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Using GIS to Analyze Some Heavy Metals Concentrations in Water of Hammar, Central and Hawizeh Marshes in Southern Iraq

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الخلاصة

استخدم برنامج (ArcGIS 9.2) لتحليل تراكيز بعض العناصر الثقيلة في مياه اهور جنوب العراق خلال شهري حزيران 2008 وكانون الثاني 2009. تضمنت الدراسة قياسات حقلية للخصائص الفيزيائية والكيميائية لنماذج المياه لستة مواقع موزعة في هور الحمار، الاهور المركزية وهور الحويزة، بينما تناولت الفحوصات المختبرية قياس تركيز بعض العناصر الثقيلة (Pb, Ni, Cd, Cr, Cu, Co, Mn, Zn) وكذلك العسرة الكلية TH. أوضحت النتائج إن أعلى قيم لدرجات حرارة الهواء والماء سجلت في شهر حزيران بينما سجل عمق الماء أعلى مستوياته في شهر كانون الثاني. تراوحت قيم الأس الهيدروجيني pH بين (6.5-8.5)، بينما تجاوزت قيم التوصيلية الكهربائية EC المحددات العراقية ومحددات منظمة الصحة العالمية. بينت النتائج إن أعلى قيم للملوحة والعسرة الكلية وتراكيز بعض العناصر الثقيلة سجلت في شهر حزيران بسبب زيادة معدلات التبخر وقلة المواد العضوية.

ABSTRACT

ArcGIS 9.2 software was used to analyze the some heavy metals concentrations in water of marshlands in southern Iraq during June 2008 and January 2009. The study included field measurements for Physical and chemical characteristics of water samples in six sites distributed in the Hammar, Central and Hawizeh marshes, and laboratory measurements have included measuring the concentration of some heavy metals (Pb, Ni, Cd, Cr, Cu, Co, Mn, Zn) and TH. The results shown that the values of air, water temperature were high in June, while water depth was high in January. pH values are lies between (6.5-8.5). EC values in all sites are exceeded Iraqi and WHO standards. The highest salinity and TH values were registered during June, as well as the highest contaminations of most heavy metals because of the evaporation and degradations of organic matter.

Keywords: Spatial analyst – Iraqi marshes – Heavy metals

INTRODUCTION

The Mesopotamian marshlands are located mostly in south-eastern Iraq but also extend across the border into Iran. They once covered an area 20000 km² between the three Iraqi cities of Amarah in the north, Basra in

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the south, Naseriyah in the west and the Iranian town of Hawizeh in the east [1]. The sources of marshland water was of multi origin namely rivers, precipitations and groundwater. Flow from the Tigris and Euphrates rivers almost wholly regulate the marshland since local rainfall, is negligible. The marshlands constitute the largest wetland ecosystem in the Middle East and Western Eurasia. These wetlands which are located at the confluence of Tigris and Euphrates rivers in southern Iraq. This area supported a marsh Arab population of 500,000 as well as numerous endemic species of birds, mammals, amphibians, reptiles, fish and invertebrates [2]. There are three major units of marshlands in Iraq:

1. Hawizeh Marsh which is located to the east of the Tigris River in Misan Governorate and extended to the Iranian territory with an the extension of about 80 km from north to south, and 30 km from east to west. Al-Hawizeh marsh covers at least 3000 Km² of area in the flood time and hundreds m² in summer time [3].
2. Hammar Marsh is situated almost entirely south of the Euphrates, extending from near Al-Nasiriyah in the west to the outskirts of Basrah on Shatt al-Arab in the east. Al-Hammar marshes are bordered by a sand dune belt of the Southern Desert. Estimates of this marsh area range from 2800 km² of contiguous permanent marsh and lake, extending to a total area of over 4500 km² during periods of seasonal and temporary inundation. Al-Hammar Lake, which dominates the marshes, is the largest water body in the lower Euphrates. It is approximately 120 km long and 25 km at its widest point. The lake is eutrophic and shallow. Maximum depth at low water levels is 1.8 m and about three meters at high water mark.
3. The Central Marshlands is located in a triangular area between the Tigris and the Euphrates this area is roughly bounded by Al-Nasiriyah, Qalaat-Saleh and Al-Qurnah cities [4].

Heavy elements are the most harmful environmental pollutants, as a continuation of the emission from various sources (natural and industrial) increase the concentration in the atmosphere. The heavy elements play a major role in body building and metabolism of living organisms, but in the case of exposure to high concentrations have a backlash where the danger lies in accumulation within the bodies of living organisms. The overall effects induced by heavy metals in biological systems lead to a range of diseases including cancer, heart disease, kidney, brain and nerve damage [5].

Spatial analysis is the study of geographic feature locations, attributes, and spatial dimensions and the relationships between each and the process of examining the locations, attributes, and relationships of features in spatial

data through overlay and other analytical techniques in order to extract or create new information from spatial data [6].

It is the aim of the present work assessment of heavy metals concentrations (Pb, Ni, Cd, Cr, Cu, Co, Mn, Zn), determine the physical and chemical characteristics in some of marshlands water samples in southern Iraq and use ArcGIS 9.2 spatial analysis to create a spatial model of heavy metals and identify areas affected by them.

STUDY AREA

The climate of the southern region characterized by long hot summers and rather short cold winters, the prevailing north-westerly winds have an pronounced influence on the area [7].

After the restoration of the marshes in southern Iraq in 2003, has been a present study to assessment some of heavy metals concentrations and determine the physical and chemical characteristics at 6 sites distributed in Hawizeh, Hammar, Central and marshes during June 2008 and January 2009, see Figure 1.

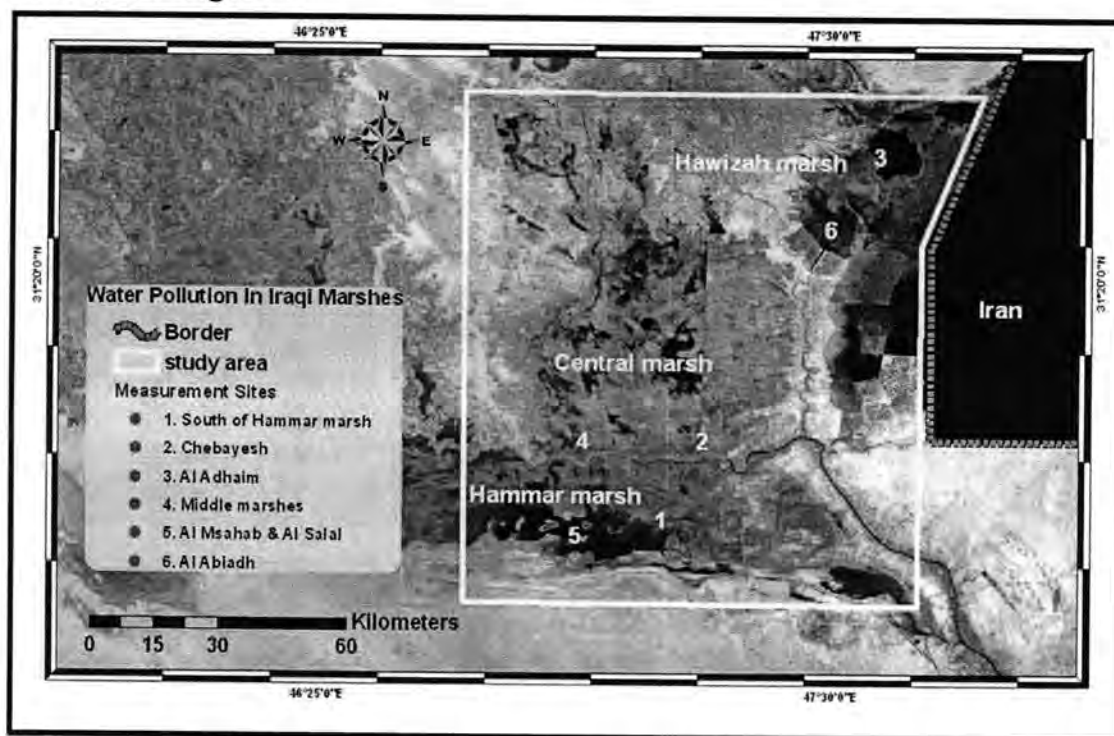


Figure 1: Study area and sites of water pollutants measurements

MATERIALS AND METHODS

In this study, the water samples were collected from the surface water (about 30 cm below the surface) in each sample, using 20 litter containers. The filtrates were placed in glass and/or plastic containers and frozen till time of analysis. The field work are included measurement physical and chemical characteristics directly in the field by digital portable multi meter to water samples, these measurements have been: Water Temperature ($^{\circ}\text{C}$),

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Water Hydrogen Ion Concentration (pH), Water Electrical Conductivity (EC) ms/cm, Water Salinity (Sal,% 0.0), Water Depth (cm) was measured during the field study period by ironic ruler, which was divided from (0-400 cm).

The Lab. Measurements which have been include:

Total Hardness (mg/L): Followed the method of [8] to measure the total brackish, taking (25 ml) of the model and commuted to (50 ml) distilled water, and the models against Shan Solution Ethylene Diamine ,Tetra Acetic Acid Disodium salt (EDTA-Na₂) index (0.01 Molari) with the addition of a few dye reagent Erickrom Black T Reagent, the titration continued to change color to purple and blue across the unit on the results mg (calcium carbonate) / liter, according to the following equation:

$$\text{Total hardness as CaCO}_3 \text{ mg/L} = \frac{A \times B \times 1000}{\text{ml of sample}}$$

A: volume (ml) EDTA used in titration.

B: weight (mg) CaCO₃, which is equivalent to 1 ml of EDTA

Heavy metals (mg/L): The determination of concentrations of heavy metals (Pb,Ni,Cd,Cr,Cu,Co,Mn,Zn) in water samples per (mg/L) by used Flame Atomic Absorption Spectrophotometry.

RESULTS AND DISCUSSION

Tables 1,2 shows Physical and chemical characteristics to water samples in June and January of 6 sites in southern Iraqi marshes. The air temperature values fall between (37.11-40.01 C°) in June and between (11.5-15.4 C°) in January. The water temperature values fall between (27.3-28.71 C°) in June and between (10.3-12.5 C°). Maximum temperature was recorded during June in June months and lowest January in January months for all monitored sites. Changes in the water temperature synchronized with air temperature. Temperature is an important parameter that controls the quality, dispersion and distribution of living organisms. The sun and air temperature are the two main factors that influence water temperature.

The pH values of water samples fall between (7.8 - 8.2) in June and between (7.4-8.1) in January. All the results are within the acceptable Iraqi limits (6.5-8.5). The pH meter is another important factor influencing the species and metabolism of organism inhabiting. The pH is greatly affected CO₂ concentration, dissolved oxygen, ammonia, photosynthesis, water temperature, organic matter content [9].

The EC values of water samples fall between (822-1203 µs/cm) in June and between (820 -1400 µs/cm) in January. The average of EC in June was (809.6 µs/cm), while the average of EC in January was (1043.3 µs/cm). All the results of EC in water samples in present study was exceeded WHO and the European standards recommended value of EC is (250 µs/cm). The

low EC values in June are because of the dilution by the relatively higher water level, and may be due to the high temperatures that causes evaporation of the water its increases with increasing temperature. The conductivity is affected primarily by geology of the area through which the water flows and the presence of naturally electrolytes [10].

The salinity of the marsh is important because of the possibility of using the water as drinking water, its important being to evaluate whether salinity is appropriate to support wildlife, primarily birds and fishes. The salinity values of water samples fall between (1.7-2.4 ppt) in June and between (1.3 -2.2 ppt)

Table 1: Physical and chemical characteristics to water samples in Summer (June)

No	Location	Air Temp (C°)	Water Temp (C°)	pH	EC (µs/cm)	Salinity (ppt)	Total Hardness (mg/L)	water Depth (cm)
1	South of Hammar marsh	37.11	28.1	7.8	951	1.9	650	84
2	Chebeyesh	38.91	28.31	7.9	918	1.7	850	81
3	Al Audhaim	38.02	27.3	7.9	853	2.2	890	70
4	Middle marshes	39.81	28.71	8.2	822	2.3	686	90
5	Al Msahab & Al Salal	39.03	28.01	7.8	111	2.1	950	90
6	Al Abiadh	40.01	27.91	8	1203	2.4	983	98
Average		38.8	28.1	7.9	809.6	2.1	834.8	85.5

Table 2: Physical and chemical characteristics to water samples in Winter (January)

No	Location	Air Temp (C°)	Water Temp (C°)	pH	EC (µs/cm)	Salinity (ppt)	Total Hardness (mg/L)	water Depth (cm)
1	South of Hammar marsh	12.2	10.5	8	1400	1.3	580	86
2	Chebeyesh	11.7	10.3	7.5	990	1.5	686	99
3	Al Audhaim	12.1	12.5	8.1	1010	2.1	861	111
4	Middle marshes	15.4	11.1	7.4	940	2	630	144
5	Al Msahab & Al Salal	13.5	12.4	7.5	1100	1.5	720	107
6	Al Abiadh	11.5	11.9	7.4	820	2.2	960	125
Average		12.7	11.5	7.7	1043.3	1.8	739.5	112

In January, The average of salinity in June is (2.1 ppt), while it average in January is (1.8 ppt). The highest salinity values were registered during June was caused by the decrease in water levels and the increase of the evaporation ratio. The lowest salinity values were registered during January was caused by increasing of rainfall and raise of water levels, whereas that

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dilute the concentration of dissolved solid materials. Salinity varied directly with agriculture, manure, sewage and effluent discharges. The total hardness is mainly caused by Ca^{+2} and Mg^{+2} ions in water. The values of TH in June fall between (650-983 mg/L) and the average is (834.8 mg/L). The values of TH in January fall between (580-960mg/L) and the average is (739.5 mg/L).

The high TH values of water samples in sites study is recorded in June that that may be due to the decrease of the water levels and the increasing of evaporation rate which led to increasing the salinity [11].

The water depth that recorded in study sites is showed that fall between (70-98 cm) and the average is (85.5 cm) in June, while the water depth values fall between (86-144 cm) and the average is (112 cm) in January. The lowest levels of water was recorded in June because decrease in surface water that fed southern marshlands and the increasing of evaporation rate.

Heavy metals in water samples

The occurrence of metal problem as a result of the rapid growth of population, increased urbanization, expansion of industrial activities, exploration and exploitation of natural resources, extension of irrigation and other modern agricultural practices as well as other sources. Heavy metals enter the aquatic environment of southern Iraq from both natural and anthropogenic sources [12]. Natural sources include storm dust fall, erosion or crustal weathering and dead and decomposition of the biota in the water, whereas the anthropogenic sources include sewage wastes, industrial effluent, automobile effluent, petroleum and fertilizer industry effluent [13].

Pb concentrations: Tables 3 and 4, shows the heavy metals concentration of water samples in southern Iraqi marshes during summer (June) and winter (January), respectively. The higher concentration of Pb in June was recorded in Al Audhaim (1.09 mg/L) and the lower concentration was recorded in Al Msahab and Al Salal (0.15 mg/L), while during winter the higher concentration was recorded in Al Audhaim (1.01 mg/L) and the lower concentration was recorded in Chebayesh and Al Msahab and Al Salal (0.12 mg/L). Pb concentrations in all the sites study is exceeded Iraqi and WHO Specifications (0.01 mg/L). That's indicator about the water marsh is polluted by Pb because the water of Tigris and Euphrates rivers and the clay minerals that content in sediments and sewage water [14].

Co concentrations : The higher concentration of Co in June was recorded in Al Abiadh (0.41 mg/L) and the lower concentration was recorded in Middle marshes (0.15 mg/L), table 3. While Table 4 shows that higher concentration in January was recorded in Al Abiadh (0.34 mg/L) and the lower concentration was recorded in South of Hammar marsh (0.11 mg/L).

The increase in the concentrations of Co is coming from the water of river and sewage water.

Table 3: Heavy metals concentrations of water samples in Summer (June)

No	Location	Pb mg/L	Co mg/L	Cu mg/L	Cr mg/L	Cd mg/L	Ni mg/L	Mn mg/L	Zn mg/L
	Iraqi specification	0.01	nil	1	0.05	0.00 3	0.02	0.1	3
	WHO Specification	0.01	nil	0.00 2	0.05	0.00 5	0.02	0.04	1.1-3
1	South of Hammar marsh	0.29	0.19	0.31	0.32	0.08	0.12	0.07	0.15
2	Chebeyesh	0.18	0.22	0.25	0.19	0.09	0.15	0.14	0.22
3	Al Audhaim	1.09	0.29	0.29	0.24	0.07	0.16	0.07	0.12
4	Middle marshes	1.04	0.15	0.22	0.34	0.06	0.18	0.15	0.11
5	Al Msahab and Al Salal	0.15	0.22	0.18	0.25	0.08	0.13	0.18	0.19
6	Al Abiadh	0.28	0.41	0.33	1.07	0.09	0.27	0.19	0.22
	Average	0.51	0.24	0.26	0.4	0.07	0.16	0.13	0.16

Table 4: Heavy metals concentrations of water samples in Winter (January)

No	Location	Pb mg/L	Co mg/L	Cu mg/L	Cr mg/L	Cd mg/L	Ni mg/L	Mn mg/L	Zn mg/L
	Iraqi specification	0.01	nil	1	0.05	0.00 3	0.02	0.1	3
	WHO Specification	0.01	nil	0.00 2	0.05	0.00 5	0.02	0.04	1.1-3
1	South of Hammar marsh	0.22	0.11	0.29	0.25	0.08	0.15	0.04	0.11
2	Chebeyesh	0.12	0.24	0.21	0.19	0.06	0.21	0.11	0.19
3	Al Audhaim	1.01	0.14	0.18	0.19	0.09	0.19	0.08	0.11
4	Middle marshes	1	0.24	0.17	0.16	0.07	0.12	0.16	0.14
5	Al Msahab and Al Salal	0.12	0.14	0.19	0.14	0.09	0.21	0.14	0.17
6	Al Abiadh	0.24	0.34	0.29	0.91	0.11	0.19	0.18	0.16
	Average	0.45	0.2	0.22	0.3	0.08	0.17	0.11	0.14

Cd concentrations : Table 3 is shows that higher concentration of Cd in June was recorded in Al Abiadh and Chebayesh (0.09 mg/L) and the lower concentration was recorded in Middle marshes (0.06 mg/L). In January, the higher concentration of Cd was recorded in Al Abiadh (0.11 mg/L) and the lower concentration was recorded in Chebayesh (0.06 mg/L). Cd concentrations are higher than Iraqi and WHO specifications (0.003,0.005 mg/L),respectively in all sites in present study. The increase in the

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concentrations of Cd are resulting from the water of river or clay minerals and sewage water.

Cr concentrations : The higher concentration of Cr in June was recorded in Al Abiadh (1.07 mg/L), Table 3, and the lower concentration was recorded in Chebayesh (0.19 mg/L). Table 4 shows that higher concentration of Cr in January was recorded in Al Abiadh (0.91 mg/L) and the lower concentration was recorded in Al Msahab and Al Salal (0.14 mg/L). In January, Cr concentration are exceeded Iraqi and WHO specification (0.05 mg/L) in all sites in present study.

Cu concentrations : Table 3 shows the higher concentration of Cu in June was recorded in Al Abiadh (0.33 mg/L) and the lower concentration was recorded in Al Msahab and Al Salal (0.18 mg/L), while in January the higher concentration was recorded in Al Abiadh and South of Hammar marsh (0.29 mg/L) and the lower concentration was recorded in middle marshes (0.17 mg/L), see Table 4. Cu concentrations are higher than WHO specification (0.002 mg/L) but its less more than Iraqi specification (1 mg/L).

Ni concentrations : The higher concentration of Ni in June was recorded in Al Abiadh (0.27 mg/L) Table 3 and the lower concentration was recorded in South of Hammar marsh (0.12 mg/L), while in January, Table 4 shows that the higher concentration of Ni was recorded in Chebayesh and Al Msahab and Al Salal (0.21 mg/L) and the lower concentration was recorded in South of Hammar marsh (0.12 mg/L). In all sites present study, Ni concentrations are higher than Iraqi and WHO specifications (0.02 mg/L). These high concentrations may be due to respectively and the clay minerals. In this study that clear different in Ni concentration due to area type and plants density.

Mn concentrations : Table 3 is shows that higher concentration of Mn in June was recorded in Al Abiadh (0.19 mg/L) and the lower concentration was recorded in South of Hammar marsh and Al Audhaim (0.07 mg/L). In January, the higher concentration of Mn was recorded in Al Abiadh (0.18 mg/L) and the lower concentration was recorded in South of Hammar marsh (0.04 mg/L). Mn concentrations are higher than Iraqi and WHO specifications (0.1 , 0.04 mg/L), respectively in all sites in present study.

Zn concentrations : The higher concentration of Zn in June was recorded in Chebayesh and Al Abiadh (0.22 mg/L), and the lower concentration was recorded in Middle marshes (0.11 mg/L), table 3. While Table 4 shows that higher concentration in January was recorded in Chebayesh (0.19 mg/L) and the lower concentration was recorded in South of Hammar marsh and Al Audhaim (0.11 mg/L). Zn concentrations are lower than Iraqi and WHO specifications (3 , 1.1-3 mg/L).

ArcGIS SPATIAL ANALYST

Using ArcGIS 9.2 spatial analysis provided for the purpose of analysis of heavy metals (Pb,Co,Cu,Cr,Cd,Ni,Mn,Zn) in water of Iraqi marshes and the preparation of maps of its distribution , as well as the creation of a spatial model for concentrations of elements, where they were in the first stage and the distribution maps for each component using spatial analysis. In the second stage the composition of another layer for each element was depicted by (Reclassify) option levels of concentration of heavy metals. Finally, the third stage collected such layers using (Raster Calculator) option using Map Algebra (the analysis language for Spatial Analysis) to allow query raster data and perform mathematical operations. One of the spatial analyst operations is adding many rasters together and reclassifying these rasters to create more efficient analysis of the area then collecting these rasters in (raster calculator) option to create modeling shows the areas most affected by heavy metals in Iraqi marshes. Figure 2 represents heavy metals model in June using spatial analysis and Figure 3 represents the heavy metals model in January using spatial analysis. Both the figures 2 and 3 are shows that Al Abiadh site in Hawizah marsh have more concentrations of heavy metals in present study.

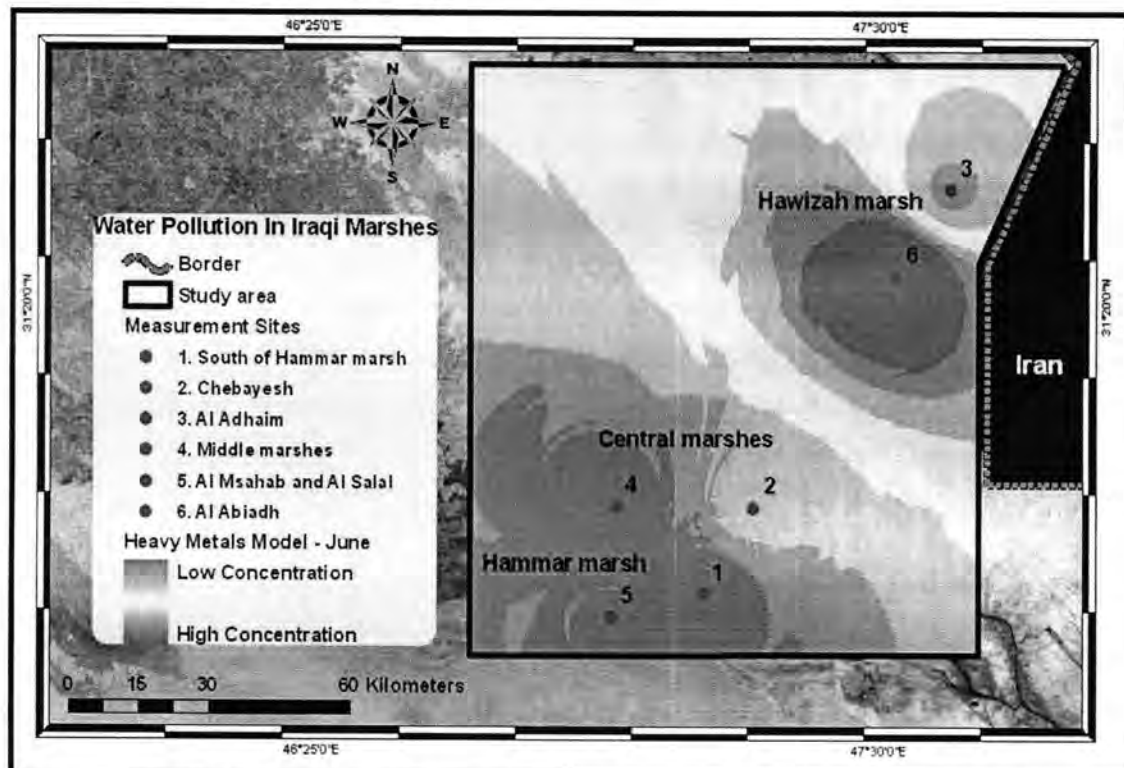


Figure 2: Heavy metals model during summer using spatial analysis

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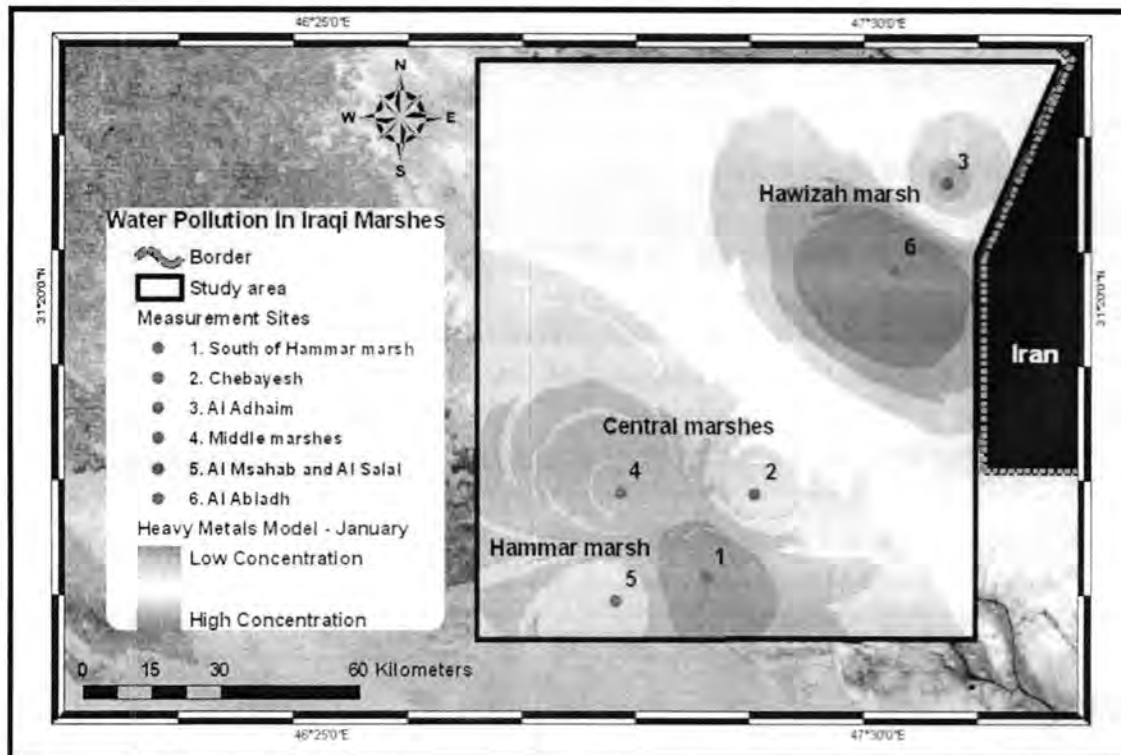


Figure 3: Heavy metals model during winter using spatial analysis

CONCLUSION

1. Results of the physical and chemical characteristics of water samples in sites of Iraqi marshes shown that the values of air, water temperature were high in June, while water depth was high in January. pH values were within the acceptable Iraqi limits (6.5-8.5). EC values in all sites are exceeded WHO and European standards. The highest salinity and TH values were registered during June was caused by the decrease in water levels and the increase of the evaporation ratio.
2. Results shown that the highest contaminations of most heavy metals in water samples have been recorded in June because of the evaporation, degradations of organic matter.
3. ArcGIS 9.2 spatial analysis tools are used to analyze and display the concentration of heavy metals in water Iraqi marshes and the preparation of maps for distribution, as well as create spatial model for concentrations of these elements during the study period June 2008

and January 2009 to show the pollutant sites by heavy metals in Iraqi marshes.

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Synthesis, Spectroscopic and Biological Studies of 2-(N-Phenyl Dithio Carboxamide)Benzothiazole with some Metal Ions

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الخلاصة

حضر الليكاند (L) ، 2- (N - فنيل داي ثايوكاربوكسي اميد) بنزو ثيازول من تفاعل 2- مركبتوبنزو ثيازول مع فنيل ايزوثايوسيانييت وبنسبة 1: 1. شخص المركب (L) بواسطة تحليل العناصر (C.H.N) ، ¹H-NMR ، الاشعة تحت الحمراء و فوق البنفسجية - المرئية. حضرت وشخصت معقدات املاح بعض أيونات العناصر الثنائية التكافؤ (Ni و Cu و Zn و Cd و Hg) مستخدمين تقنيات طيف تحت الحمراء والاشعة فوق البنفسجية - المرئية و التوصيلية الكهربائية و الامتصاصية الذرية و النسبة المولية لبعض الايونات المختارة مثل (Ni²⁺ , Cu²⁺). واستنتج من التحاليل ان المعقدات لها شكل ثماني السطوح في حالة (Ni, Cu) ورباعي السطوح في حالة (Hg, Cd, Zn). تم دراسة الفعالية البيولوجية لليكاند ومعقداته في تركيزين مختلفين (1 و 5) ملغم/مل تجاه *E-coli* و *taphylococcus aureus* وأظهرت النتائج فعالية متباينة عند التركيزين تجاه الصبغة الموجبة. في حين مع الصبغة السالبة أظهر تأثير التركيز بشكل واضح فعند استعمال التركيز 1 ملغم/مل يكون التأثير تجاه *E-coli* متباين ما عدا معقد الزئبق لم يظهر أي تأثير في حين عند التركيز 5 ملغم/مل لم يظهر الليكاند ومعقداته أي تأثير ما عدا معقد الزئبق له تأثير 5 ملغم.

ABSTRACT

The synthesis of 2(N-phenyl dithio carboxamid) benzothiazol Ligand (L) from reaction of 2-Mercaptobenzothiazol with phenylisothiocyanate using ratio 1:1. The ligand was characterized by elemental analysis (C.H.N), ¹H-NMR, IR and UV-Vis. The complexes with bivalent ions (Ni, Cu, Zn, Cd and Hg) have been prepared and characterized. The structural diagnosis was established using IR, UV – Visible spectro photometer, molar conductivity, atomic absorption and molar ratio with selected metal ions (Ni²⁺ , Cu²⁺). The complexes of (Ni, Cu) gave octahedral structural while the complexes of (Zn, Cd, Hg) gave tetrahedral structural. The study of biological activity of the ligand (L) and its complexes (Ni, Cu, Hg) in two deferent concentration (1 and 5) mg/ml with *staphylococcus aureus* and *E-coli*. The results showed deference effect towards positive in two concentration (1 and 5)mg/ml. while the effect towards negative showed variety effect except Hg-complex didn't

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show effect in 1mg/ml but in 5mg/ml the ligand and complexes did show effect except Hg-complex showed effect 5 mm.

INTRODUCTION

Heterocycles bearing nitrogen, sulphur and thiazole moieties constitute the core structure of a number of biologically interesting compound. 2-Mercaptobenzothiazole derivatives are known to possess various pharmacological activities(1-3). Our current interest is in heterocyclic Bis-oxadiazol and trizol derivatives and their complexes have been prepared and reported(4-5). In the present work the efforts have been made to synthesize 2(N-phenyldithiocarboxamide) benzothiazol which has more than one sulphur and nitrogen atoms and study of its reaction with some metal ions and their bactericidal activities.

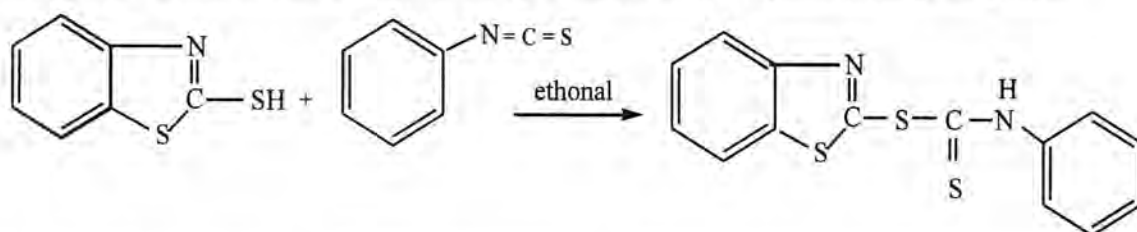
MATERIALS AND METHODS

- a- Chemicals; All reagents used were analar or chemically pure grade by British Drug Houses (BDH).
- The chemical materials: 2-Mercaptobenzothiazol $C_7H_5NS_2$, phenyl isothiocyanate (C_7H_5NS), Nickelchloridehexahydrate ($NiCl_2.6H_2O$), Copperchloridedehydrate ($CuCl_2.2H_2O$), Zincchloride $ZnCl_2$, Cadimunchloride dehydrate ($CdCl_2.2H_2O$), Mercurychloride ($HgCl_2$), Ethanol (CH_3CH_2OH) 99%, Dimethylformamide (DMF) 99%, Dimethylsulphoxide (DMSO) 99% , carbontetrachloride (CCl_4) 99%.
- b- Instruments;
- Elemental analysis for the new (L) (C, H, N) was determined by calibration type : Linear Regression Euro EA Elemental Analysis.
 - Melting points were determind by Gallen-Kamp apparatus.
 - 1H -NMR- Bruker, Mondel: Ultra shield 300MHz origin, Swizerland (Jordan) in CH_3OD using TMS as an internal standard.
 - IR spectra were recorded as KBr disc in the rang $(4000-400)cm^{-1}$ using shimad Zu-FTIR.
 - UV-Visible spectra were recorded by shima Zu-UV-Vis. 160 A Ultra violet spectro photometer at $25^\circ C$, using 1cm quartz cell and examined at the range of $(200-1100)nm$ in DMF at $10^{-3}M$.
 - Atomic Absorption (A.A) technique using a shimad Zu AA680G atomic absorption spectrophotometer.
 - Molar conductivity of the complexes were measured on pw 9526 digital conductivity in DMF at $10^{-3}M$.

Snythesies of 2(N-phenyl dithio carboxamid) benzothiazol (L)

2-Mercaptobenzothiazole (0.17g, 1mmol) in ethanol (10 ml) was added to a solution of phenylisothiocyanate (0.14g, 1mmol) in ethanol

(10ml). The resulting mixture was stirred at room temperature and then followed by refluxing for 4hrs to give a yellow solid. The product filtered and dried. Then it was crystallized by ethanol to give yellowish precipitate.



2-Mercaptobenzothiazole phenylisothiocyanate 2(N-phenyl dithio carboxamid)benzothiazol(L)

Figure 1: Preparation of the ligand (L) with formula $C_{14}H_{10}N_2S_3$

Synthesis of metal complexes.

An ethanolic solution of the following metal salts $NiCl_2 \cdot 6H_2O$ (0.237g, 1mmol), $CuCl_2 \cdot 2H_2O$ (0.17g, 1mmol), $ZnCl_2$ (0.136, 1mmol), $CdCl_2 \cdot H_2O$ (0.201 g, 1mmol) and $HgCl_2$ (0.271g, 1mmol) were added to a solution of the ligand (L) (0.302 g, 1mmol) in ethanol. The mixture was stirred for 30 min. The product was filtered and washed with distilled water and dried under vacuum. Physical properties for the ligand and its complexes are given in Table(1).

Table 1: Physical properties for(L) and its complexes

No	Compound	Color	m.p C° or (D)	Yield %	Metal analysis Found (calculated)					solubility
					Mwt	C%	H%	N%	M%	
1	(L) $C_{14}H_{10}N_2S_3$	Yellowish	90	75	302.44	55.54 (55.43)	3.306 (3.302)	9.25 (9.23)	-	CCl_4 DMF,DMSO
2	$[LNiCl_2(H_2O)_2]5H_2O$	Green	160	80	558.13	-	-	-	10.56 (10.52)	DMF,DMSO
3	$[LCuCl_2(H_2O)_2]2H_2O$	Green	140	87	508.98	-	-	-	12.29 (12.48)	DMF,DMSO
4	$LZnCl_2$	White-yellow	165	79	438.83	-	-	-	15.85 (14.90)	DMF,DMSO
5	$LCdCl_2$	White-yellow	286	80	524.85	-	-	-	21.68 (21.41)	DMF,DMSO
6	$LHgCl_2$	Yellow	110	85	574.03	-	-	-	34.79 (34.94)	DMF,DMSO

D = Decomposition

RESULTS AND DISCUSSION

Elemental analysis (C.H.N)

The ligand was characterized by (C.H.N) analysis as shown in Table (1).

¹HNMR

The results are summarized in Table (2) Fig.2 displays the ¹HNMR spectrum of the ligand (L). The chemical shift at 7.0-7.8 ppm are to aromatic protons. The chemical shifts at 4.9 ppm is assigned for (N-H) protons, while the chemical shift at 4.0 ppm is due to solvent(6).

Table 2: ¹HNMR data for the synthesized ligand

L	δ (p.p.m)	
	Aromatic C-H N-H	7.0 – 7.8 4.9

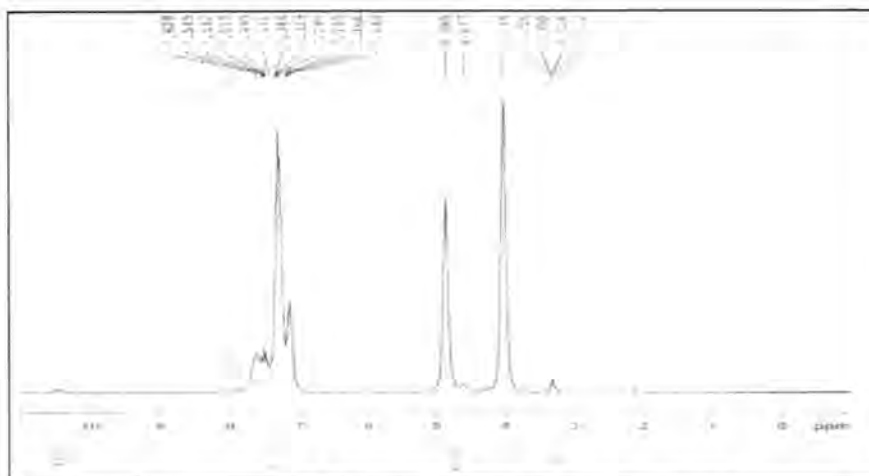


Figure 2: The ¹HNMR of the ligand(L)

The FTIR spectrum of (L)

Because the ligand consist of the SCNH group which may be available either the thion form (S=C-N-H) or the thiol form (H-S-C=N). from the study of infrared spectroscopy as shown in Fig.3, indicated the ligand can exist in tautomeric thion (H-N-C=S) and thiol (-N=C-SH) forms and hence give characteristic thioamide bands in its IR spectrum(7). Sharp band at 3182 cm^{-1} due to $\nu(N-H)$ indicates the thion form while a weak band in the region $2576-2526\text{ cm}^{-1}$ suggests thiol form of the ligand. Another band at $1593, 1535, 1138, 1014$ and 676 cm^{-1} are assigned to $\delta(N-H), \nu(C=N), \nu(C-N) + \nu(C=S), \nu(C-S)$ respectively(7-8).

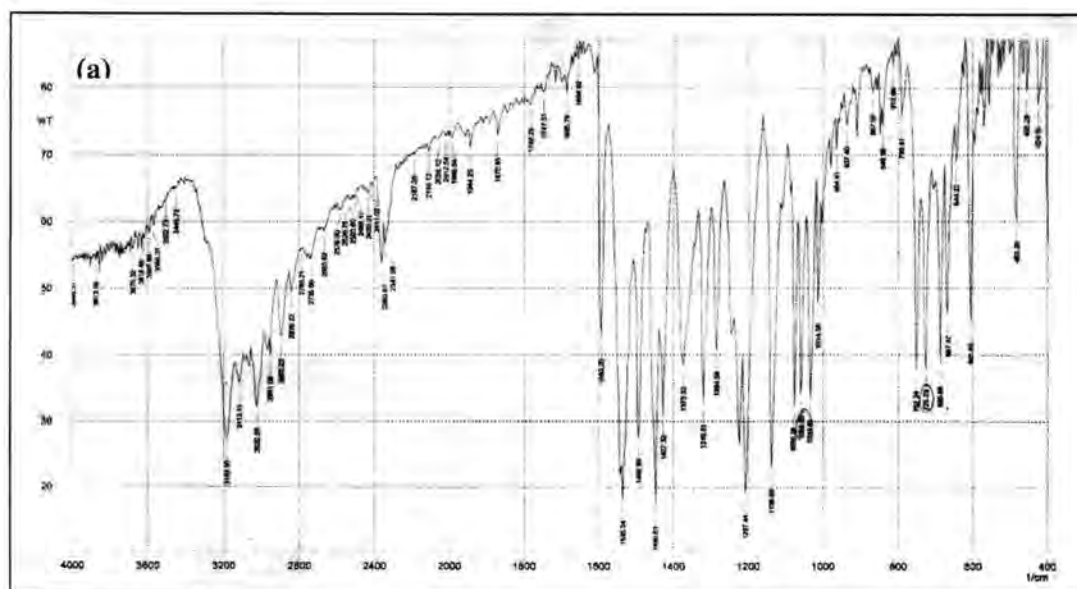
I.R spectra of L-complexes

The mode of ligand bonding is decided on the basis of shifts of $\nu(N-H)$, $\nu(C=S)$ and four thioamide bands on complexation. The thioamide band II and III have contributions from:

$$\delta(N-H), \delta(N-H) + \nu(C-N) + \nu(C-S).$$

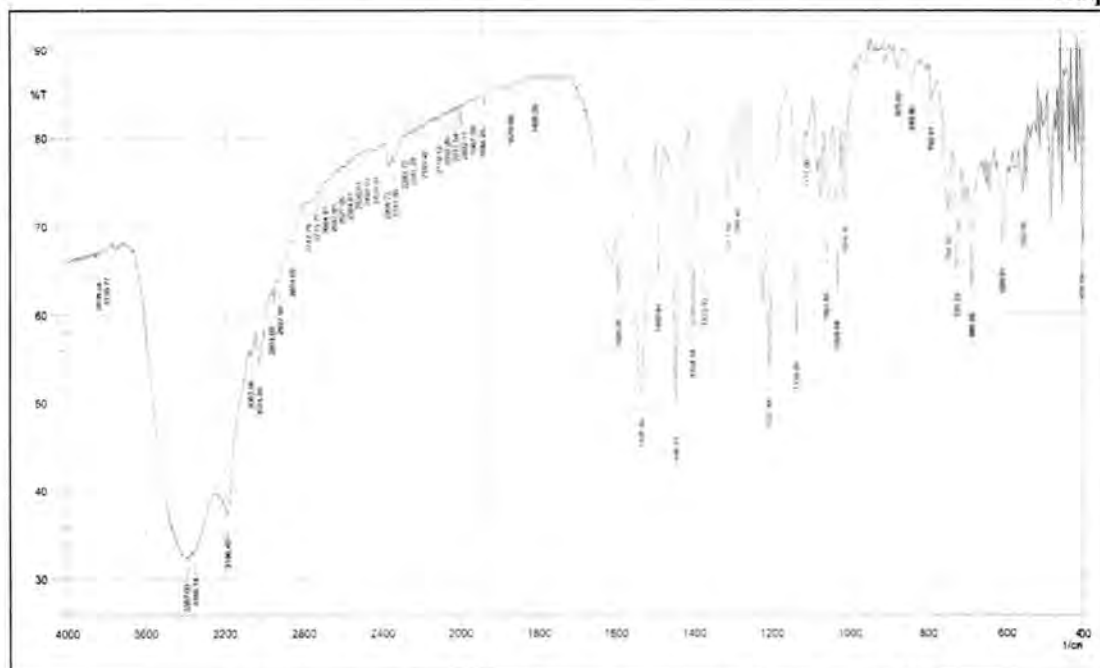
The high frequency N-H absorption bands in the spectrum of the ligand is appeared in multibands 3186-3300 cm^{-1} on the formation of the metal-ligand complexes. The infrared absorption bands observed at about 1535 cm^{-1} assigned to $\nu(C=N)$ stretching vibration. The broaden and increase in frequency observed for the complexes Ni (1545, 1535), Cu (1560, 1543), Zn (1562, 1512), Cd (1558, 1531) and Hg (1550)(9). Can be explained as resulting from the greater double bond character of the carbon to nitrogen bond on the complexes formation.

A difference in the spectra of ligand and its metal complexes appears in the region at about 1014 cm^{-1} , which is due $\nu(C-N) + \nu(C-S)$. A multibands or broaden banas on complexes formation (Table-3). This observation can be explained by the participation of $\nu(C-N) + \nu(C=S)$ in bonding on complexation. The appearance of $\nu(M-N)$ and $\nu(M-S)$ at region (513-410) cm^{-1} and (489-424) cm^{-1} respectively (10-11), suggesting the coordination through nitrogen and sulphur atom(12). The bands characteristic of coordinated water and (M-O) are seen in Ni and Cu complexes in (827, 555) cm^{-1} and (832, 551) cm^{-1} respectively(13-14). Table (3) showed the characteristic stretching vibrational frequencies (cm^{-1}) located in the FT-IR of the ligand and its complexes.



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**Figure 3: a Infrared spectrum of the ligand(L)
b Infrared spectrum of the [LNiCl₂.(H₂O)₂]5H₂O**

**Table 2: Characteristic stretching vibrational frequencies (cm⁻¹) located
(b) in the FT-IR the ligand (L) and its complexes.**

No	Compound	$\nu(N-H)$ $\delta(N-H)$ cm ⁻¹	$\nu(C-N)$ cm ⁻¹	$\nu(C-N) +$ $\nu(C=S)$ cm ⁻¹	$\nu(C=S)$ cm ⁻¹	$\nu(M-N)$ cm ⁻¹	$\nu(M-S)$ cm ⁻¹	$\nu(M-O)$ cm ⁻¹	Other band $\nu(O-H)$ cm ⁻¹
1	(L)C ₁₄ H ₁₀ N ₂ S ₃	3182 1593	1535	1138 1014	667	-	-	-	-
2	[LNiCl ₂ 2H ₂ O] 5H ₂ O	3186 1610	1545 1535	1138 1014	671	525	430	555	3387
3	[LCuCl ₂ 2H ₂ O] 2H ₂ O	3186 1600	1560 1543 1520	1130 1010	678	532	432	551	3398
4	LZnCl ₂	3059 1599	1562 1512	1134 1026	671	581	432	-	-
5	LCdCl ₂	3059 1589	1558 1531	1130 1010	694	536	424	-	3525
6	LHgCl ₂	3182 1597	1550	1138 1037	690	532	420	-	-

UV-Visible spectra of the ligand (L) and complexes

The UV-Visible spectra of the ligand (L) in dimethyl formamide solution (Table-4) exhibited strong absorption bands at (220 nm, 4545 cm^{-1}), (279 nm, 35842 cm^{-1}) and (326 nm, 30675 cm^{-1}). This may be attributed to the ($\pi \rightarrow \pi^*$) and ($n \rightarrow \pi^*$) transition(15).

The UV-Visible spectrum of Ni^{2+} -complex showed multibands in the region (640 nm, 15625 cm^{-1}) are due to ${}^2E_g \leftarrow {}^3A_{2g}(\nu_2)$ and (430 nm, 23256 cm^{-1}) is due to ${}^3T_{1g(p)} \leftarrow {}^3A_{2g}(\nu_3)$. The absence of transition (ν_1) which is equal to (10 Dq) was calculated by fitting the ratio (ν_3/ν_2) to the Tanabe-sugans digram for d^8 ion(15-16). The ratio 23256 to 15625 equal 1.49 $E(\nu_3)/B=30$, $B = 23256 / 30 = 775$ and $\Delta O / B = 9$. $\Delta O = 6975 \text{ cm}^{-1}$. B for free $\text{Ni}^{2+} = 775$ β (nephelauxetic effect) = $B \text{ complex} / B \text{ Ni}^{2+} = 755/1030 = 0.756$, which indicates of d-electron delocalization on the ligand hence a some covalent character in complex Bonds. Cu^{2+} complex appeared band at (650nm, 15385 cm^{-1}) is due to ${}^2T_{(2g)} \leftarrow {}^2E_{(g)}$. The yellowish L-complexes (Zn, Cd, Hg) spectra that have d^{10} configuration have shifting from a free ligand band, which presented at (316 nm, 31645 cm^{-1}), (379 nm, 26385 cm^{-1}) and (311 nm, 32102 cm^{-1}) are due to charge transfer(17-18). Table(4).

The molar conductance

The molar conductance of all complexes in DMF Table(4) was found to be low which suggested coordination of anion to the metal(18).

Table-4: Electronic spectra and conductance in DMF of ligand (L) and its complexes

No.	Compound	$\lambda(\text{nm})$ (cm^{-1})	Assignment bands	$\Lambda \text{ S.cm}^{-1}$ DMF (10^{-3}M)
1	(L) $\text{C}_{14}\text{H}_{10}\text{N}_2\text{S}_3$	4545 (220) 35778(279.5) 30627(326.5)	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	-
2	$[\text{LNiCl}_2(\text{H}_2\text{O})_2] \cdot 5\text{H}_2\text{O}$	23256(430) 15625 (640)	${}^3T_{1g(p)} \leftarrow {}^3A_{2g}$ ${}^2E_g \leftarrow {}^3A_{2g}$	10.4
3	$[\text{LCuCl}_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$	15385 (650)	${}^2T_{(2g)} \leftarrow {}^2E_{(g)}$	12.4
4	LZnCl_2	31645 (316)	Charge-transfer	2.26
5	LCdCl_2	26385 (379)	Charge-transfer	0.20
6	LHgCl_2	32102 (311.5)	Charge-transfer	3.98

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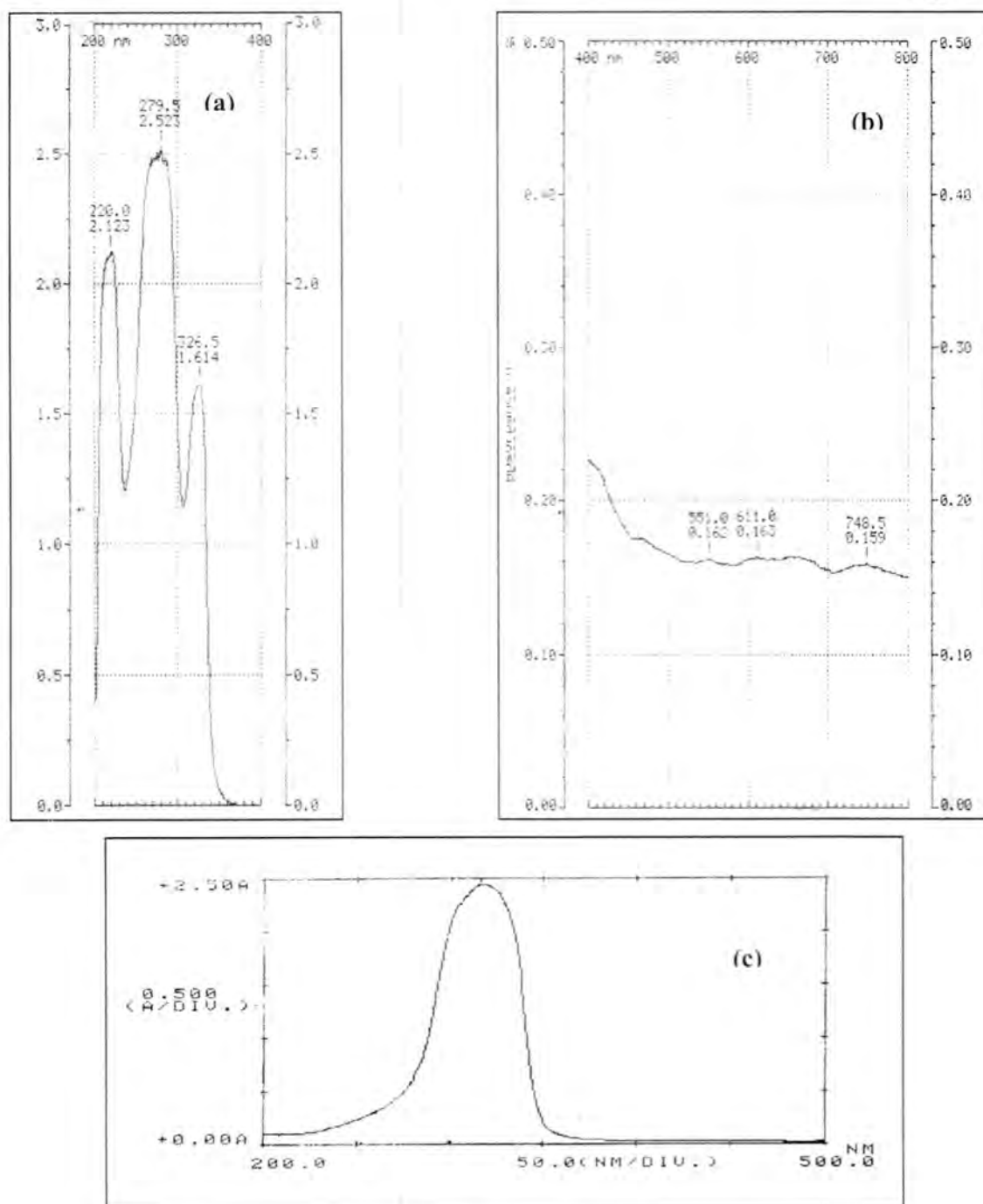


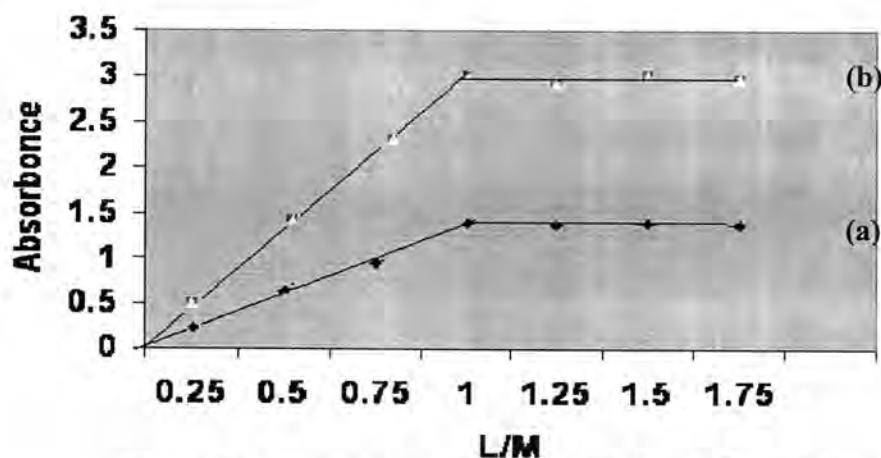
Figure 4(a):uv-visible spectrum of the ligand(L)
 (b):uv-visible spectrum of the [LNiCl₂.(H₂O)₂]5H₂O the [LNiCl₂.2H₂O]5H₂O
 (c):uv-visible spectrum of the [LCdCl₂]2H₂O

Molar ratio

The complexes of the ligand (L) with selected metal ions (Ni^{2+} and Cu^{2+}) were studied in solution using ethanol as a solvent, in order to determine (M:L) ratio in the prepared complexes, following molar ratio method(19). A series of solutions were prepared having a constant concentration (C) 10^{-3}M of the hydrated metal salts and the ligand (L). The (M:L) ratio was determined from the relationship between the absorption of the absorbed light and the mole ratio (M:L) found to be (1:1). Fig-5 (a),(b). The result of complexes formation in solution are show in Table(5).

Table 5: (a,b): V_M , V_L and absorption of (L), V_M = volume of metal in ml, V_L = volume of ligand in ml

(a)			(b)		
[$\text{LNiCl}_2 \cdot 2\text{H}_2\text{O}$] $5\text{H}_2\text{O}$			[$\text{LCuCl}_2 \cdot 2\text{H}_2\text{O}$] $2\text{H}_2\text{O}$		
V_M	V_L	Abs	V_M	V_L	Abs
1ml	0.25	0.32	1ml	0.25	0.45
1	0.5	0.68	1	0.5	0.85
1	0.75	0.94	1	0.75	1.45
1	1	1.4	1	1	1.60
1	1.25	1.38	1	1.25	1.55
1	1.5	1.39	1	1.5	1.62
1	1.75	1.38	1	1.75	1.60



**Figure 5: (a): molar ratio slop for Ni^{2+} ion $\lambda(352\text{ nm})$
(b): molar ratio slop for Cu^{2+} ion $\lambda(617\text{ nm})$**

Study of biological activity

The biological activity of the prepared new ligand and its complexes were studied against selected type of microorganisms which include gram positive bacteria like *staphylococcus aureus* and gram Negative bacteria like *E.coli*, in agar diffusion method(20), which is used (DMF) as a solvent,

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and we are used these Antibiotics disc which include cephalosporin and Amoxicillin as control. Agar diffusion method involves the exposure of the Zone of inhibition toward the diffusion of microorganisms on agar plate. The plates were incubated for (24)hrs at (37C°). The Zone of inhibition of bacterial growth around the disc was observed.

Biological effects of new ligand and its complexes exhibited antibacterial activity against gram positive bacteria in two defferent concentration (1and5) mg/ml while with gram negative, the effect was clear in 1 mg/ml concentration except Hg-complex didnt have effect but in 5 mg/ml the ligand and its complexes didnt show any effect except Hg-complex gave 5mm. Fig-6 .

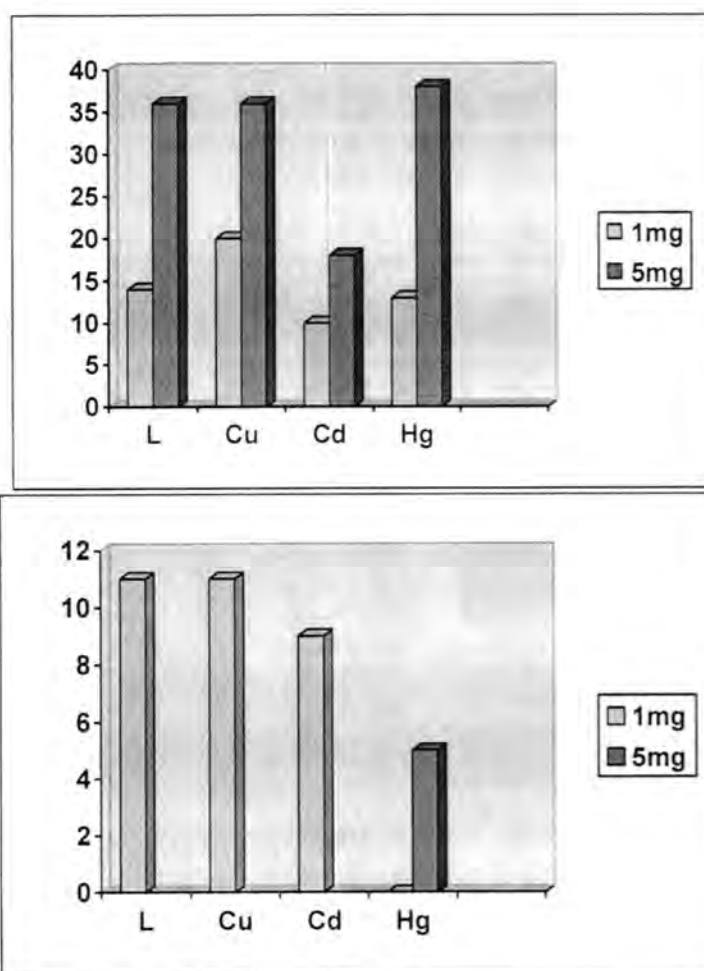


Figure 6: (a): Effect of ligand and its complexes on *Staphylococcus aureus*.

(b): Effect of ligand and its complexes on *E. coli*.

CONCLUSION

A series of complexes (Cu^{2+} , Ni^{2+} , Zn^{2+} , Cd^{2+} and Hg^{2+}) with 2(N-phenyldithio carboxamid) benzothiazol (L) have been prepared and

characterized. The bidentate ligand (L) (N, S) is binding metal ions ($M^{2+} = \text{Cu, Ni}$) and with two molecule H_2O forming octahedral structure while with metal ion ($M^{2+} = \text{Zn, Cd, Hg}^{2+}$), forming tetrahedral structure and as follow; Fig-7.

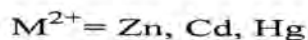
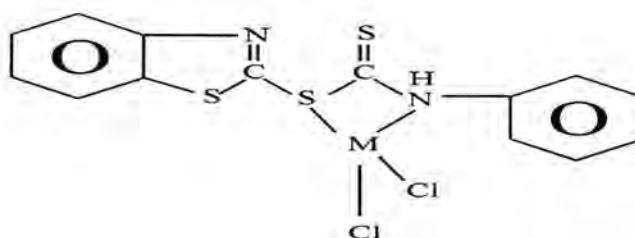
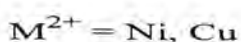
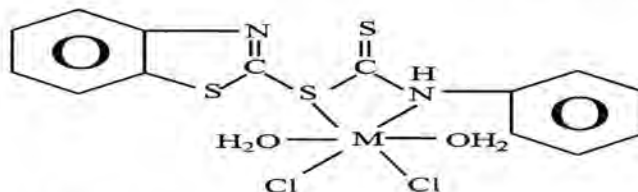


Figure 7: The structure of these complexes may thus be represented

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Experimental and Theoretical Study for The Photo degradation of Chlorpyrifos and Cypermethrin Insecticides on γ -Alumina Surface

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الخلاصة

تم في هذا البحث دراسة عملية ونظرية لامتناهية و التحلل الضوئي للمبيدين الحشريين (الكلوربايرفوس والسايبيرمثرين) باستخدام ضوء الـ (UV) والكاما - الومينا كعامل محفز. تم التحلل باستخدام مذبيبي الماء والهكسان عند (pH=7-7.5) ووزن (0.1g) من العامل المحفز حيث وجد زيادة في سرعة التحلل لكلا المبيدين، حيث كانت تفاعلات التحلل الضوئي من المرتبة الاولى. ولوحظ ان زيادة درجة الحرارة تؤدي الى زيادة ثابت سرعة التفاعل $(0.8 \times 10^{-2} - 1.4 \times 10^{-2}) \text{min}^{-1}$ للكلوربايرفوس و $(1 \times 10^{-2} - 1.6 \times 10^{-2}) \text{min}^{-1}$ للسايبيرمثرين. وتم حساب طاقة تنشيط المبيدين وكانت القيم كالتالي $(22.971 \text{KJ. mol}^{-1})$ للكلوربايرفوس و $(13.127 \text{KJ. mol}^{-1})$ للسايبيرمثرين ووجد ان تفاعلات التحلل من النوع السريع. وتم حساب حراريات التكوين لكلا المبيدين عمليا ونظريا باستخدام برنامج hyper chem.8.0/semi-empirical(PM3) فكانت القيم $(20.452 \text{KJ. mol}^{-1})$ للسايبيرمثرين وكانت القيم موجبة والتي تدل على ان تفاعلات التحلل هي تفاعلات ماصة للحرارة. كما تم متابعة الاطياف الالكترونية والاهتزازية للمبيدين عمليا ونظريا قبل وبعد عملية التشعيع فوجد تغير واضح في الحزم خلال وبعد عملية التشعيع.

ABSTRACT

In this research, experimental and theoretical study of the adsorption and photodegradation of two insecticides (chlorpyrifos and cypermethrin) using the (UV) light and (gamma-alumina) as sensitizer. The photolysis of insecticides by using water and hexane as solvents at (pH=7-7.5) and (0.1g) of sensitizer were found increase the rate of decomposition of both insecticides. The reactions of photodegradation of insecticides followed the first order reactions. It was observed that the increasing in reaction temperature led to increase the rate constant of the reaction $(0.8 \times 10^{-2} - 1.4 \times 10^{-2}) \text{min}^{-1}$ for chlorpyrifos and $(1 \times 10^{-2} - 1.6 \times 10^{-2}) \text{min}^{-1}$ for cypermethrin. Activation energy of degradation were calculated and found $(22.971 \text{KJ. mol}^{-1})$ for chlorpyrifos and $(13.127 \text{KJ. mol}^{-1})$ which was relatively low, it explain the rapid reactions of insecticides. The values of heats of formation were calculated for both insecticides experimentally and theoretically using

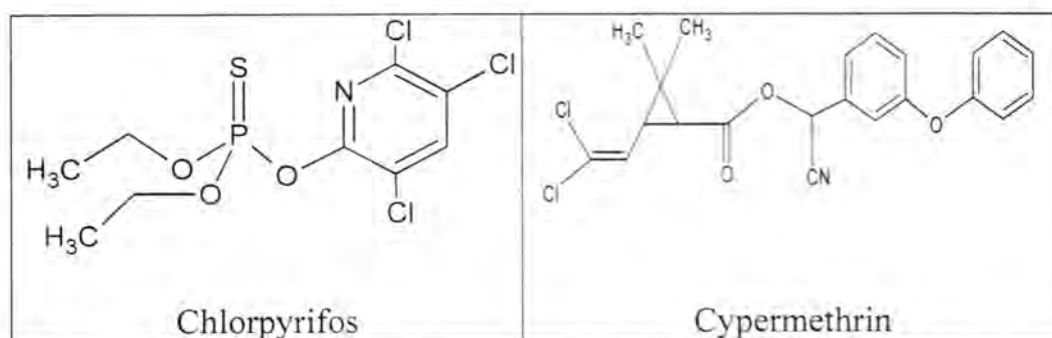
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the hyper chem.8.0/semi-empirical(PM₃) and the values were as follows (20.452 KJ. mol⁻¹, (21.56)_p KJ. mol⁻¹) for chlorpyrifos and (10.608KJ.mol⁻¹, (17.348)_p KJ. mol⁻¹) for cypermethrin, they showed a positive values which means that the decomposition processes of insecticides is an endothermic process. The electronic and vibrational spectra of both insecticides were identified experimentally and theoretically and found obvious changes.

INTRODUCTION

Chlorpyrifos and cypermethrin are two of the most important insecticides, which are widespread use. Chlorpyrifos as organophosphorus insecticides is acrySTALLINE solid dissolves, in water in addition to the solubility in acetone and ethylacetate and have a short half-life, the chemical name is (O,O-diethyl-O-(3,5,6-trichloro-2-pyridinyl)phosphorothioate(1). Cypermethrin is a pyrethroid insecticide, low solubility in water but it is soluble in organic solvents such as hexane, cyclohexane and chloroform(2).



Heterogeneous photocatalytic study were carried out for both insecticides experimentally by using UV light as a source and gamma-alumina as a catalyst(3), its formula is (γ -alumina) and molecular weight (101.96), insoluble in water and organic solvents. The reason for use of alumina is the presence within the contents of the soil well proportioned. The figure (1) show the crystal structure of γ -alumina(4):

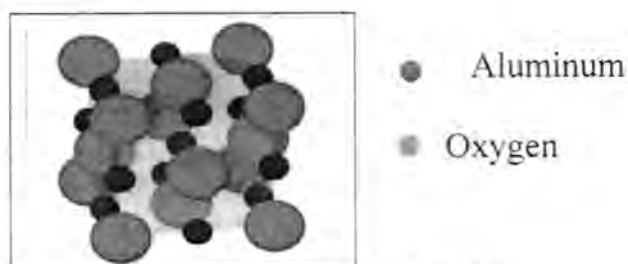


Figure 1: The crystal structure of γ -alumina

These two insecticides were studied theoretically using the program(hyper chem.8.0/ semi-empirical (PM₃)), this method is the most computational

speed and accuracy, applied to large molecules and are useful in the study of reactions of organic compounds(5).

Experimental

Chemical Materials

Common name	Molecular formula	Molecular weight	Purity	Company
Chlorpyrifos	$C_9H_{11}Cl_3NO_3PS$	350.5	98%	IPROCHEM(China)
Cypermethrin	$C_{22}H_{19}Cl_2NO_3$	416.3	93.5%	BILAG(Gordan)
Hexane	C_6H_6	78	99.8	GCC
γ - alumina	$\gamma - Al_2O_3$	101.69	99%	BDH

Instruments

- 1- UV-Visible spectra measurements by CARY 100 from VARIAN Co.
- 2- Infrared spectra measurements by SHIMADZU
- 3- pH meter (HANA)
- 4- Gas-Chromatography by Buck Model 910
- 5- Electronic balance AE220 Model by METLER

Preparation of Standard Solutions

1- Preparation of Standard Solution for Active Ingredient of Chlorpyrifos

The standard solution of chlorpyrifos was prepared by dissolving (0.3505g, 1mmol) of chlorpyrifos in 100ml of distilled water to get a concentration of ($1 \times 10^{-2}M$), which represents (Stock Sol.) of the active ingredient of chlorpyrifos and using the law of mitigation to prepare concentrations used in the process of Irradiation (2×10^{-3} $9 \times 10^{-3}M$).

2- Preparation of Standard Solution for Active Ingredient of Cypermethrin

The standard solution of cypermethrin was prepared by dissolving (0.416g 1mmol,) of cypermethrin in (100ml) of hexane to get a concentration of ($1 \times 10^{-2}M$), which represents (Stock Sol.) of the active ingredient of cypermethrin and using the law of mitigation to prepare concentrations used in the process of irradiation (4×10^{-5} $8 \times 10^{-5}M$)

Procedure

Placed 100ml of a solution of the active ingredient for chlorpyrifos or cypermethrin using the concentrations founding in (1,2) and (0.1g) of catalyst (gamma-alumina) was added. The mixture was placed in irradiation cell and connecting plastic pipes to the thermostat to regulate temperature, the samples using a UV-Visible light source (125 W), medium mercury pressure lamp. The pyrex cell has a quartz window, which was 15cm a put from the light source with a magnetic stirrer.

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Figure 2: The irradiation system used in the photocatalytic process

RESULTS AND DISCUSSION

Catalyst Effect

The effect of the presence of a catalyst (γ - alumina) on the rate of photolysis of the active ingredients of chlorpyrifos and cypermethrin through a comparison between the presence of the catalyst and its absence. This process has been carried on by irradiation of chlorpyrifos at concentration (8×10^{-3} mol/L) and cypermethrin at concentration (8×10^{-5} mol/L) at a temperature of (303^0K) and in the presence (0.1g) of a catalyst (γ -alumina). The change in the concentration of the active ingredients through the process of irradiation were followed in different times. Figures (3) and (4) showing the effect of the catalyst on the degradation rate of the active ingredients for chlorpyrifos in water and cypermethrin in hexane at temperature (303^0K) using (UV) light.

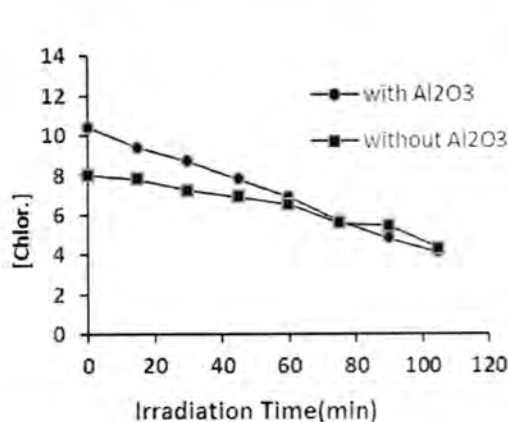


Figure 3: the effect of catalyst on degradation of chlorpyrifos

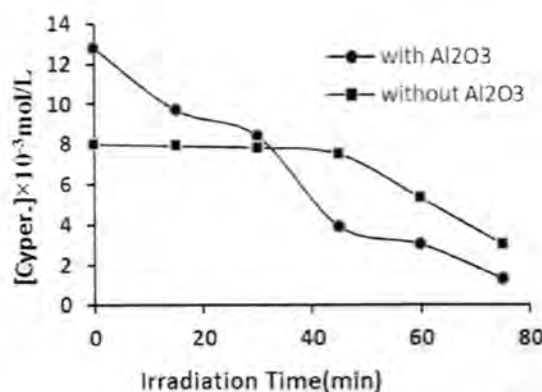


Figure 4: The effect of catalyst on degradation of cypermethrin

The results have shown that the degradation of the active ingredients of chlorpyrifos and cypermethrin using light through providing the

compounds with energy that needed and decomposition for excitation (6) as it has proved that the presence of the catalyst (gamma - alumina) increases the rate of reaction due to increase the absorption of a photon by the catalyst, leading to different mechanical degradation of the materials and this has proven by other researchers (7), where they have observed increasing the real concentration for the active ingredients with the addition of the catalyst and before irradiation process ($t = 0$) and the reason is due to adsorption of the active substances on the surface of alumina and the occurrence of reaction between them

Effect of initial concentration change

The study of initial concentration change of chlorpyrifos and cypermethrin on the reaction rate using UV light and gamma-alumina of weight (0.1g) in different times at constant temperature:

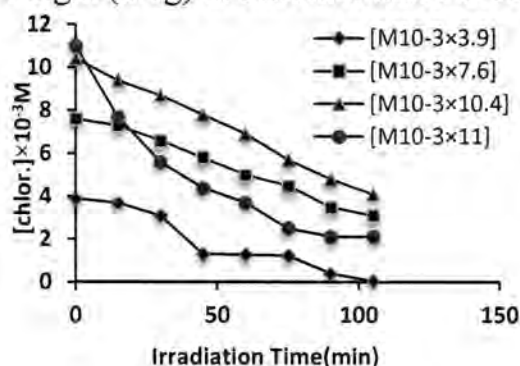


Figure 5: The relationship between the conc. of chlorpyrifos and irradiation time

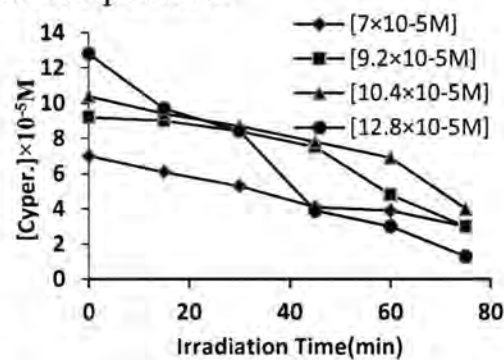


Figure 6: The relationship between the con. of cypermethrin and irradiation time

Kinetic studies

The UV-Visible spectroscopy is a good technology for follow-up the change in the concentration of chlorpyrifos in water at (pH=7.5) and cypermethrin in hexane at (pH=7) in different times with constant temperature (303⁰K) at wavelengths of ($\lambda_{max} = 318\text{nm}$) for chlorpyrifos and ($\lambda_{max} = 278\text{nm}$) for cypermethrin at a range between (200-500)nm during the irradiation of (105min) for chlorpyrifos and (75min) for cypermethrin. Figures (7) and (8) show the absorption spectra in the ultraviolet region for the active ingredients of chlorpyrifos in water and cypermethrin in hexane before and after irradiation process.

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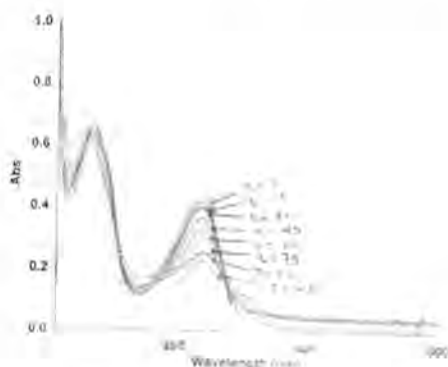


Figure 7: UV-Vis. absorption spectra for chlorpyrifos in water after and before irradiation process

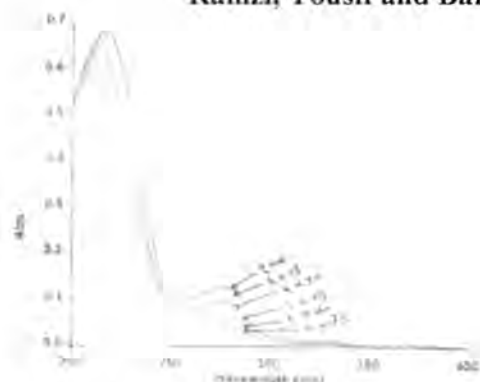


Figure 8: UV-Vis. Absorption spectra for cypermethrin in hexane after and before irradiation process

The decline in absorbance during the irradiation process every (15min) led to a decline in concentration of compounds, which was also accompanied by changing the pH from basic to the acidic medium and this is evidence for the degradation of both compounds(8).

Theoretically by using the hyper chem..8.0/semi-empirical(PM₃), table (1) show the comparison between the spectrum of electronic for active ingredients of chlorpyrifos and cypermethrin experimentally and theoretically.

Table 1: Comparison between the electronic spectrum of active ingredients for chlorpyrifos and cypermethrin

No.	Compound	Band (I)	Band (II)
		λ (nm)	λ (nm)
1	C ₉ H ₁₁ Cl ₃ NOPS	318 (322) _p	237 (250) _p
2	C ₂₂ H ₁₉ Cl ₂ NO ₃	278 (273) _p	218 (228) _p

P: semi-empirical(PM₃)

Figures (9) and (10) show the theoretical UV spectra for chlorpyrifos and cypermethrin theoretically:

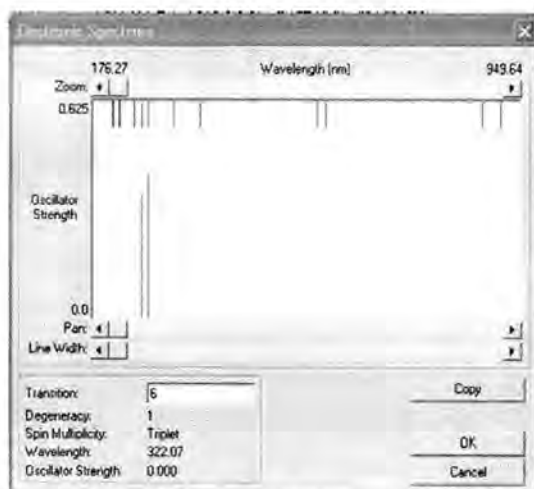


Figure 9: The theoretical UV spectra for chlorpyrifos

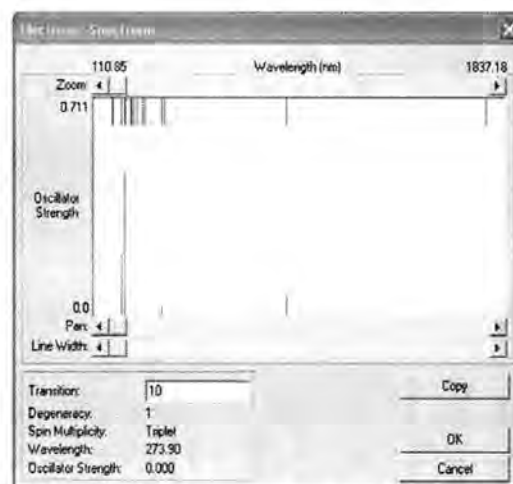


Figure 10: The theoretical UV spectra for cypermethrin

The reaction order was determined by the following equation:

$$\ln \text{Rate} = \ln k + n \ln [\text{Conc.}] \quad \dots(1-3)$$

k: rate constant

n: reaction order

A straight line was given by draw $\ln \text{Rate}$ versus $\ln [\text{Conc.}]$. The slope of the straight line represent the reaction order. Figures (11) and (12) represent the relationship between $\ln[\text{conc.}]$ and $[\ln \text{Rate}]$ of chlorpyrifos and cypermethrin:

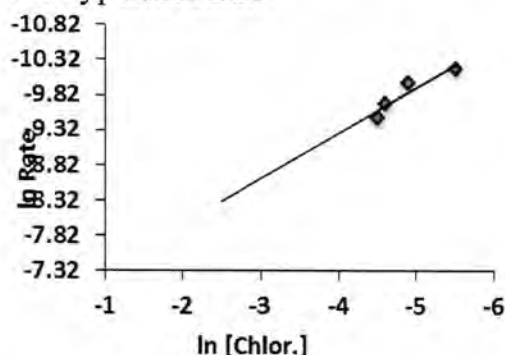


Figure 11: The relationship between $\ln[\text{chlor.}]$ and $\ln \text{Rate}$

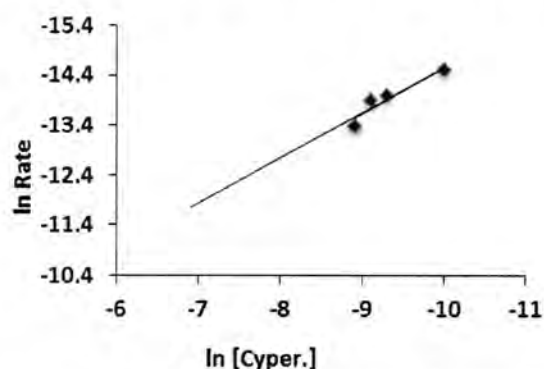


Figure 12: The relationship between $\ln[\text{cyper.}]$ and $\ln \text{Rate}$

The catalytic photodegradation reaction for both insecticides showed first order reaction and therefore these reactions are simple reactions (one step). The reaction rate constant is calculated by drawing the relationship between $\ln [\text{conc.}]$ versus irradiation time for insecticides. Figures (13) and (14) demonstrated the relationship between $\ln [\text{conc.}]$ versus time of irradiation for chlorpyrifos and cypermethrin at a temperature of (303^0k) .

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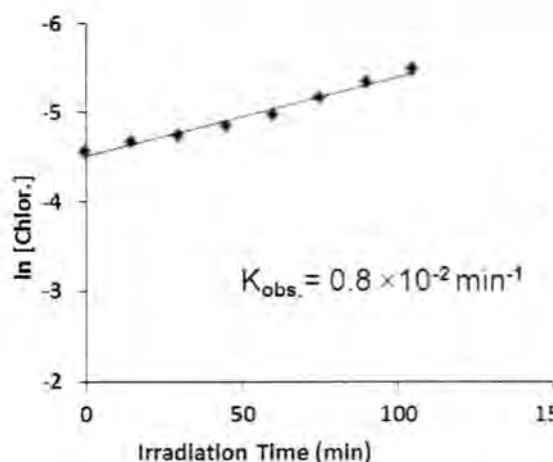


Figure 13: The relationship between $\ln[\text{chlor.}]$ versus irradiation time

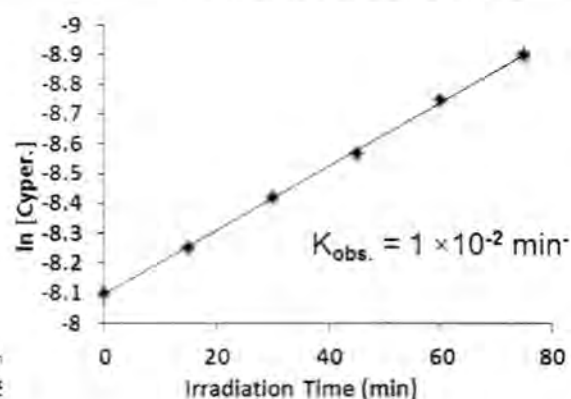


Figure 14: The relationship between $\ln[\text{cyper.}]$ versus irradiation time

The tendency of this relationship was obtained the rate constants. The half-life time of the reactions as a first order were obtained through the following relationship:

$$t_{1/2} = 0.693 / K \quad \dots\dots(2-3)$$

Table (2) shows the values of rate constant (K) and half-life time ($t_{1/2}$) of chlorpyrifos and cypermethrin:

Table 2: The values of K and $t_{1/2}$ for chlorpyrifos and cypermethrin

No.	Compound	$K \times 10^{-2} (\text{min}^{-1})$	$t_{1/2} (\text{min})$
1	$\text{C}_9\text{H}_{11}\text{Cl}_3\text{NOPS}$	0.8	86.62
2	$\text{C}_{22}\text{H}_{19}\text{Cl}_2\text{NO}_3$	1	69.3

Effect of Temperature Change

The effect of temperature change on rate constant of photolysis reaction were studied for the active ingredients of chlorpyrifos and cypermethrin in the solvents water and hexane using (UV) light and the presence of (0.1g) catalyst (gamma-alumina). The irradiation process carried out under different thermal conditions (303° , 313° , 323° , 333°)K, Where the following equation was applied to find the rate constant:

$$\ln [C_t] = \ln [C_0] - k_{\text{obs.}} \cdot t \quad \dots\dots(3-3)$$

Table (3) represent the values of rate constant in different temperatures for both insecticides:

Table 3: The values of rate constant in different temperatures for chlorpyrifos and cypermethrin

Temperature(K)	303 ⁰	313 ⁰	323 ⁰	333 ⁰
$K \times 10^{-2}(\text{min}^{-1})$ for chlorpyrifos	0.8	1.1	1.3	1.4
$K \times 10^{-2}(\text{min}^{-1})$ for cypermethrin	1	1.2	1.4	1.6

It was observed that increasing temperature led to increase the rate constant of decomposition.

The activation energy which show the type of the reactions were calculated, it was showed whether the reaction rapid or slow from arrhenius equation

$$k = A \cdot e^{-E_a/RT} \quad \dots\dots(4-3)$$

By taking the logarithm of the parties....

$$\ln k = \ln A - \frac{E_a}{RT} \quad \dots\dots\dots(5-3)$$

Plotting the relationship between $1/T$ versus $\ln K$ as in figures (15) and (16). the slope gave activation energy .

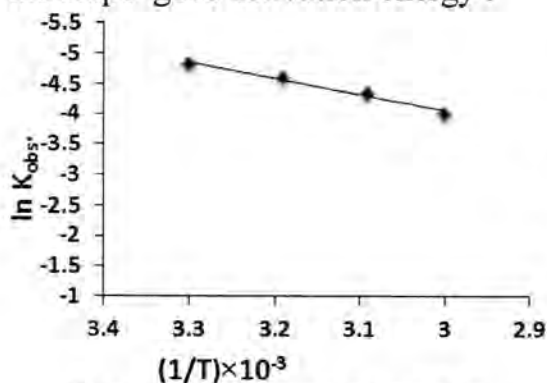


Figure 15: The relationship between $\ln K$ versus $1/T$ for chlorpyrifos

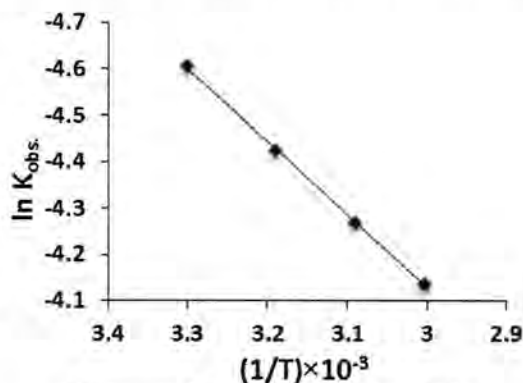


Figure 16: The relationship between $\ln K$ versus $1/T$ for cypermethrin

We note that the value of activation energy ($E_a=22.971\text{KJ.mol}^{-1}$) for chlorpyrifos and ($E_a=13.127\text{KJ.mol}^{-1}$) for cypermethrin, these values are low that means the reactions were fast and the reason is the surface of alumina contributes to reduce the activation energy by adsorbing the insecticides molecules on the surface and makes it easier to decompose(9).

The heats of formation values for the two insecticides are calculated experimentally by using the equation(10):

$$E_a = \Delta H + RT \quad \dots\dots\dots(6-3)$$

Theoretically by using hyper chem.8.0/semi-empirical(PM₃), table (4) show the values of heats of formation for chlorpyrifos and cypermethrin experimentally and theoretically.

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Table 4: The values of ΔH_f for chlorpyrifos and cypermethrin experimentally and theoretically

No.	Compound	ΔH_f (KJ. mol ⁻¹)
1	C ₉ H ₁₁ Cl ₃ NOPS	20.452 (21.56) _P
2	C ₂₂ H ₁₉ Cl ₂ NO ₃	10.608 (17.348) _P

P: semi-empirical(PM₃)

I.R. Spectroscopy

Active ingredients for chlorpyrifos and cypermethrin possesses many of the bands belonging to the groups consisting in molecules (chlorpyrifos and cypermethrin). Figures (17), (18), (19) and (20) show the IR spectra for chlorpyrifos and cypermethrin before and after the photolysis process:

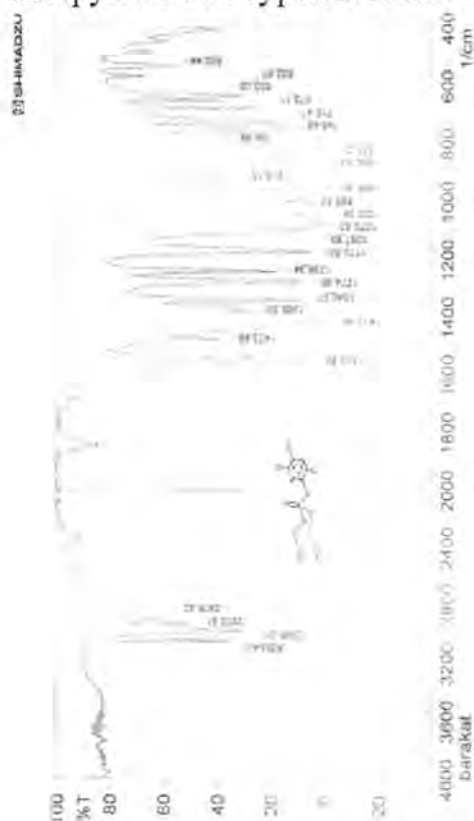


Figure 17: IR spectra for chlorpyrifos before photolysis



Figure 18: IR spectra for chlorpyrifos after photolysis process

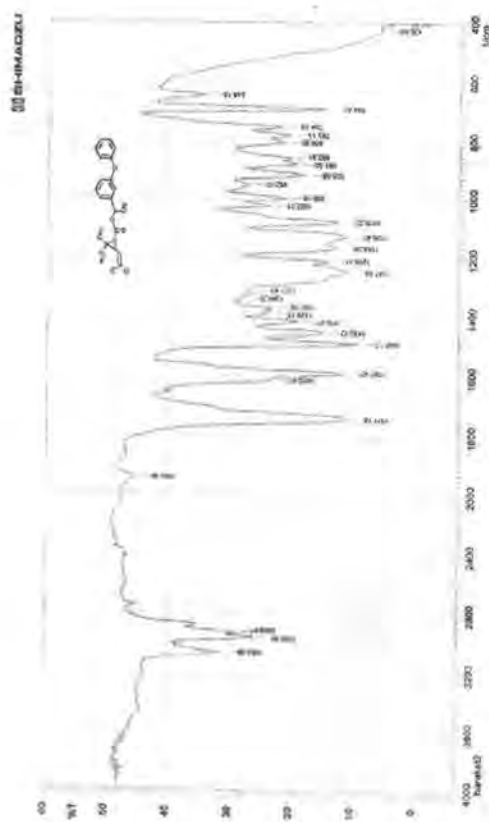


Figure 19: IR spectra for cypermethrin before photolysis

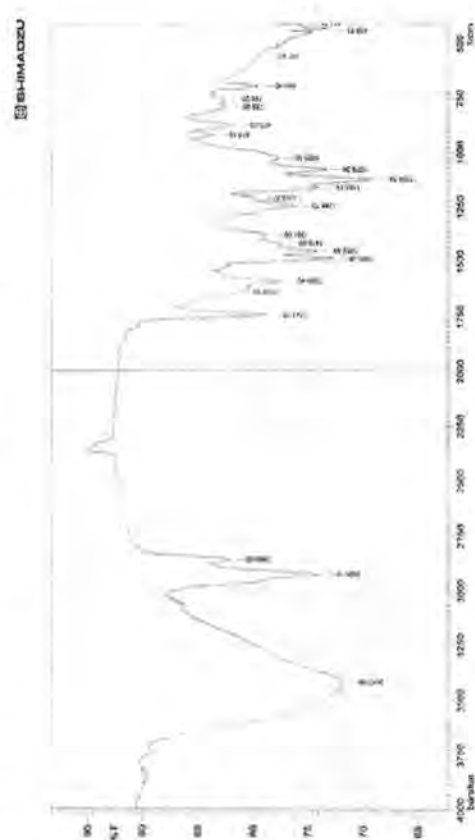


Figure 20: IR spectra for cypermethrin after photolysis process

Theoretically by using hyper chem..8.0/semi-empirical(PM₃), tables(5) and (6) show the comparison between the spectrum of IR for chlorpyrifos and cypermethrin experimentally and theoretically.

Table 5: The comparison between the vibrational spectra of chlorpyrifos experimentally and theoretically

No.	Compound	V _{P=S}	V _{C=N}	V _{C=C}	V _{C-H} aliphatic	V _{C-H} aromatic	V _{C-O}
1.	C ₉ H ₁₁ Cl ₃ NOPS	850.2 (837.67) _P	1550.8 (1555.28) _P	1647.26 (1667.9) _P	1411.9 (1411) _P	3053.4 (3004) _P	1274.9 (1277) _P

P: semi-empirical(PM₃)

Table 6: The comparison between the vibrational spectra of cypermethrin experimentally and theoretically

No.	Compound	V _{C-Cl}	V _{C=N}	V _{C=O}	V _{C=C} aliphatic	V _{C=C} aromatic	V _{Aryl-O}
1.	C ₂₂ H ₁₉ Cl ₂ NO ₃	694.4 (686.2) _P	2100 (2019) _P	1741.78 (1752.8) _P	1410.01 (1403.8) _P	1487.47 (1511) _P	1247 (1253.4) _P

P: semi-empirical(PM₃)

Figures (21) and (22) show the vibrational spectra for chlorpyrifos and cypermethrin theoretically by using hyper chem..8.0/semi-empirical(PM₃)

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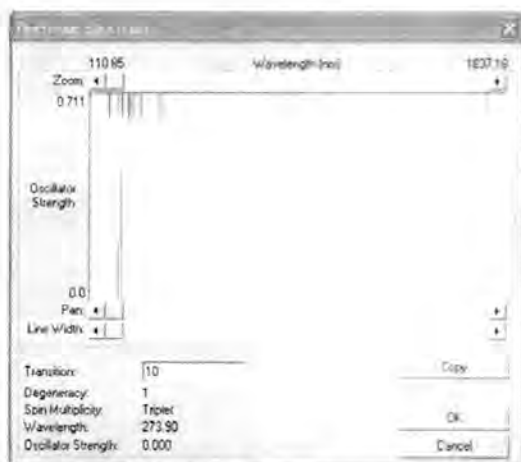


Figure 21: The vibrational spectra of chlorpyrifos theoretically



Figure 22: The vibrational spectra of cypermethrin theoretically

-The photolysis mechanism for chlorpyrifos and cypermethrin

A mechanism for degradation of chlorpyrifos and cypermethrin were suggest depending on the results of the UV-Vis., I.R. technique and determination Cl^- . figures Figures (23) and (24) show the mechanism for the both compounds:

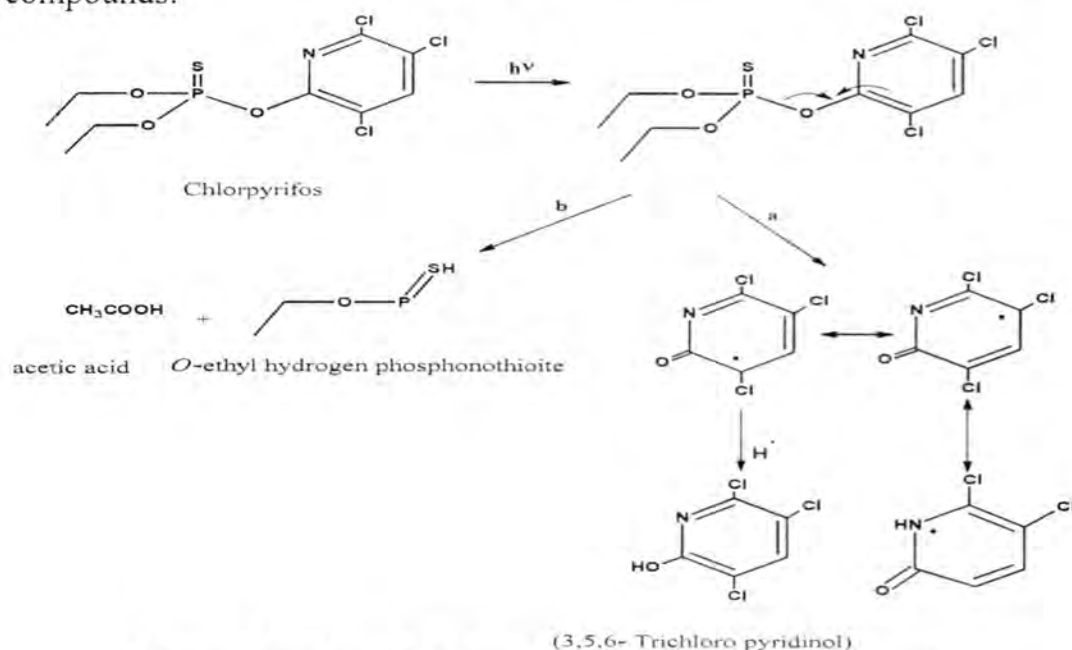


Figure 23: The photolysis mechanism for chlorpyrifos

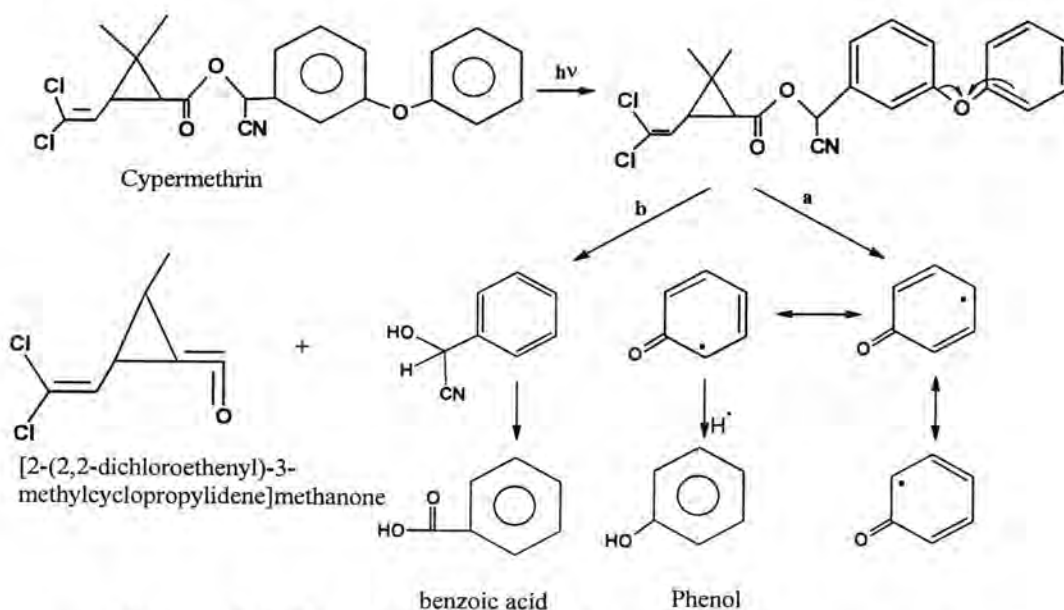


Figure 24: The photolysis mechanism for cypermethrin

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Some Hormonal changes in Women With Polycystic Ovary Syndrome (PCOS)

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الخلاصة

يعد مرض تكيس المبيض من الامراض الشائعة في الاباضة المزمنة المصحوبة بزيادة تكون الاندروجين ويحدث بنسبة 5-10% في النساء في مرحلة البلوغ. وكذلك يعد من أمراض الغدد الصماء الشائعة في النساء ما قبل سن اليأس. يصاحب اعراض هذا المرض انقطاع الطمث، انقطاع الطمث المتعدد، الشعر وخشونة الصوت، وعادة يصاحبه زيادة في الوزن مصحوبا بمقاومة الأنسولين. ان اكثر النساء المصابات ب PCOS لديهم مقاومة ملحوظة للأنسولين اكثر مما عن زيادة معامل كتلة الجسم BMI. وجد في دراستنا ان 32 مريضة بتكيس المبيض منهن 91.4% يقعون ضمن الفئة العمرية 15-35 سنة. ولوحظ ان 29.4% من النساء المصابات الغير متزوجات يعانين من زيادة في الوزن وال 58.8% منهن يعانين من السمنة إلا ان 55.6% من النساء المصابات المتزوجات يعانين من زيادة في الوزن و 44.4% منهن يعانين من السمنة. ولقد وجد ان 80% (28) من المرضى لديهم مصابين بالمرض ضمن تاريخ العائلة. لوحظ هناك زيادة معنوية ($P < 0.05$) عند قياس مستوى السكري (FPG) و (C-peptide) في النساء المصابات المتزوجات والغير متزوجات مقارنة بالاصحاء. في ال PCOS يزداد افراز ال LH بشكل تضاعفي في حين تكون زيادة ال FSH قليلة جدا او قد لا يتغير، ان نسبة LH:FSH يمكن ان تزداد الى اكثر من 2.5. اما بالنسبة لهرمون البرولاكتين (PRL) فلا توجد زيادة معنوي ($p < 0.05$) . ولقد لاحظنا بوجود زيادة ملحوظة في مستويات Prog، Testo، E_2 في المرضى المصابين للمتزوجات وغير المتزوجات مقارنة بالنساء الطبيعيات ب ($p < 0.05$).

ABSTRACT

Polycystic Ovary Syndrome (PCOS) is the most common form of chronic anovulation associated with androgen excess, occurring in 5-10% of reproductive age women. It is also the most common endocrine abnormality in premenopausal women. It is typically presents with amenorrhoea, oligomenorrhoea, hirsutism and acne, and commonly occurs at mid-twenties of age. It is now known that weight gain in both normal women and those with PCOS is associated with increasing insulin resistance. Most women with PCOS have insulin resistance to a significantly greater extent than in age and body mass index (BMI). In our study, 32(91.4%) of patients with PCOS fall in the age group 15-35 years. In single patients (not married)

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29.4% of them suffering over weight and 58.8% suffering obesity, but 55.6% of married patients suffering over weight and 44.4% of them was obesity. There were 28(80%) of patients with positively family history. A significant increase ($p < 0.05$) in Fasting Plasma Glucose (FPG) and C-peptide levels in patients with PCOS (in both single and married) as compared to normal women. In PCOS, the normal pulsatile secretion of LH is increased by an increased frequency and amplitude of pulses, while that of FSH is unchanged or muted, and the LH: FSH ratio can be increased to more than 2.5. There was no significant increase in PRL level ($p > 0.05$). We notice that there were a significant increases in progesterone (prog), testosterone (Testo) and Estradiol (E_2) levels in both single and married patients as compared with normal women ($p < 0.05$).

INTRODUCTION

Polycystic Ovary Syndrome (PCOS) is the most common form of chronic an ovulation associated with androgen excess, occurring in 5-10% of reproductive age women[1]. It is also the most common endocrine abnormality in premenopausal women[2]. It is typically presents with amenorrhoea, oligomenorrhoea, hirsutism and acne, and commonly occurs at mid-twenties of age [3-5].

In 1935, Stein and Leventhal published their findings in seven women with amenorrhoea, hirsutism, obesity, and a characteristic polycystic appearance to their ovaries, which was one of the first descriptions of this complex phenotype known as the PCOS [6,7].

A precise and uniform definition of the syndrome is lacking. An international consensus group [8] recently proposed that the syndrome can be diagnosed after the exclusion of other medical conditions that cause irregular menstrual cycles and androgen excess, and the determination that at least two of the following are present:

Oligoovulation or anovulation (usually manifested as oligomenorrhoea or amenorrhoea), elevated levels of circulating androgens (hyperandrogenemia) or clinical manifestations of androgen excess (hyperandrogenism), and polycystic ovaries as defined by ultrasonography[9].

These criteria acknowledge the condition as functional: polycystic ovaries need not be present to make a diagnosis of the PCOS [10], and conversely, their presence alone does not establish the diagnosis [11, 12]. Women with PCOS almost always some aberration in gonadotropin secretion as compared with women who have normal menstrual cycles [13]. While insulin resistance is not part of the diagnostic criteria for PCOS, its importance in the pathogenesis of PCOS cannot be defined. PCOS is associated with insulin resistance independent of total or fat free body mass. Post-receptor defects in the action of insulin have been described in PCOS which are similar to those found in obesity and type 2 Diabetes [14].

It is now known that weight gain in both normal women and those with PCOS is associated with increasing insulin resistance. However, most women with PCOS (between 50% and 90% depending on the diagnostic criteria used) have insulin resistance to a significantly greater extent than in age and body mass index (BMI). Matched control women, this disparity being more marked for higher BMIs [15-17].

Hirsutism is defined as excessive hair growth in area usually associated with male sexual maturity, that is, on the face, chest, lineal alba, lower back, buttocks, and anterior thighs. Hirsutism results from androgen effects on the pilosebaceous unit and is commonly associated with acne and oily skin. It is usually due to increased androgen production from the ovaries or adrenal glands [18].

Luteinizing hormone (LH) and Follicle stimulating hormone (FSH) are two hormones from the pituitary glands, which are associated with the normal cycling of the ovary. In PCOS, the normal pulsatile secretion of LH is increased by an increased frequency and amplitude of pulses, while that of FSH is unchanged or muted. Thus, LH values may elevate, and the LH:FSH ratio can be increased to more than 2.5, even in ovulatory cycles. On the other hand, these values may be normal in as many as 12% to 20% of women with PCOS [19].

MATERIALS AND METHODS

This study performed on (15) normal women and (35) women with proved polycystic ovary syndrome (PCOS), (18) women was married and (17) single (i.e. not married), attending the specialized center of Endocrinology and Diabetes in Baghdad, from July till December 2010.

In addition to measuring body mass index (BMI) and hirsutism. The C-peptide level and fasting plasma glucose (FPG) level were estimated for normal and all patients, also the level of a number of hormones were tested by enzyme linked fluorescent assay (ELFA) method using Biomerieux kit, as part of the investigations for menstrual disturbances, hirsutism, or infertility, and these included: serum Luteinizing hormones (LH), Follicle stimulating hormone (FSH), Prolactin (PRL), progesterone (prog), testosterone (Testo), Estradiol (E_2).

RESULTS AND DICSSION

Our results from table (1) shows that the most common prevalence of PCOS falls in the age group 15-35, and family history was positive for PCOS in 28 patients(80%) which stresses that an effort should be spent on detecting and managing these cases.

Table 1: Age, Duration and FH of PCOS.

Age group (years)	No. & %	Duration	No. & %	FH	
15-25	16 (45.7%)	< 5 y	13(37.1%)	Yes	No
26-35	16 (45.7%)	6-10 y	18(51.4%)	28(80%)	7(20%)
36-45	3 (8.6%)	> 10 y	4(11.5%)		
Total	35 (100%)		35(100%)		

No. = Number, FH = Family history, PCOS = Polycystic ovary syndrome.

Thirty two patients (91.4%) fall in age group of 15-35 which is the child-bearing age. This is in agreement with other studies [20].

Table (2) shows the Body Mass Index (BMI) in normal women and Patients with PCOS (in single and married).

Table 2 : BMI for normal and Patients with PCOS (S & M).

BMI range (Kg/m ²)	Control No. & %	Patients	
		(*S) No. & %	(**M) No. & %
< 20	0	0	0
19 – 24.9	15(100%)	2(11.8%)	0
25 – 29.9	0	5(29.4%)	10(55.6%)
≥ 30	0	10(58.8%)	8(44.4%)
Total	15(100%)	17(100%)	18(100%)

*S = Single Patients (not married), **M = Married Patients.

From this table we concluded that all control women in normal range of BMI (19-24.9 Kg/m²), but in single patients with PCOS there were only 2(11.8%) patients in normal range and 5(29.4%) patients were over weight (25-29.9 Kg/m²). But in married patients there were 10(55.6%) patients was over weight, and 8(44.4%) were suffering obesity. This is in agreement with Panidis *et al.*(2005) and Legro (2000), which explained that many women with PCOS (between 38% and 88%) were over weight or obese [21,22].

Table (3) shows that thirty patients (85.7%) have increased weight with hirsutism.

Table 3: The presentation & Duration.

Presentation	< 3y No.& %	>3 y No.& %	Total
Increase wt +Hirsuit.	28 (80%)	2 (5.7%)	30 (85.7%)
Increase wt only	3 (8.6%)	2 (5.7%)	5 (14.3%)

Wt. = weight.

Hirsuit. = Hirsutism.

Hirsutism and increased weight were present in 30 patients (85.7%) which go with the international percentage of hirsutism among women with PCOS, which is around 80% [23].

A significant increase ($p < 0.05$) in Fasting Plasma Glucose (FPG) and c-peptide levels in patients with PCOS (in both single and married) as compared to normal women as shown in table (4), and there were no different in single and married values.

Table 4 : The FPG & c-peptide levels in normal women and PCOS patients

Groups	Mean \pm SD			
	FPG	p-value	c-peptide	p-value
Normal	4.683 \pm 0.562		3.012 \pm 0.156	
Single patients	5.908 \pm 1.358	0.018	3.536 \pm 0.174	0.032
Married patients	5.016 \pm 0.793	0.022	3.825 \pm 0.176	0.030

These findings were in agreement with previous reports of increased FPG & c- peptide with AL-Lehibi study in 2009, which explained when the pancreas produces more insulin, excessively high levels of insulin stimulate the ovaries to dramatically over produce androgens, insulin resistance may lead diabetes mellitus [24].

The hormones tests of LH, FSH and PRL shows that there was significant increase of LH and FSH levels in women with PCOS as compared to there normal levels in an elevation ($p < 0.05$), but there was no significant increase in PRL level ($p > 0.05$). And there were a little different between single and married patients in there levels.

Table 5: The LH, FSH and PRL levels in normal and PCOS patients.

Groups	Mean \pm SD						LH:FSH ratio(≥ 2.5) No. & %
	LH	p-value	FSH	p-value	PRL	p-value	
Normal	6.750 \pm 1.647		7.966 \pm 1.711		10.041 \pm 3.652		
Single Patients	17.075 \pm 4.592	0.016	7.508 \pm 2.303	0.017	20.141 \pm 8.429	0.152	3 (17.6%)
Married patients	22.250 \pm 8.745	0.021	10.883 \pm 6.406	0.021	30.866 \pm 7.259	0.134	5 (27.7%)

LH and FSH are the pituitary hormones that control ovarian function. Normally, FSH is higher than LH. In women with PCOS, this ratio can be reversed, with LH being higher than FSH [25]. In PCOS, the normal pulsatile secretion of LH is increased by an increased frequency and amplitude of pulses, while that of FSH is unchanged or muted. Thus, LH values may be elevated, and LH: FSH ratio can be increased to more than 2.5, even in ovulatory cycles. On the other hand, these values may be normal in as many as 10% to 20% of women with PCOS [26].

In this study the serum concentrations of LH to FSH ratio increased (≥ 2.5) in 3 (17.6%) single patients with PCOS and 5 (27.7%) in married patients. This ratio at the end of 1985 was still perceived as a "gold standard" for diagnosis of PCOS, and the coexistence of insulin resistance and hyperinsulinemia was only emerging as a potential pathogenic factor. The over production of LH and consequently the incorrect LH: FSH ratio is nowadays considered not to be a characteristic attribute of all PCOS patients[27].

Elevated Prolactin levels can cause irregular periods. It is a pituitary hormone that controls breast milk production. If mildly elevated, it can adversely affect ovulation [26].

When the hormones progesterone (prog), testosterone (Testo) and Estradiol (E_2) were tested, we notice that there were significant increases in these hormones in both single and married patients as compared with normal women, and there were no difference in the increasing in single and married patients as shown in table (6).

Table 6: Prog, testo and E_2 levels in normal and patients with PCOS .

Groups	Mean \pm SD					
	Prog	p-value	Testo	p-value	E_2	p-value
Normal	6.525 \pm 2.854		0.483 \pm 0.225		237.083 \pm 85.088	
Single Patients	10.266 \pm 5.245	0.049	1.358 \pm 0.389	0.023	265.916 \pm 99.885	0.034
Married patients	10.050 \pm 5.490	0.028	1.433 \pm 0.441	0.021	283.583 \pm 110.23	0.042

These results were in agreement with Dunaif study in (1993) that explained, elevated total testosterone is the most direct evidence for androgen excess, varying levels of progesterone and testosterone are present in women with PCOS. It is much more common to observe high normal levels or border line elevations of testosterone in women with PCOS [28].

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Synthesis, Characterisation of Palladium (II) and Zirconium(IV) complexes with Schiff base N-(2-Azo-3-Sulphonic-2-Naphthol) 6- Carboxylic Anilino 2- hydroxyl benzildene, and 5- amino-3-[4-O-hydroxyphenyl thiosemicarbazido]-1,2,4- thiadiazol, and Study of Activation on GPT Enzyme by these complexes

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الخلاصة

تم في هذا البحث تحضير معقدي البلاتيوم (II) والزركونيوم (IV) مع قاعدة شف (L1) -N (2- أزو - 3 - سلفونك-2-نفثول) 6- كاربوكسيلك أنيلينو 2- هيدروكسيل بنزيلدين و الليكاند (L2) 5- امينو-3-[4-اورثو- هيدروكسي فنييل ثايو سيميكاربازيدو] -1,2,4- ثياديازول، شخّصت ودرست تراكيب المعقدات باستخدام الطرائق الفيزيائية المناسبة وهي تحليل طيف الأشعة تحت الحمراء (IR) ، طيف الأشعة فوق البنفسجية المرئية (UV-Vis.) ، قياس درجة الانصهار. كما تم قياس النسبة المولية في المحلول ووجدت ان النسبة كانت (1:1) وتم اقتراح التراكيب المحتملة للمعقدات المحضرة . كما درس تأثير هذه المعقدات على فعالية أنزيم النين امينو ترانسفيريز في مصل الدم . أظهرت المعقدات تأثير تنشيطي على فعالية انزيم النين امينو ترانسفيريز. وان قدرة هذه المعقدات على تغيير فعالية الانزيم تزداد طردياً مع زيادة تركيزها.

ABSTRACT

The Schiff base (L1) N-(2-Azo-3-Sulphonic-2-Naphthol) 6- Carboxylic Anilino 2- hydroxyl benzildene and (L2) 5- amino-3-[4-O-hydroxyphenyl thiosemicarbazido]-1,2,4- thiadiazol were used as ligands to prepare of metal complexes with metal ion such as {Pd (II) , Zr (IV) }the prepared complexes were studied and characterized by appropriate physical measurements , i.e., IR , UV-Vis., melting point . Molar ratio measurements in DMSO solution give (1:1) results, probable structures of the prepared complexes were assigned. Complexes were studied to show their effects on the GPT activity of enzyme in the human serum. Complexes demonstrated activation on GPT enzyme, and these effects increased with increasing the concentration of the complexes.

INTRODUCTION

Compounds that contains the -N-C= moiety is included in many basic structures of drugs either to be a part of open chain , e.g.thiocarbamates (R-N-C-S-) , isothiocy-anates (R-N=C=S) and thiosemicarbamates (R-N-C-N-

Synthesis, Characterisation of Palladium (II) and Zirconium(IV) complexes with Schiff base N-(2-Azo-3-Sulphonic-2-Naphthol) 6- Carboxylic Anilino 2- hydroxyl benzildene, and 5- amino-3-[4-O-hydroxyphenyl thiosemicarbazido]-1,2,4-thiadiazol, and Study of Activation on GPT Enzyme by these complexes

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NR2), or involved in heterocyclic ring, e.g. mercapto derivatives of triazole, oxadiazole, imidazole, and thiodiazole. These are important and versatile class of well established biologically active compounds (1), with interesting structural features and behavior. Thiotriazoles are considered to be good coordinating compounds because they contain the NCS group, and presence of unsaturated group in these ligands make them capable to form of organometallic compounds by coordination to a number of metal ions(2). The synthesis of transition metal complexes with thiosemicarbazone ligand due to the pharmacological properties of both ligand and complexes great variety of biological activities, such as anti tumor, antifungal properties. The deprotonated thiosemicarbazone ligands usually coordinate to osmium through oxygen, nitrogen, and sulphur donor atoms in tridentate form, to form metallic complexes of different molecular(3). The present work the researcher report synthesis of metal complexes with 1,2,4-thiadiazole derivatives and biological studied. The structures of the prepared compounds were suggested on the basis of spectral analyses. Schiff bases from stable complexes with metals that perform important role in biological systems, they find also wide application in analytical chemistry since they allow simple and inexpensive bases complexes were found to be very effective catalysts for hydrolytic cleavage or transesterification of RNA phosphate diester back bone, therefore metal complexes of Schiff bases attained a prominent place in coordination chemistry (4,5). complexes of Pd (II), Pt (II) and Ru (II) with ligands containing amide and thioamide groups described in our laboratory are likely to possess anti-cancer activity(6).

Glutamate Pyruvate Transaminase (GPT) activity(EC 2.6.1.2) :-

Transaminase, GPT It's also called alanine amino transferase (ALT) it's one of the thousands kind of liver enzymes, and kind of transfers, having the function of transferring amino group of amino acids from alpha -amino acid to alpha -keto acids, therefore; named transaminase (7). GPT which is prevalent in mammalian tissue catalyzes the transfer of the amino group of alanine to α -ketoglutarate. The transamination reaction is important in intermediary metabolism because of function in the synthesis and degradation of amino acids. The keto acids formed by the reaction are ultimately oxidized by the tricarboxylic acid cycle to provide a source of energy(8). GPT found in a highest concentration in liver in spite of its active occurrence in skeletal muscles, heart and kidney. The GPT activity in tissues is generally less than GOT.

Elevation of the serum level mainly due to damages of liver, myocardial, striated muscle and red blood cell, according to Wroldewski and La Due

(karmen unit /1gm wet weight), in 1954, La Due first reported the elevation of serum GOT in acute myocardial infraction, in 1955, De Ritis reported the elevation of GOT & GPT in hepatitis, it has been used as the marker of liver damage since then until now (9-13).

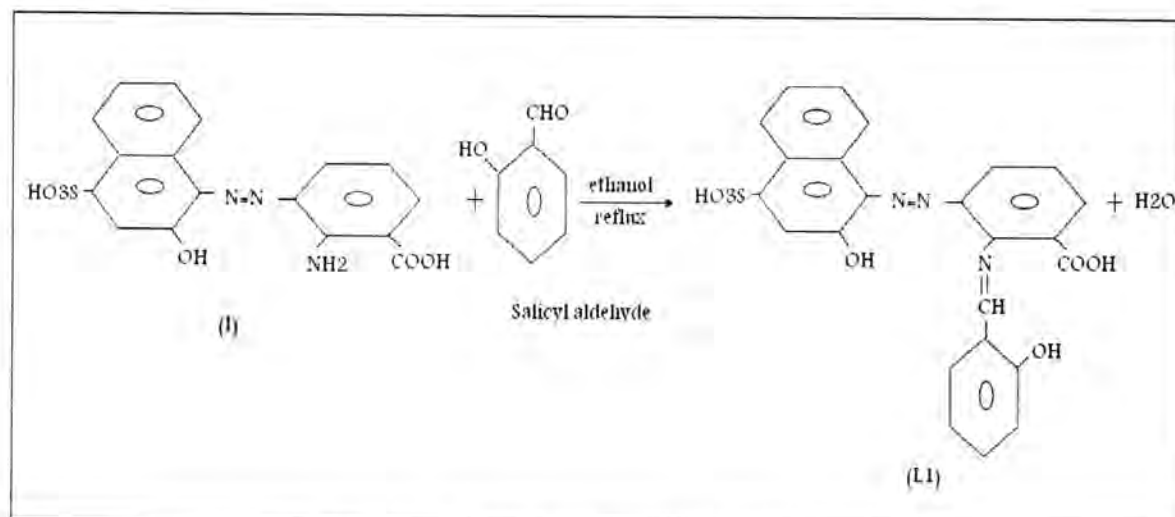
GOT, GPT exist mainly in liver and myocardium, and in less kidney and pancreas (14). The concentration of GOT and GPT are 1,000-10,000 times of serum, in liver or cardiac damages, large amount of transaminase are released in to serum, therefore; it show very high sensitivity in detection of liver and cardiac damages, GPT is more sensitive and specific than GOT in detection of liver damages (15). GPT is contained only in cytosol of cell, but GOT present in both cytosol and mitochondria cell (16).

MATERIALS AND METHODS

All materials were supplied from (BDH) and fluk CO. Ethanol absolute (99.96%), (3%) NH_3 solution. Salicylaldehyde (98%), {3-(2-naphthol-4-sulphonic) Azo-2-aminobenzoic acid} (I) was prepared according to the literature (17,18). Melting points were recorded SMP1. IR spectra were obtained using pye-Unicam SP3-300 infrared spectrophotometer for the range $(200-4000) \text{ cm}^{-1}$ by using CsI discs. Electronic spectra (UV-Vis.) were obtained using shimadzu UV-1600 series spectrophotometer in DMSO solvent. Kit of GPT was supplied from Biomegrebe Co.

1-Synthesis of ligands:-

a- (L_1): The Schiff base ligand (L_1) was prepared by reacting (0.0011 mol, 0.27 gm) salicyl aldehyde in 15 ml absolute ethanol and (0.0011 mol, 0.74 gm) azo compound (I) the reaction mixture was refluxed gently for (4 hr.) cool and leave in a refrigerator for (48 hr.), the product was filtered off and recrystallized from ethanol and dried under vacuum, scheme (1).

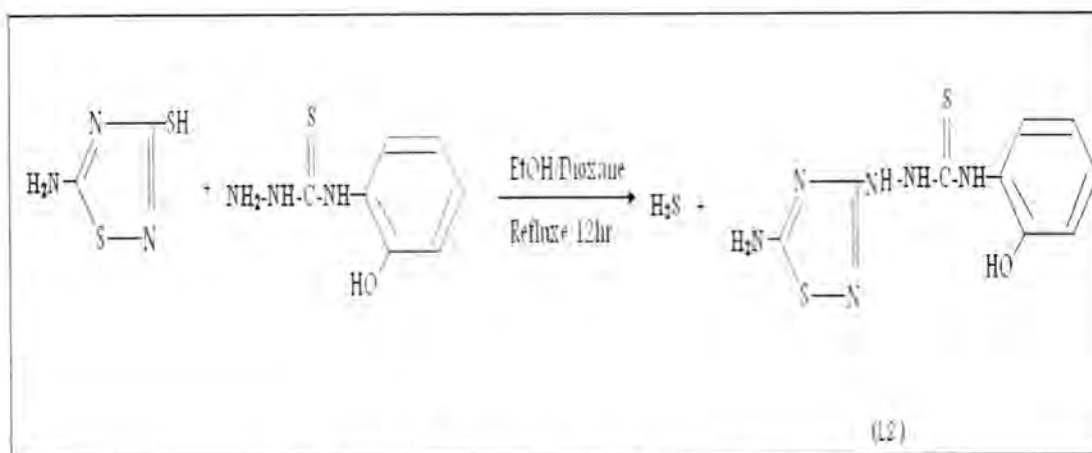


Scheme 1: Synthesis of ligand (L_1)

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b-(L₂): An ethanolic solution of (25 ml) of 5-amino-3-mercapto-1,2,4-thiadiazole (0.01 mole, 1.33 gm) was added to a solution of (0.01 mole, 1.83 gm) O- hydroxyl phenyl thiosemicarbazide dissolved (15 ml ethanol absolute+5 ml Dioxane). The mixture was refluxed gently for (12 hr.) upon – cooling , a yellow solid was separated. The product (1.9 gm ,70%) was recrystallized from ethanol , and dried , scheme (2).



Scheme 2: Synthesis of ligand (L₂)

2-Synthesis of complexes:-

a- [M(L₁)Cl₂]: Complexes were prepared by addition of metal salts (1.05 mmole , 0.147 gm PdCl₂ , 0.24 gm ZrCl₄) in 10 ml a hot ethanol solution then 3 % NH₃ solution was added with stirring the above solution was gradually added to (1 mmole , 0.49 gm) of ligand (L₁) in 10 ml of ethanol , the mixture was refluxed for (2 hr.) and the product was filtered off and recrystallization from ethanol yielded colored crystals of the complexes, the physical and analytical data of the ligand and its metal complexes given in table (1)

b- [M(L₂)Cl₂]: An ethanol solution of (1 m mole , 0.147 gm PdCl₂) in ethanol was added to an ethanolic solution of (1mmole , 0.282 gm of L₂) in 10 ml ethanol . The mixture of reaction was refluxed for two hours .The product was filtered off and recrystallization from ethanol yielded colored crystals of the complexes table (1).

3-Effect of complexes on GPT activity:-

Colorimetric determination of GPT activity according to the following reactions:-



The pyruvate formed was measured in its derivated form 2,4-dinitrophenylhydrazone, which was absorbed at wave length 505 nm (19-21, A₁).

A- A stock solution (0.1 M) of compounds were prepared and the following concentration of (1x10⁻², 1x10⁻³, 1x10⁻⁴, 1x10⁻⁵)M were prepared by diluting with DMSO.

The enzyme GPT activity was measured in human serum by using the same method of this enzyme with replaces 100μl of DMSO with 100μl of compounds.

The activation percentage was calculated by comparing the activity with and without the activator and under the same conditions, according to the equation(22):-

$$\%Activation = 100 \times \frac{\text{The activity in the presence of activator}}{\text{The activity in the absence of activator}} - 100$$

B- A constant concentrations of compounds (1x10⁻¹, 1x10⁻⁵) M was used with different substrate concentrations of (40, 80, 120, 160, 200)mmol/L for GPT to study of activation. Buffer was used to prepare different substrate concentrations of this enzyme (phosphate buffer pH 7.4, 100 mmol/L).

C-The effect of (DMSO), which was used as diluents, was determined by adding aquantiy equivalent to the sample and all steps completed as in A.

D- Absorption of all compounds was measured at wave length 505 nm to concentrations of (1x10⁻², 1x10⁻³, 1x10⁻⁴, 1x10⁻⁵)M, A₂. Absorption of pyruvate derivative was calculated by the equation:- A = A₁ - A₂

The enzyme activity was determined with and without compounds, by using the Lineweaver-Burk equation and plotting 1/v against 1/[s] were evaluated values (23) :-

a) k_a, b) Apparent v_{max} (v_{mapp}), c) Apperent k_m (k_{mapp}).

RESULTS AND DISCUSSION

a-Synthesis of complexes:-

The complexes of L₁ of Pd (II) complexes were obtained as products with a metal ion to ligand ratio of 1:1 and the general formula [Pd (L₁) Cl₂], their colours are following black for complex A₁, Maronite crystal for complex A₂ (Table 1). The compounds were characterized by UV-Vis. and FTIR spectra (Table 2). IR spectra of the (L₁) exhibits a band at (3300 cm⁻¹) assignable to νOH and intense band at (1532 cm⁻¹) corresponding to the (N=N) stretching also we show band at (1610 cm⁻¹) assignable to azo methine group(23). The comparison of the positions of these bands with those observed in the IR spectra of the complexes indicated that the band at (1610 cm⁻¹) shifted to a higher region by about (87 cm⁻¹) this behavior suggests the coordination of (L₁) through the azo methine N. proof of coordination of the N atom is provided by the occurrence of the new bands at (480 cm⁻¹) in the IR spectra of the compounds the band of (M ---O) are

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observed at (270 cm^{-1}) the band in the ($300\text{-}320\text{ cm}^{-1}$) characteristic for (M—Cl) vibrations while that did not show a marked shift azo group and (C=O) group this behavior suggests did not coordination of oxygen atom about carbonyl group and metal ions that proof of clearly demonstraling the ligand via the oxygen atom through OH and nitrogen atom through the azo methane . Table (2), fig (1) and fig(2).

The IR spectrum of the ligand(L₂) exhibits a band at (1107 cm^{-1}) assignable to ($\nu\text{ C=S}$) of the thiosemicarbazone and an intense band at (1537 cm^{-1} ; 1340 cm^{-1}) corresponding to (C=N ; $\nu\text{ S-N}$) respectively. The comparison of the positions of these bands with those observed in the IR spectra of the complexes indicated that the band at (1363 cm^{-1}) shifted to a lower region by about (27 cm^{-1}) proof of coordination of the N atom is provided by the occurrence of the new bands at ($472\text{-}490\text{ cm}^{-1}$) in the IR spectra of the compounds the band of (M-S) are observed at ($340\text{-}380\text{ cm}^{-1}$) characteristic for (M-S) while the band at (3450 cm^{-1}) show a marked shift (-OH) phenol group this behavior suggests did not coordination of oxygen atom about phenol group. The observed band at (1170 cm^{-1}) in the free ligand , which is ascribed to $\nu\text{ C=S}$, shifted to a higher values for two complexes , suggesting the involvement of the sulfur atom in the bonding with the metal s ions. Table(3) ,fig(1) and fig(2).

UV-Vis. spectra for the named complexes have been found to contain absorption bands as shown in fig (3). The ϵ values are (1.623×10^3 ; 0.60×10^3) $\text{L.mol}^{-1} . \text{cm}^{-1}$ for complex A₁ & A₂ respectively . The band at due to (IL) transition and (25062.6 ; 23612.7 cm^{-1}) due to charge transfer (C.T) transition which supported the square planer structure . Electronic absorption for complex A₂ shows bands transition at (36630.03 cm^{-1} and 40983.60 cm^{-1}) due to intra ligand (IL) transition and at (29673.5 cm^{-1}) due to C.T transition , these transition indicative of tetra hyderal (T.h) geometry. UV-Vis. spectra for the named complexes have been found to contain absorption bands as shown in fig (3). The ϵ values are (1.7×10^3 ; 1.5×10^3) $\text{L.mol}^{-1} . \text{cm}^{-1}$ for complex A₃ & A₄ respectively. The band at (40160 and 41666 cm^{-1}) due to intra ligand (IL) transition and at (33003 cm^{-1}) due to charge transfer transition (C.T), these transition indicative of tetrahedral (T.h) geometry. Electronic absorption for complex A₄ shows two bands transition at (39370 cm^{-1}) due to (IL) transition and (32362 cm^{-1}) due to C.T transition which supported the tetrahedral structure ,fig(4).

b-Effect of complexes on GPT activity:-

This research addresses investigation of the effects of L1, L2, PdL1, PdL2, ZrL1, ZrL2 on GPT enzyme .The effect of the solvent (DMSO) showed a slight inhibitory effect on serum of GPT, which was calculated to be 0.2%

of original activity. The biochemical tests revealed that all compounds caused activatory effects on GPT enzyme. Figure (5).

The normal value of the GPT enzyme activity was (16.5 U/L). The relationship between compounds concentration versus and the activity of enzyme as shown in figure (6), these results observed that any increase in compound concentrations caused increase in percentage of activation of enzyme. The greater activation of compounds were demonstrated at concentration (0.1M) as shown in figure(6) and table (4). From these figure and table they were observed that compound (ZrL2) exhibits higher percentage of activation (1384.84 %) than other compounds. In contrast compound (L2) exhibits lower percentage of activation (45.45%) than other compounds. The complexes PdL1, PdL2, ZrL1, ZrL2 exhibits percentage of activation higher than ligands L1, L2.

Competitive, noncompetitive and uncompetitive inhibition can be easily distinguished with the use of double reciprocal plot of the Lineweaver-Burk plot. Two sets of rate determination in which enzyme concentration was held constant, were carried out. In the first experiment the velocity of enzyme without inhibitor was established, in the second experimental constant amount of inhibitor is included in each enzyme assay. Varieties of substances have the ability to reduce or eliminate the catalytic activity of specific enzyme (24).

Table(5) and figure (7) showed that the enzyme activation using Lineweaver-Burk plot for compounds on serum GPT activity. The V_{max} and K_m without compounds were (6.67 U/L, 200 M) of respectively. A liquate 10^{-1} M and 10^{-5} M of compounds were activation for enzyme activity. Activation changed the V_{max} of the enzyme but not the K_m . When concentration 10^{-1} M of L1, L2, PdL1, PdL2, ZrL1, ZrL2 the V_{max} were (50, 50, 20 , 1000, 1000, 1000) U/L respectively, the 10^{-5} M concentration of L1, L2, PdL1, PdL2, ZrL1, ZrL2 the V_{max} were (10, 10, 10 , 12.5, 11.11, 16.67) U/L respectively. By using Lineweaver-Burk equation was calculated the K_a values of enzyme for compounds which was studied in different concentrations. When concentration 10^{-1} M K_a of L1, L2, PdL1, PdL2, ZrL1, ZrL2 were (12×10^{-2} , 12×10^{-2} , 15×10^{-2} , 9.4×10^{-2} , 10×10^{-2} , 10×10^{-2}) M respectively. The 10^{-5} M concentration of L1, L2, PdL1, PdL2, ZrL1, ZrL2 the K_a were (3×10^{-4} , 3×10^{-4} , 15×10^{-6} , 21×10^{-6} , 25×10^{-6} , 16×10^{-6}) M respectively.

Non-competitive inhibition occurs when the inhibitor and substrate bind at different sites on the enzyme. Noncompetitive inhibition can not be overcome by increasing the concentration of substrate thus non-competitive inhibitors decrease the apparent V_{max} of the reaction, Since non-competitive inhibitors donot interfere with the binding of substrate to enzyme. Thus the enzyme shows the same K_m in the presence or absence of the non-

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competitive inhibitor, there are no studies in the literature about the effect of ligand and complexes on GPT.

The variable activatory effect of the compounds under study on serum GPT is due to that compounds molecules have (N=N, N=C, HSO₃, COOH and OH) groups by which, it activates the active sides of amino acids of GPT enzyme by increasing affinity of active sides of enzyme to react with the substrate, or the change in the stereostructure of the enzyme in the presence of such compounds caused to activate the enzyme.

The enzyme play important role in amino acid metabolism and in the urea and tricarboxylic acid cycles (25). The differences in potency of activation from any compound to another are due to the differences in nature of groups substituted (donating groups) which results increased efficiency of enzyme.

Table 1: Physical properties and suggested molecular formula for the prepared compounds

compound	colour	m.p (C°)	Yield %	Suggested formula	geometry
L ₁	Leaden	271-272	51	[C ₂₄ H ₁₇ O ₇ N ₃ S]	-----
L ₂	yellow	256-258	70	[C ₉ H ₁₀ N ₆ S ₂ O]	-----
A ₁	black	290	75	[Pd (L ₁) Cl ₂]	S.q
A ₂	Maronite crystall	297-300	65	[Zr (L ₁) Cl ₂]	T.h
A ₃	Olive-green	290	45.16	Pd (L ₂)Cl ₂]	T.h
A ₄	Pale-orange	280	53.39	Zr (L ₂)Cl ₂]	T.h

Table 2: Characteristics stretching vibrational frequencies (cm⁻¹) located in the (F.T.I.R) of the L₁ ligand and its metal compounds

Comp.	ν (C=N)	ν (N=N)	ν (CO)	ν (OH)	M-Cl	M-N	M-O
L ₁	1610	1532	1720	3300	----	-----	-----
A ₁	1697	1527	1714	3005-3745	300-320	420	270(w)
A ₂	1606	1523	1701	3219	200-230	447(w)	655

Table 3: Characteristic infrared absorption frequencies (cm⁻¹) of the ligand and complexes

Comp.	ν NH	ν C-N	ν C=S	ν C=N	ν M-N	ν M-Cl	ν M-S	ν -OH
L ₂	3250	1363(m)	1107	1537(s)	-----	-----	-----	3450
A ₃	3250	1336	1130	1533	490	240	350	3423
A ₄	3248	1336	1128	1539	472	320	340-380	3423

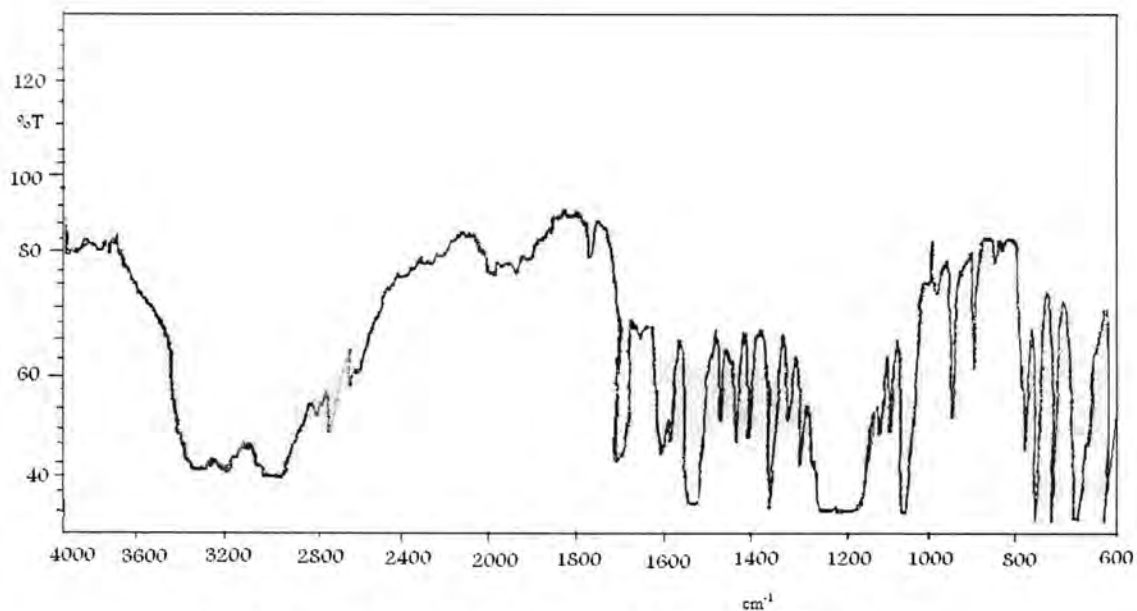


Figure 1: IR Spectrum of $L_1 = C_{24}H_{17}O_7N_3S$

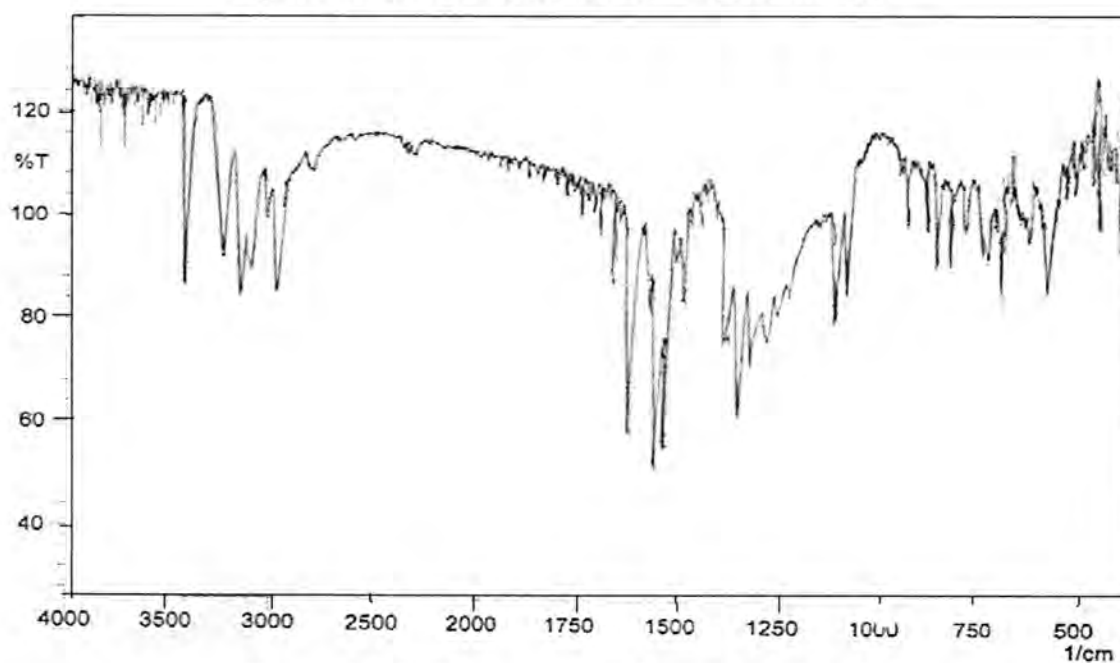
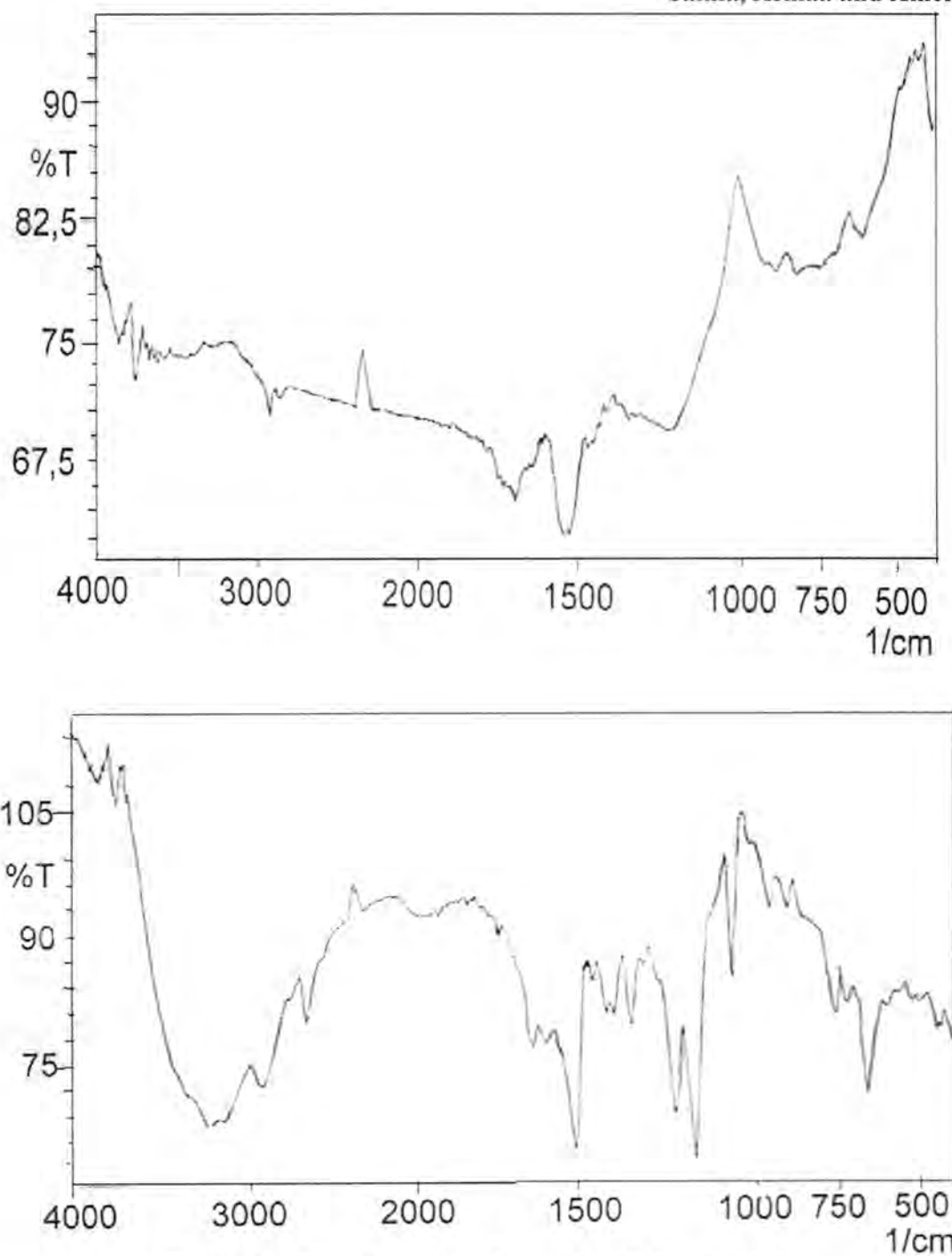


Figure 1: IR Spectrum of $L_2 = C_9H_{10}N_6S_2O$

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**Figure 2: IR spectrum of (a) [Pd(L₁)Cl₂]
(b) [Zr (L₁)Cl₂]**

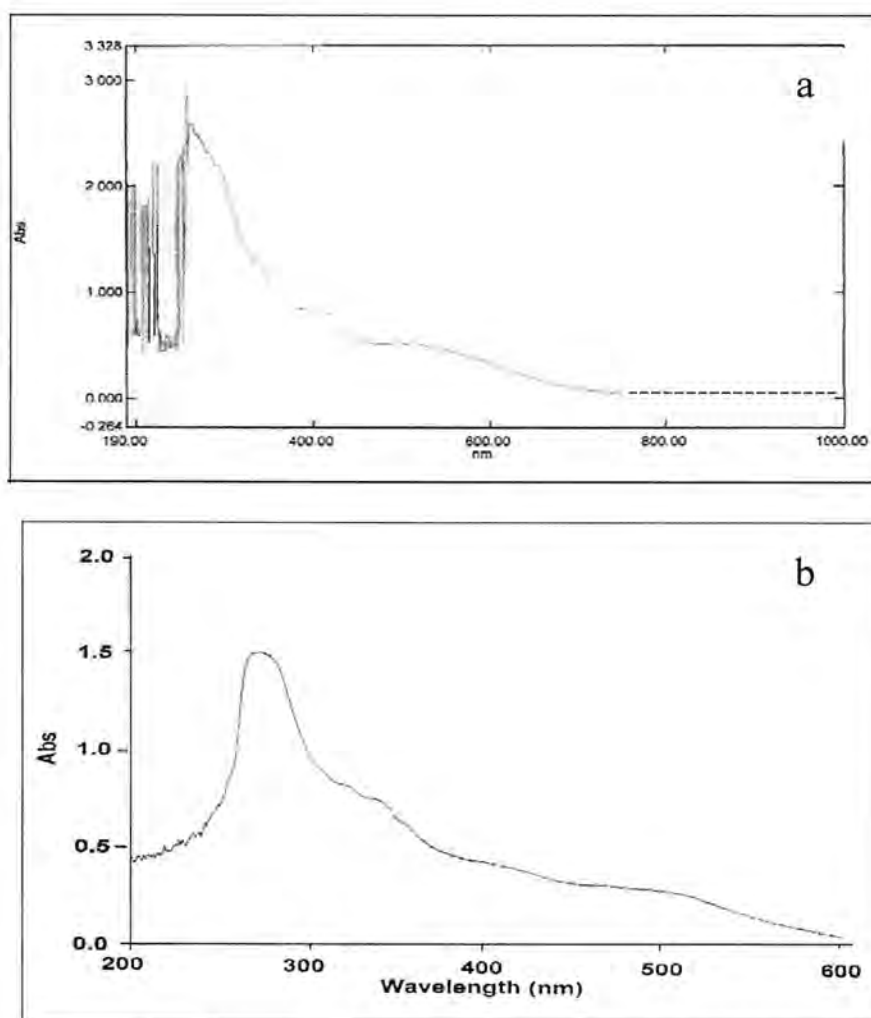


Figure 3: Electronic spectra of (a) $[\text{Pd}(\text{L}_1)\text{Cl}_2]$
(b) $[\text{Zr}(\text{L}_1)\text{Cl}_2]$

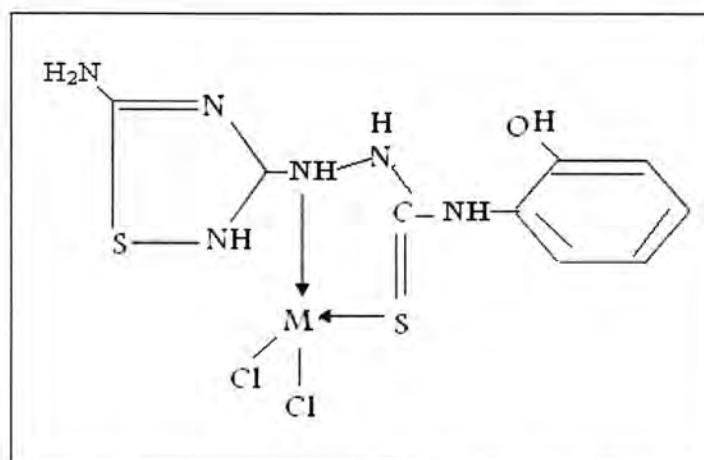


Figure 4: Tetrahedral geometry of A_3 & A_4 complexes, $\text{M} = \text{Pd}(\text{II})$, $\text{Zr}(\text{IV})$

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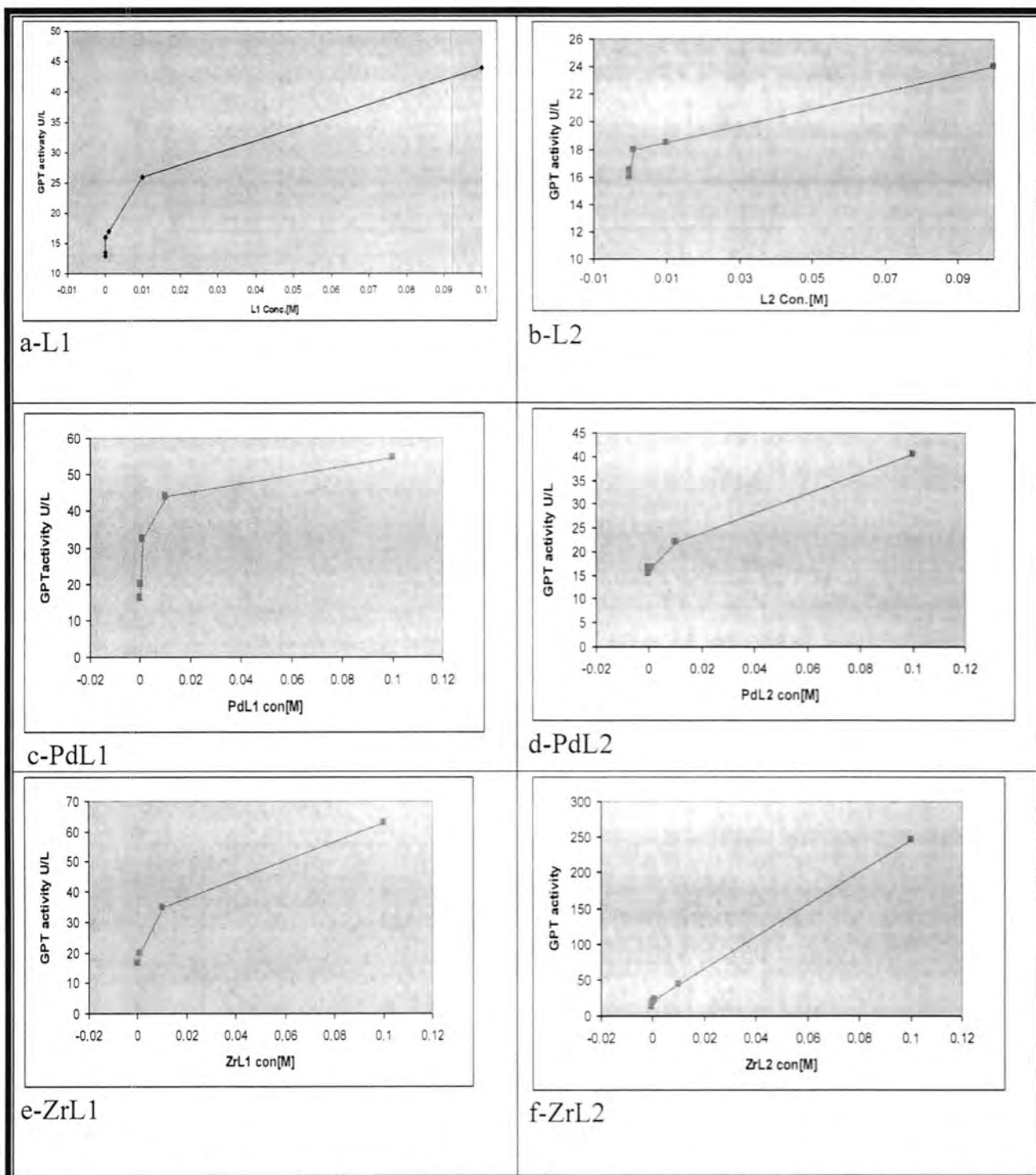


Figure 5: The relationship between concentration of L1, L2, PdL1, PdL2, ZrL1, ZrL2 and GPT enzyme activity

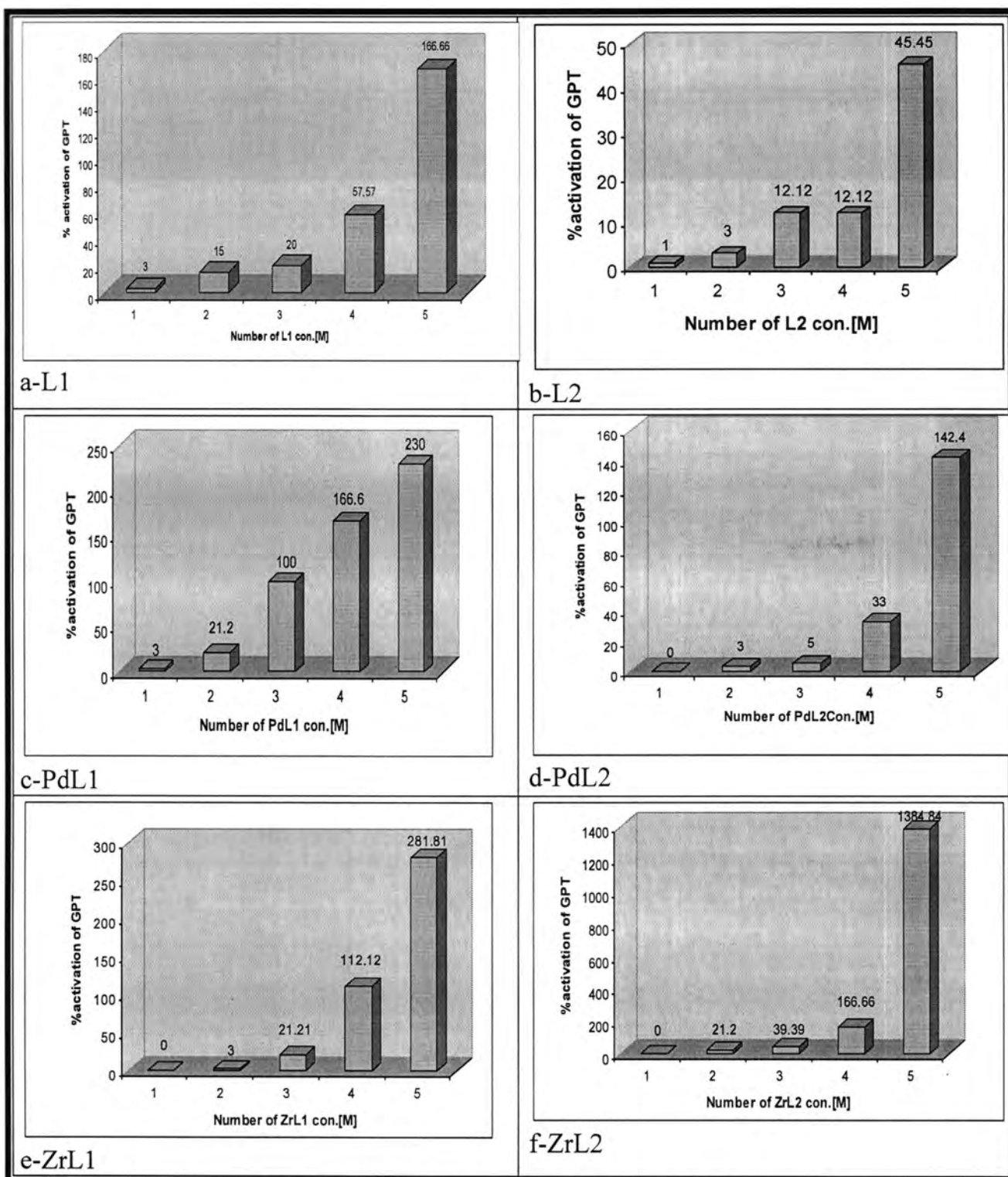


Figure 6: % activation of GPT enzyme activity with 0.1 M L1, L2, PdL1, PdL2, ZrL1, ZrL2

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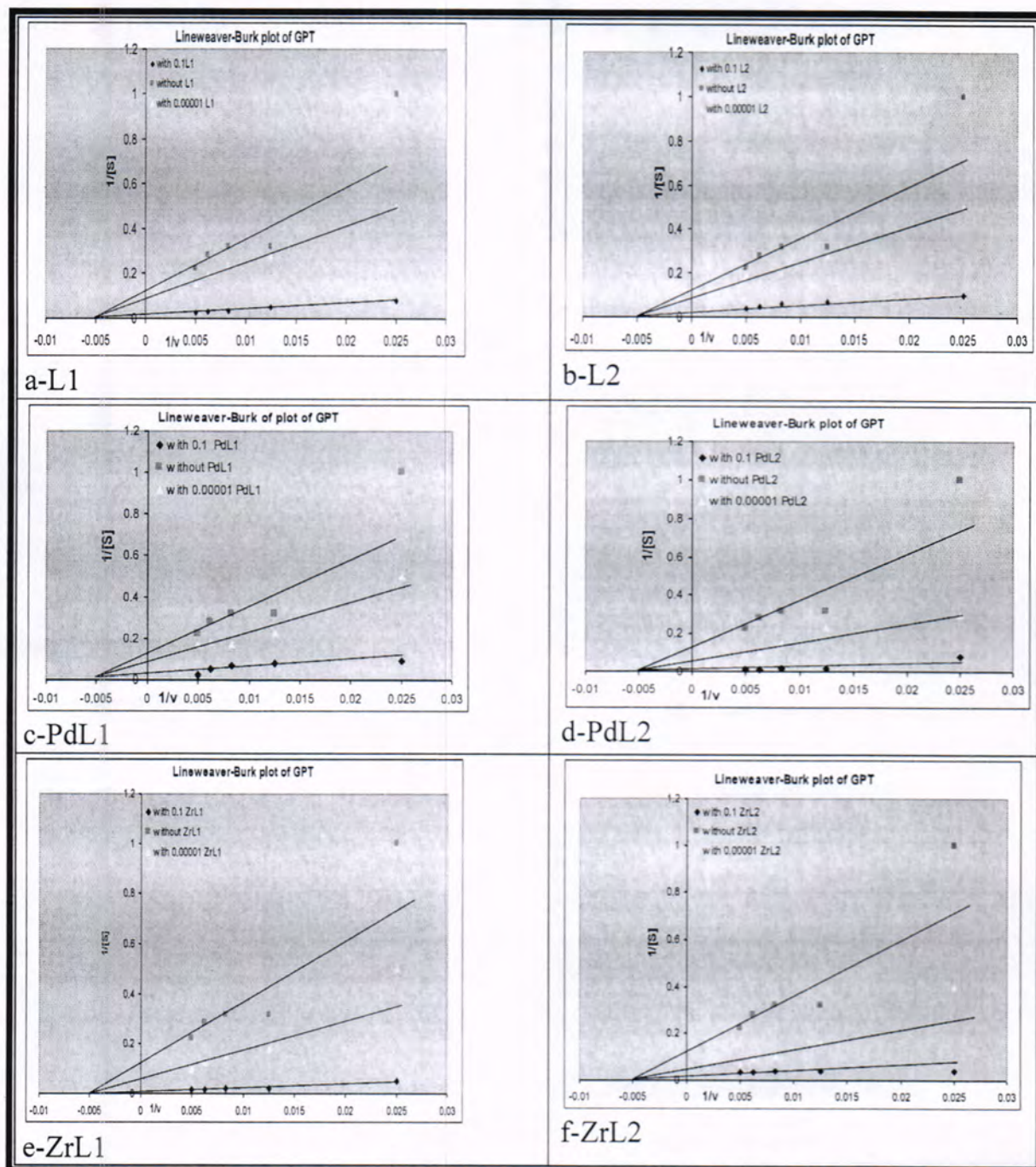


Figure 7: Lineweaver-Burk plots for L1,L2,PdL1,PdL2,ZrL1, ZrL2 effects on GPT

Table 4: The effect of different concentrations of compounds on the activity of GPT enzyme in human serum

Effect	0	$[10^{-1}]$ M	$[10^{-2}]$ M	$[10^{-3}]$ M	$[10^{-4}]$ M	$[10^{-5}]$ M
GPT activity U/L of L1	16.5	44	25	17	16.5	16.5
% Activation of L1	0	166.66	57.57	3.0	0	0
GPT activity U/L of L2	16.5	24	18.5	18	16.5	16.5
% Activation of L2	0	45.45	12.12	12.12	0	0
GPT activity U/L of PdL1	16.5	54.5	44	32.5	20	16.5
% Activation of PdL1	0	230	166.6	100	21.2	0
GPT activity U/L of PdL2	16.5	40	22	18	17	16.5
% Activation of PdL2	0	142.4	33	9.0	3	0
GPT activity U/L of ZrL1	16.5	63	35	20	16.5	16.5
% Activation of ZrL1	0	281.8	112.12	21.21	0	0
GPT activity U/L of ZrL2	16.5	245	44	23	20	16.5
% Activation of ZrL2	0	1384.84	166.66	39.39	21.2	0

Table 5: The kinetic properties of GPT with 0.1 M of compounds

Com.		V map U/L	Ka(M)
L1	10^{-1}	50	12×10^{-2}
	10^{-5}	10	3×10^{-4}
L2	10^{-1}	50	12×10^{-2}
	10^{-5}	10	3×10^{-4}
PdL1	10^{-1}	20	15×10^{-2}
	10^{-5}	10	15×10^{-6}
PdL2	10^{-1}	1000	9.4×10^{-2}
	10^{-5}	12.5	21.4×10^{-6}
ZrL1	10^{-1}	1000	10×10^{-2}
	10^{-5}	11.11	25×10^{-6}
ZrL2	10^{-1}	1000	10×10^{-2}
	10^{-5}	16.667	16×10^{-6}

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Analysis of Pyrazinamide and Salbutamol using triethanolamine-glycerol-maleate copolymer as HPLC stationary phases

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الخلاصة

تم تحضير بوليمير متشابك بواسطة بلمرة التكثيف من تفاعل (Glycerol) و (Triethanol amine) مع (Maleic anhydride). حيث ان البوليمر الناتج يتميز بصلادة وسهولة الطحن لذلك استخدم كطور ثابت لجهاز HPLC حيث تم استخدام البوليمر في فصل (Pyrazinamide and Salbutamol) بواسطة استخدام خليط بنسب مختلفة من الطور المتحرك حيث استخدم (Buffer phosphate at pH 8: 85% : ethanol 15%) كطور متحرك ومعدل جريان (1.2ml/min) وطول موجي 245nm وجد ان زمن احتجاز Pyrazinamide & Salbutamol 3.24 min and 7.46 min و ان فصل جميع هذه المركبات قورن مع فصل هذه المركبات باستخدام عامود C-18. وكان لكل من المركبات المحللة وقت احتجاز مختلف عن الاخرى بالاضافة الى انتقائية مختلفة مما سمح بفصل المركبات الدوائية.

ABSTRACT

A cross-linked polymer was synthesized by condensation reaction between mixture of glycerol and triethanol amine with maleic anhydride. The resulted polymer have high rigidity and easily grinded, with high stability and used as stationary phase for HPLC column. Drugs (Pyrazinamide and Salbutamol) were analyzed with triethanolamine-glycerol-malate column with gradient (15-85) % ethanol in buffer phosphate as a mobile phase with flow rate of 1.2ml/min and UV detection of 245nm. The retention times for Pyrazinamide and Salbutamol were 3.24 min and 7.46 min. The results obtained were compared with commercial column C-18. The method of analysis was applied for determination of the drugs in pharmaceutical as well as in serum samples.

INTRODUCTION

Cross-linked organic polymer was introduced as packing in columns at liquid chromatography since 1960 (1). Kwang et al.(2) have prepared cyclodextrin (CD) polymers from the reaction of CD with a hexamethylene diisocyanate in dried DMF solution. The column backing is CD polymer as a stationary phase for separation of phenol isomers. Kanazawa et al.(3) have proposed a thermo-responsive polymer carrying an amino acid residue as

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HPLC stationary phase, they have investigated a new concept of chromatography.

They have, also used HPLC adsorbents stationary phase by modifying the surface of micro particulate silica gel using functional polymer (4). The thermo responsive co-polymer, poly (N-isopropylacrylamide co-n-butyl metaacrylate) was used to modify the silica stationary phase surface. Kobayashi et al. (4) have used a cross-linked poly N-isopropylacrylamide co-acrylic acid grafted silica bead surface and applied as new column matrix materials that exploit temperature responsive anionic chromatography to separate basic bioactive compounds. Meyer et al. (5, 6) have used three poly ethylene-co-acrylic acid co-polymers with different chain lengths and mass fractions of acrylic acid and covalently immobilized as stationary phase on silica via two variants of molecular spacer namely; 3-aminopropyltriethoxysilane and 3-glycidoxypentyltrimethoxysilane. Redelinghuys et al. (7) have been determined Pyrazinamide in blood by using Shim-pack CLC-ODS column, mobile phase gradient consist of acetonitrile, water, and acetic acid and using fluorescent detection, retention time was 15 min and detection limit was as low as 5 ng/ml.

In this work triethanolamine-glycerol-maleate co-polymer was prepared and used as a new stationary phase for HPLC column. It is used for analysis of several material asthma drugs. Isocratic and gradient elution programs were applied for separation as well as the percent composition of the mobile was studied. The results obtained from this column were compared with commercial column ODS-C18.

MATERIALS AND METHODS

Experimental

Apparatus

1. High performance liquid chromatograph type Shimadzu (Japan) which consisted of a system controller model SCL-10 AVP, a degasser model DGU-12A, two liquid delivery pumps model LC-8AVP, UV-Visible detector model SPD-10AVP, and injector model SIL-10A, equipped with 20 μ l sample loop was used. The HPLC system has been interfaced with computer via a Shimadzu class-VP5 chromatography data system program supplied by the manufacturer.
2. Epson LQ-300 printer model P852A (Japan).
3. Shimadzu Fourier transforms infrared model FTIR 8300 (Japan) was used to measure the IR spectra for the prepared polymers.
4. X-Ray diffract meter, Siemens SRS D500 (Germany).
5. Combination glass electrode was used to measure the pH of polymer solutions (Germany).

Preparation of Triethanolamine-Glycerol-Maleate Polymer

In a 100ml round-bottom flask placed in a sand-bath and equipped with a thermometer and stirrer, a mixture of 7.45gm (0.05mole) triethanolamine and 4.61gm (0.05mole) glycerol were placed. The mixture was stirred for 15min. and 14.7gm (0.15mole) of maleic anhydride was added to the mixture. The temperature was rise gradually to 160°C. The reaction was performed under vacuum. Continued heating at this temperature, for 3 hours, caused an increase in viscosity of the solution until crystalline polymer was formed. The final product was washed with warm water and methanol for several times, and then dried in vacuum oven at 50°C over night.

Preparation of Stock Solutions

Preparation of 50ppm of standard drugs were prepared by dissolving 5mg Salbutamol in ethanol and diluted to 100ml. The same procedure was followed in the preparation of Pyrazinamide stock solutions. Other standard stock solutions were prepared by subsequent dilution of the stock solutions. The solvent used to prepare these solutions before injection into HPLC was the mobile phase employed for their separation.

Analysis of Samples:

All the prepared samples, standard solutions, and mixtures of then have been chromatographically analyzed with the prepared new packed columns using different mobile phases. Mobile phase gradient 15% phosphate buffer-85% EtOH as a mobile phase with flow rate of 1.2ml/min and UV detection of 245. The same samples were analyzed with C-18 column using the literate parameter.

RESULTS AND DISCUSION

Synthesis of co-polymers used as a stationary phase in this work was done via condensation reaction of triethanolamine-glycerol with maleic anhydride in which produces a hard and rigid. The high degree of cross linking of the co-polymer prevented the solvation process and for this reason it was difficult to determine the molecular weight and the degree of polymerization. The co-polymer was identified by FTIR in which the appearance of absorption band at 1732 cm^{-1} due to the stretching vibration of the C = O of the formed ester and a band at 1296 cm^{-1} for C-N. Also an X-ray diffraction was used to identify the nature of the polymer whether it is a crystalline or not. The results showed that the polymer have different crystalline forms. Swelling test for prepared polymeric stationary phase was performed according to the ASTM procedure (8). The degree of cross-linking has been measured using polar, moderately polar and non polar that are usually used in HPLC such as (water, acetone, acetonitrile and hexane). The results of the swelling ranged from 1% to 4% which are theoretically

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expected, except for unexpected value for water 4% which could be attributed to the presence of hydrogen bonding forming moiety on the polymer surface. The solubility has been examined using different solvents such as acetonitrile, benzene, chloroform, dioxane, DMF, DMSO, hexane, methanol and water. It is found that the polymer insoluble and undecompose in all the above solvents and it is very stable. These results were attributed to high cross-linking of the polymer. However, at pH higher than 10 the polymer being decompose due to hydrolysis of the ester bond of the polymer. Column packing was done by using the slurry formed by mixing the triethanolamine-glycerol-maleate powder with 100 ml acetonitrile and homogenized in an ultrasonic bath and placed in the slurry reservoir and the column was packed using down-flow packing system. The study was carried out for the analysis of drugs by using the co-polymer triethanolamine-glycerol-maleate column (25 x 0.4 cm). The drugs, Pyrazinamide and Salbutamol were analyzed by using the co-polymer triethanolamine-glycerol-maleate column (25 x 0.4 cm). The effect of the pH and phosphate buffer concentration of these drugs was studied. The results of pH showed that at pH <6 and at higher pH > 9 the drug cannot be detected. The capacity factor K' using ethanol and phosphate buffer as eluent at different pH were calculated and shown in figure 1. The K' values was ranged from 0.82-1.23, 1.32-1.89, 2.30-3.22 and 4.21-4.93 at pH 6.0, 7.0, 8.0 and 9.0, respectively. The separation factor (α) values for Pyrazinamide and Salbutamol were ranged from 1.15-1.18, 1.25-1.26, 1.09-1.21 and 1.24-1.29 at pH 6.0, 7.0, 8.0 and 9.0, respectively. These variations in capacity factors and separation factors of these analytes may indicate that the pH 8.0 is the best pH buffer that can use for separating. The variation of the capacity factor and separation factor for Pyrazinamide and Salbutamol with different percentage of phosphate buffer (percentage in ethanol) ranged from 5% to 25% are listed in table 1. The results indicate that a good competitive interaction of these drugs with the stationary phase and the best mobile phase of ethanol at 15% phosphate buffer.

Table 1: Capacity K' and separation α factors variation with changing of composition of mobile phase for drugs using triethanolamine-glycerol column

Compounds	Percentage of phosphate buffer in mobile phase									
	5%(0.01M) of buffer		10%(0.02M) of buffer		15%(0.04M) of buffer		20%(0.05M) of buffer		$\geq 25\%(0.06M)$ of buffer	
	K'	α	K'	α	K'	α	K'	α	K'	α
Pyrazinamide	2.66		1.81		1.59		1.82		--	--
Salbutamol	4.12	1.56	2.22	1.23	1.85	1.19	2.15	1.18	--	--

Figure 4 shows a chromatogram of the separation of two drugs; 0.2 ppm Salbutamol, and 0.3 ppm Pyrazinamide, using gradient elution of 15% phosphate buffer and 85% ethanol at pH=8, flow rate of 1.2 ml/min and wavelength at 245 nm. The retention time and other parameters for separation of the drugs are listed in table 2.

Table 2: Retention time (t_r), capacity (K') and separation (α) factors, resolution and peak asymmetry for drugs using triethanolamine-glycerol-maleate column, eluent gradient 15% phosphate buffer-85% EtOH, flow rate 1.2ml/min and detection wavelength 245nm

Compounds	Retention time(t_r)	Capacity factor(K')	Separation factor (α)	Resolution	Peak Asymmetry
Pyrazinamide	3.24	1.59	--	--	1.12
Salbutamol	7.46	1.85	1.19	1.14	1.02

The order of interaction of the drugs with the stationary phase due to the retention time is: **Salbutamol > Pyrazinamide**

The interaction of these drugs depends on the hydrogen bonding between N-H group of the drug and O-H groups of triethanolamine-glycerol-maleate co-polymer. The separation of two drugs in mixture was improved by using gradient elution programming as shown in figure 4.

The column triethanolamine-glycerol-maleate column was compared with commercial column ODS-C18. Pyrazinamide and Salbutamol drugs were chromatogram on C-18 with flow rate of 2.0 ml/min. The mobile phase for elution the drugs as follows: Pyrazinamide was consisted of ammonium acetate and copper acetate monohydrate in water (pH=5) / methanol (94/6 v/v), and wavelength 245nm gives retention time of 15.5 min, for Salbutamol was phosphate buffer (with 0.2% sodium 1-octanesulfate pH=2.5) and acetonitrile (85/15 v/v), and wavelength 245nm gave a retention time of 13.35 min. The separation of a mixture cannot be performed because of the different in the composition of the mobile phases. Therefore, ODS-C18 was very good column for determination of each drug individually.

Quantitative analysis was studied from the construction of calibration curves for Pyrazinamide and Salbutamol. The linear calibration curves for these compounds are shown in figure 5.

Table 3: Linear equation, correlation coefficient and detection limits for the drugs using two types of columns

Triethanolamine-glycerol-maleate column				
Compounds	Linear Equation $Y^*=mx^*+b$	Conc. Range	R	Detection Limit (ppm)
Pyrazinamide	$Y=37780.6x-2264.4$	0.1-10	0.9998	0.05

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Salbutamol	$Y=38452.1x-2331.6$	0.05-10	0.9996	0.10
ODS-C18 column				
Compounds	Linear Equation $Y*=mx*+b$	Conc. Range	R	Detection Limit (ppm)
Pyrazinamide	$Y=19944.6x-18660.4$	0.05-10	0.9998	0.05
Salbutamol	$Y=21743.1x-19244.6$	0.05-10	0.9997	0.10

The linear equations and concentration range with the detection limit using triethanolamine-glycerol-maleate and ODS-C18 columns, eluent gradient (15-85) % phosphate buffer in ethanol, flow rate 1.2ml/min and detection wavelength 245nm are listed in table 3.

The slopes for the linear calibration curves using triethanolamine-glycerol-maleate column ranged from 56221.6 – 59495.9 depends upon the kind of drugs. The correlation coefficients ranged from 0.9996 – 0.9998 with detection limit ranged from 0.05 to 0.10 ppm. While for ODS-C18, the slopes for the linear calibration curves of the analyzed drugs ranged from 23935.6 – 28636.9.

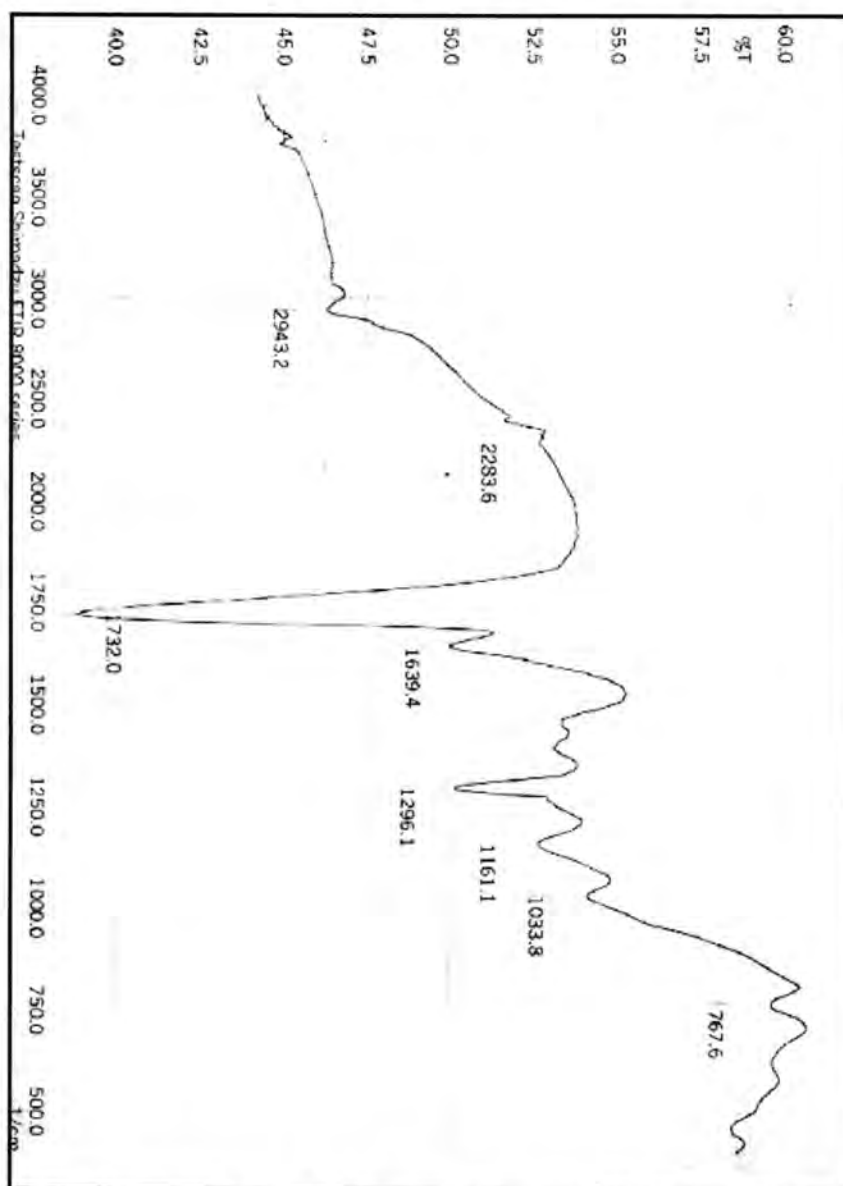
Table 4: Recovery and percentage relative error of drugs eluted on two columns for the drugs using gradient eluent (0-15) % phosphate buffer in ethanol

Triethanolamine-glycerol-maleate column				
Drugs	Conc. Injected (ppm)	Conc. Found(calculated*) (ppm)	Recovery %	Relative error%
Pyrazinamide	4.00	3.94	98.50	1.50
Salbutamol	3.00	2.97	99.00	1.00
ODS-C18 column				
Drugs	Conc. Injected (ppm)	Conc. Found(calculated*) (ppm)	Recovery %	Relative error%
Pyrazinamide	4.00	3.89	97.25	2.75
Salbutamol	3.00	2.86	96.50	4.66

The detection limit for the three amino acids was 0.05 ppm. And also the detection limit for the two drugs was 0.05 ppm. Standard solutions were injected for at least three times under the same condition for both columns triethanolamine-glycerol-maleate and ODS-C18. The %RSD are; 0.849% and 0.811%, recovery ranged from 96.5% to 99.0% and relative errors ranged from 1.00% to 4.66% for Pyrazinamide and Salbutamol respectively the results are listed in table 4. Also the drugs were determined in serum under the same column. The value for Salbutamol ranged from 1.67 – 1.76 after two hours, and for Pyrazinamide ranged from 4.54 – 4.67 after two hours.

Table 5: Analysis of Pyrazinamide (5mg), and Salbutamol (2mg) in tablets using triethanolamine-glycerol-maleate column.

Companies		Pyrazinamide	Salbutamol
Iraq	Wt.(mg) injected	5.00	2.00
	Wt.(mg) calculated	4.98	1.95
	Recovery %	99.25	99.77
India	Wt.(mg) injected	5.00	2.00
	Wt.(mg) calculated	4.84	1.78
	Recovery %	96.24	88.28
Egypt	Wt.(mg) injected	5.00	2.00
	Wt.(mg) calculated*	4.91	1.84
	Recovery %	98.16	94.23

**Figure 1: FTIR spectrum of the co-polymer(triethanolamine-glycerol-maleate)**

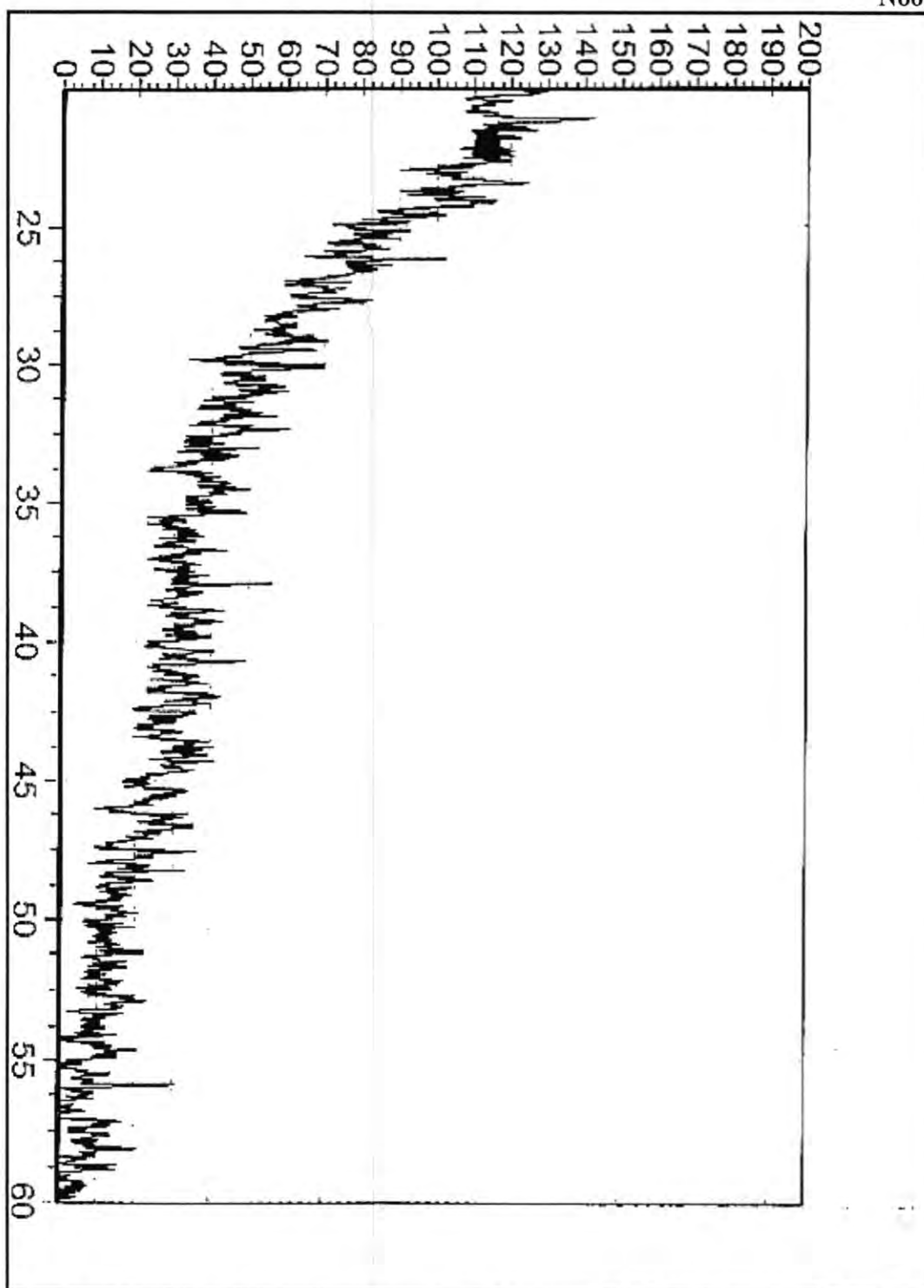


Figure 2: X-ray diffraction of the co-polymer (triethanolamine-glycerol-maleate)

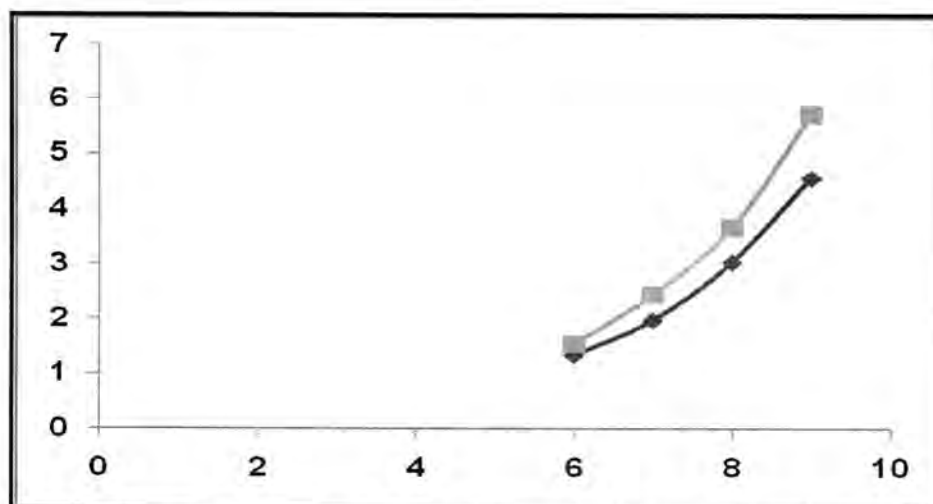


Figure 3: Plot of Capacity factor, versus pH, using triethanolamine-glycerol-maleate column, flow rate 1.2ml/min, detection wavelength 245nm and 2ppm Salbutamol and Pyrazinamide sample

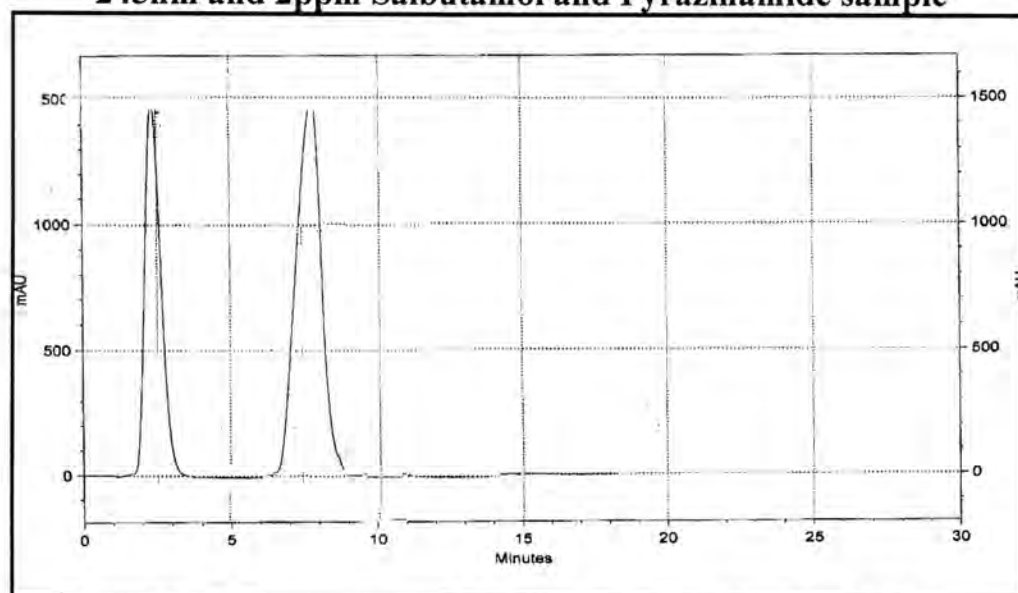
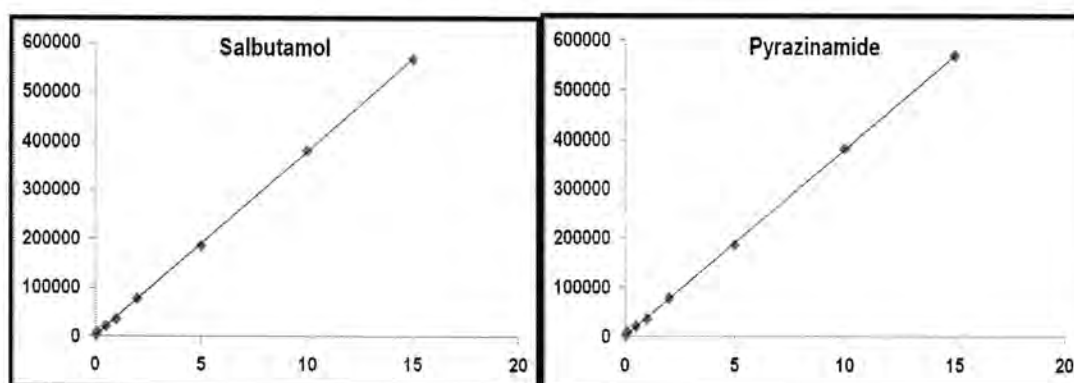
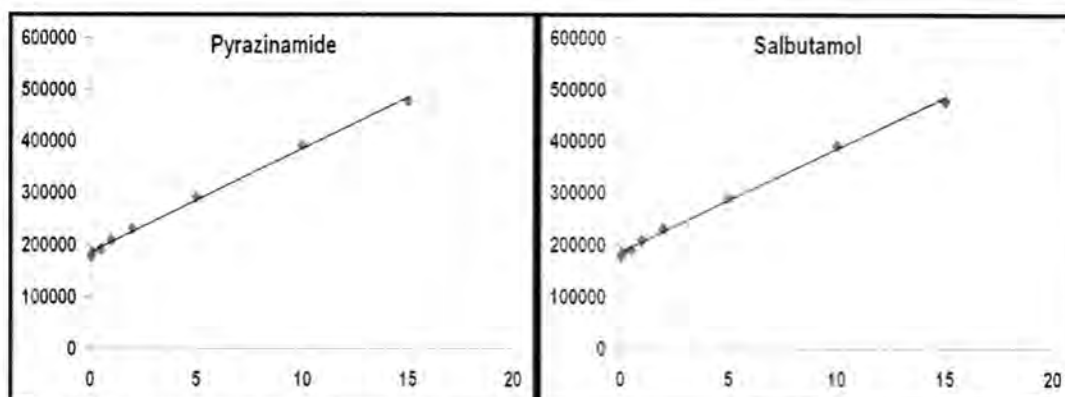


Figure 4: Chromatogram of 0.2ppm Salbutamol and 0.3 ppm Pyrazinamide, using gradient elution of 15% phosphate buffer and 85% ethanol at pH=8, flow rate of 1.2 ml/min and wavelength at 245 nm.



(A)



(B)

Figure 5: Calibration curve of Pyrazinamide and Salbutamol using (A) triethanolamine-glycerol-maleate and (B) ODS-C18 column (25×0.4 cm (id))

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Synthesis and characterization of new aza sugar derivatives

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الخلاصة

يتضمن البحث تحضير مشتقات جديدة لسكريات الأزا من خلال العديد من التفاعلات المتسلسلة لتحضير المشتق الألدهيدي الذي كثف مع بعض مشتقات الأنيلين لانتاج قواعد شف جديدة. تم متابعة سير التفاعلات بواسطة تقنية TLC وشخصت المشتقات المحضرة بواسطة طيف الأشعة تحت الحمراء وطيف الرنين النووي المغناطيسي وجهاز تحليل العناصر الدقيق كما وتم قياس درجات الانصهار لجميع المركبات الجديدة المحضرة.

ABSTRACT

Synthesis new derivatives for aza sugar through many chain reactions to prepare the aldehydic derivative which condensed with aniline derivatives to prepare a new Schiff bases. The synthesized compounds have been characterized by TLC ,element analysis FTIR and ^1H NMR spectroscopy and the melting points were measured to all new prepared compounds.

INTRODUCTION

A number of hydroxylated piperidines and pyrrolines occur in nature in plants and microorganisms(1). These nature products which have been called "sugar-shaped" alkaloids and plants(2), are reversible, competitive inhibition of glycosidases. The purpose of these nature products is possibly to inhibit the carbohydrate metabolism and consequently the growth of plant consuming pests. Since selective glycosides inhibitors have a large number of interesting potential application including treatment of AIDS(3), diabetes(4) and anticancer agents(5), they have a considerable attention.

The "sugar shaped" alkaloids (aza sugar) closely resemble monosaccharides by being analogues of these where the ring oxygen has been exchanged with a nitrogen atom. Thus nojirimycin(1) (6) and 1-deoxynojirimycin:2 (7) are analogues of D-glucose and they are glycosidase inhibitors . Similarly nature (+)-galactonojirimycin (4) have been shown to display strong inhibitory activity toward several β -glucosidase (Figure 1)(8).

MATERIALS AND METHODS

All chemicals used were from (BDH, Fluka and merck). The solvent were further purified by distillation further purified by distillation before used.

Melting points were recorded on a Stuart Melting point apparatus. IR spectra were taken using KBr disc and film on Testcan Shimadzu FTIR 8000 series. Elemental analysis were carried out by C.H.N analyzer type Euro vector, EA 3000 A Italy. The ^1H NMR spectra were recorded on Bruker, ultra shield 300 MHz, Switzerland using TMS as internal standard.

Reaction progress were monitored by T.L.C technique using silica gel coated plates type linear K(20×20) mm Watman company, in the presence (benzene : methanol) (8:2) .

Synthesis:

Synthesis of N,N-di [(methyl sulphide)(5,6-O- isoprplidine-N-methyl gluconamide)] derivative(S1):

It was prepared by addition of (0.043 mol,10.5 gm) of systin to amixture from (8gm ,0.043 mol) sodium in(30 ml) absolute ethanol with mixing for (10 min), then the compound (2,3 diacetyl 5,6-O-isopropylidine L-ascorbic acid) (0.032 mol,10gm) was added to the mixture above . the reaction condensed for (60 min) ,Cooling and filtered .We got a white crystals. Some physical properties and analytical data in the tables (1,2)

Synthesis of N,N-di [(methyl sulphide)(5,6-O- isoprplidine-N-methyl aza ascorbic acid)] derivative (S2):

A solution of (0.018 mole,10 gm) from S1 in 20 ml of pyridine was prepared then (0.018 mole ,1.47 gm) of Sodium acetate was added to the mixture with drops of acetic anhydride with mixing through addition . The mixture left for (24 hr) at room temp with continuous mixing finally extracted by chloroform (25 ml×3) we got a milky crystals . Some physical properties and analytical data in the tables (1,2)

Synthesis of N,N-di [(methyl sulphide)(2,3-O- di acetyl -5,6-O-isoprplidine-N-methyl aza ascorbic acid)] derivative S3:

It was prepared by mixing (0.017 mole,9 gm) of S2 in pyridine (20 ml) with acetic anhydride (25 ml, 0.026 mole) with continuous stirring at room temp. for (24 hr). The mixture is extracted with chloroform (25 ml×3) then with (0.05 HCl) (50 ml). The solution is evaporated to obtained brown crystals. Some physical properties and analytical data are summarized in (Tables 1 and 2).

Synthesis of - N,N-di [(methyl sulphide)(2,3-O- di acetyl , N-methyl aza ascorbic acid)] derivative S4:

A solution of iodine (0.0146 mole , 1.82 gm) in (30 ml) methanol was added with continuous stirring to (0.012 mole,8.5 gm) of S3 derivative in (40 ml) of chloroform. The mixture was refluxed for (1 hr). Cooled and filtered. Recrystallised from ethanol gives brown crystals.

Synthesis of N,N-di [(methyl sulphide)(N-methyl-5-formyl 3,4-di hydroxy -2-N- pyroline)] derivative S5:

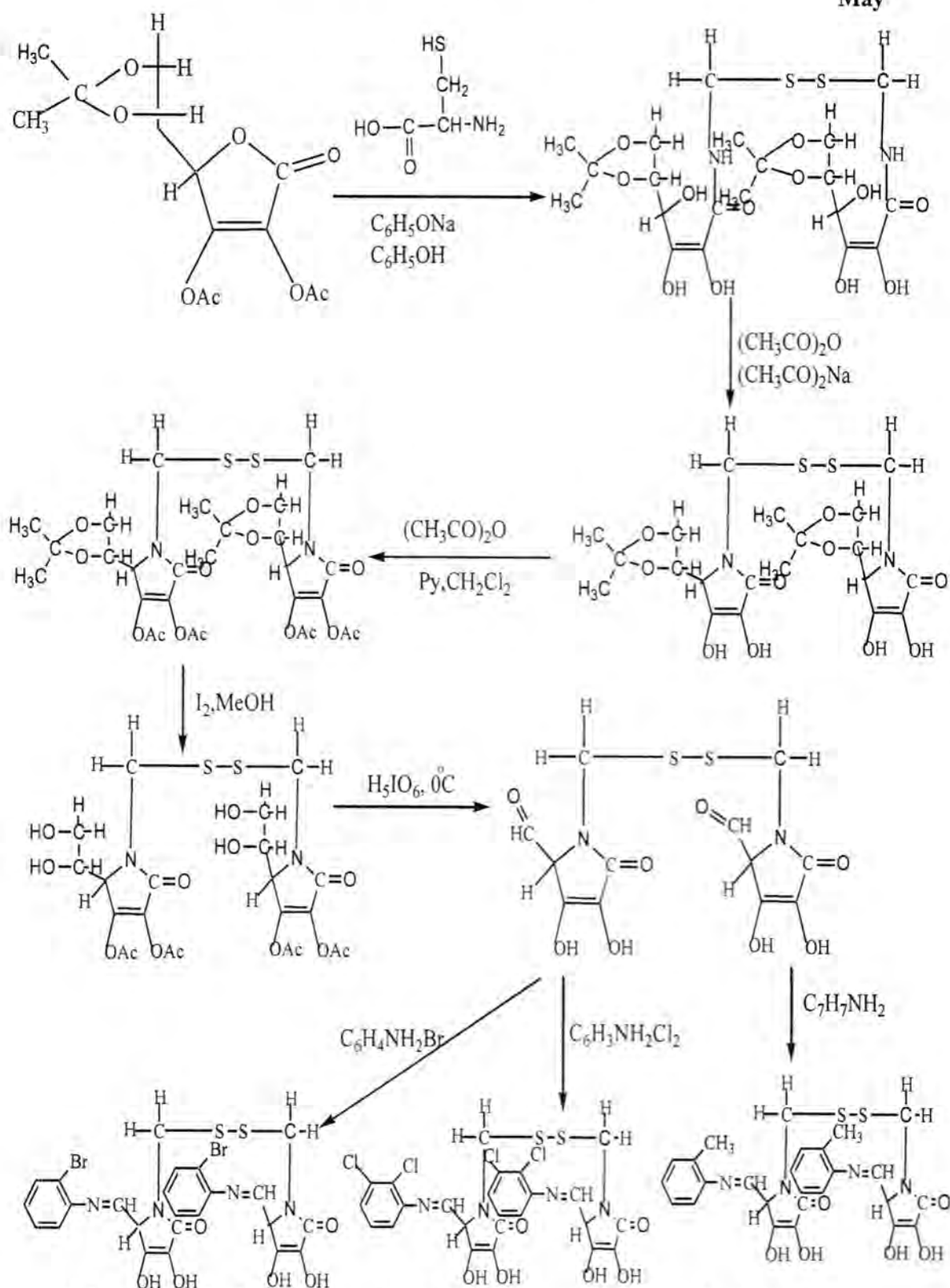
A solution of periodic acid (0.014 mole ,3.2 gm) in distilled water (25 ml) was added to (0.013 mole,8 gm) of an appropriate derivatives of S4 through (30 min.) at (0°C). The ethylene glycol (0.5 ml) is added. The mixture was extracted with ethyl acetate (30 ml×3). The organic layer is evaporated to obtained white crystals.

Synthesis of the Schiff bases (ST,SCI,SBr).

The Schiff bases were synthesized by the condensation of S5 (0.018 mole,7gm) in (30 ml) absolute ethanol with (0,018 mole) of adifferent aromatic amines (ortho toludene, 2-bromo aniline ,2,3-di chloro aniline). The resulting reaction mixtures were refluxed for \approx 3 hr. The solid precipitates of Schiff bases obtained were filtered, washed with ethanol, recrystallised from ethanol. Some physical properties and analytical data are summarized in Tables (1,2).

Synthesis and characterization of new aza sugar derivatives

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Scheme 1: Methods of preparation of new aza sugar derivatives

RESULTS AND DISCUSSION

Derivatives of pyrrolidine and piperidine are used as starting material for prepared many derivatives of aza sugar compounds. (9) , The first derivative prepared by addition the cystine in a mixture of sodium in ethanol to prepare the second derivative which synthesized by treated it with pyridine then sodium acetate the third were prepared by treated the compound above with acetic anhydride at (25°C) in pyridine ., The last product were reacted with iodine in methanol then with periodic acid at (0°C) to produce the aldehydic derivative. From other hand Schiff bases were synthesized by treated the product aldehyde with aniline derivative which are (O-Toluidine, 2-bromo aniline, 1,2-di chloro aniline) as in scheme -1-, some physical properties with analytical data are summarized in tables (1,2).

FTIR spectroscopic studies shows for the first derivative S1 fig (1) appear a weak peak at (3400) cm^{-1} represented stretching vibration of hydroxyl group . The carbonyl amide group shows strong peak at 1680 cm^{-1} . Also another peak at (3300) cm^{-1} for (N-H) amide which is enclosed with hydroxyl group (10)., and weak peak at (2910) cm^{-1} due to CH_2 stretching . S2 derivative fig (2) show a weak peak at (3450) cm^{-1} belong to hydroxyl group . and a strong peak at (1640) cm^{-1} represented stretching vibration of carbonyl lacton group with appear of a weak peaks in (2840 ,2930) cm^{-1} for stretching vibration of methyl groups(11).

S3 derivative fig (4) show division of carbonyl lacton group peak into two peaks one of them for ester carbonyl group and the other for lactonic carbonyl group also appear of sharp peak at (2800-2950) cm^{-1} belong to (CH) aliphatic stretching and strong peak at (1326-1380) cm^{-1} due to (CH) bending of methyl group finally weak peak at (1438-1600) cm^{-1} represented stretching vibration peak of (C=C) group(12). , For S4 derivative fig (6) show a new strong peak at (1683.74) cm^{-1} belong to stretching vibration of lacton group and middle stretching peak at 3800 cm^{-1} due to hydroxyl group and weak peak in 2812 cm^{-1} for CH_2 group and finally strong peak at 1508 cm^{-1} due to (C=C)(13).

S5 derivative fig (8) show a middle peak at 3300 cm^{-1} due to hydroxyl group with another middle peak at 1600 cm^{-1} belong to carbonyl lacton group and weak peak at 2758 cm^{-1} represented stretching vibration of (C-H)

aldehyde and weak peak at 1600 cm^{-1} belong to $\text{C}=\text{O}$ stretching for aldehyde group which enclosed with (CO) lactonic (14) ., At last Schiff bases SCl derivative fig (12) show appear a middle stretching vibrational peak at (3340-3280) cm^{-1} for hydroxyl group and a sharp peak at 1480 cm^{-1} for methen group .ST fig (10) derivative show strong peak at 1600 cm^{-1} due to

Synthesis and characterization of new aza sugar derivatives

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(C=N) stretching and weak peak at 3137 cm^{-1} belong to (OH) stretching

finally middle peak at 1683 cm^{-1} belong to $\text{C}=\text{O}$ lacton stretching (15).

^1H NMR spectra for new derivatives of aza sugars show in S2 derivative fig (3)w singlet signal at ($\delta=2.5\text{ ppm}$) due to solvent and singlet signal at ($\delta=3.7\text{ ppm}$) belong to hydroxyl groups protons ., so that there is a singlet signal at ($\delta=0.8\text{ ppm}$) for protons of methyl groups and singlet signal at ($\delta=0.5\text{ ppm}$) for protons of carbon atoms that attach with sulfa atoms and doublet signal at ($\delta=1\text{ ppm}$) due to methylene group protons(16).,

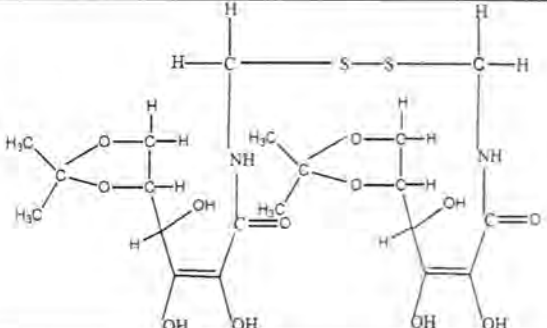
^1H NMR spectra for S3 derivative fig (5) show a new siglet signal appear at ($\delta=2.8\text{ ppm}$) belong to protons of estic group(17).

^1H NMR spectra for S4 fig (7) derivative show a new singlet signal at ($\delta=4\text{ ppm}$) for protons of hydroxyl group .,S5 fig (9) derivative show appear a new singlet signal at ($\delta=9.3\text{ ppm}$) for aldehydic protons(18).

^1H NMR spectra for new Schiff bases ,for ST fig (11) derivative show a singlet signal at ($\delta=2.5\text{ ppm}$) belong to solvent and singlt signal at ($\delta=0.5\text{ ppm}$) due to protons of methyl group and singlet signal at ($\delta=3.5\text{ ppm}$) belong to protons of hydroxyl group ., The proton of imine group show singlet signal at ($\delta=8.1\text{ ppm}$) and also there is a multiplet signal at ($\delta=7.2\text{ ppm}$) due to protons of aromatic ring .,At last singlet signal at ($\delta=0.8\text{ ppm}$) for protons of carbon atom that attach with sulfa atoms(19).

SC1 fig (13) derivative show a change in the position of phenyl ring as a singlet signal at ($\delta=7.5\text{ ppm}$) because of the effectiveness of chloride groups(20).

Table 1:Some physical properties of a new aza sugar derivatives

No.	Structure	M.F	MWt.	M.P °C	Yield%
S1		$\text{C}_{20}\text{H}_{32}\text{O}_{12}\text{S}_2\text{N}_2$	556	230	80-79

S2		$C_{20}H_{28}O_{10}N_2S_2$	520	210	78-76
S3		$C_{28}H_{36}O_{14}N_2S_2$	688	300	76-75
S4		$C_{22}H_{28}O_{14}N_2S_2$	608	270	75-74

Table 2: Some physical properties of a new aza sugar derivatives

No.	Structure	M.F	MWt.	M.P °C	Yield %
S5		$C_{12}H_{12}O_8N_2S_2$	376	205	73-71
ST		$C_{26}H_{26}O_6N_4S_2$	554	210	70-69

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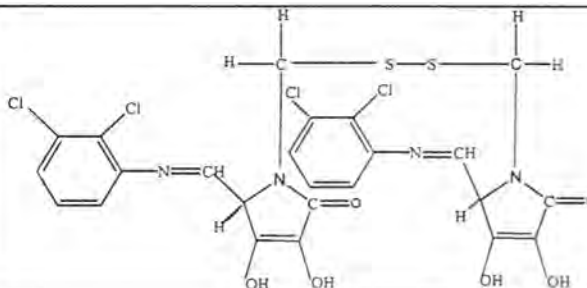
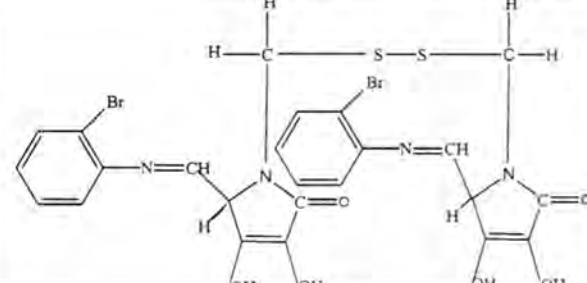
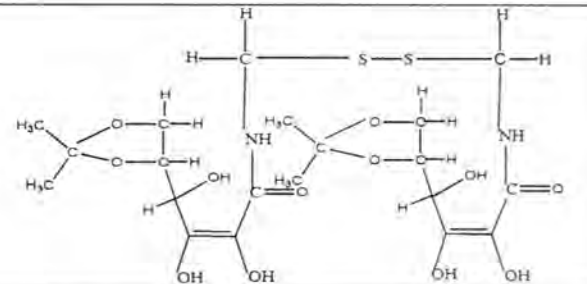
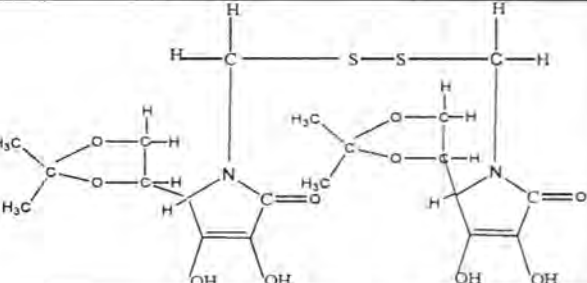
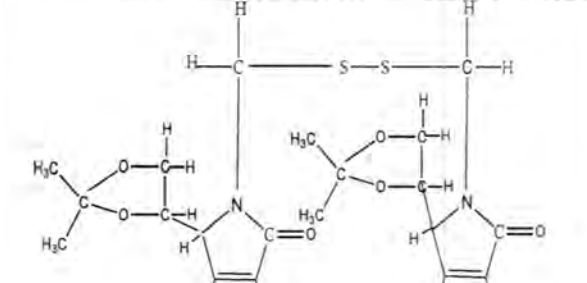
SCI		$C_{24}H_{18}O_6N_4S_2Cl$ 4	662	350	71-69
SBr		$C_{24}H_{20}O_6N_4S_2Br$ 2	684	370	71-70

Table 3: Analytical data and R_f of a new aza sugar derivatives

No.	Structure	R_f	C% Calc. Found	H% Calc. Found	N% Calc. Found	S% Calc. Found
S1		0.9	31.37 31.02	5.62 5.66	11.60 11.63	26.36 26.44
S2		0.87	31.79 31.25	5.56 5.36	9.76 9.40	19.69 19.21
S3		0.8	30.44 30.11	5.50 5.42	11.91 12.30	25.16 24.92

S4		0.5	30.28 30.58	5.52 5.36	12.90 13.11	27.28 27.02
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Table 4:Some physical properties of a new aza sugar derivatives

No.	Structure	R_f	C% Calc. Found	H% Calc. Found	N% Calc. Found	S% Calc. Found
S5		0.79	30.26 30.56	5.52 5.55	13.17 13.33	27.04 26.41
ST		0.9	74.43 74.60	8.11 8.44	14.49 14.61	2.43 3.06
SCI		0.81	32.80 31.02	5.49 5.47	12.43 12.69	24.02 23.62
SBr		0.8	47.67 47.36	3.81 3.33	8.92 9.31	10.85 11.00

Synthesis and characterization of new aza sugar derivatives

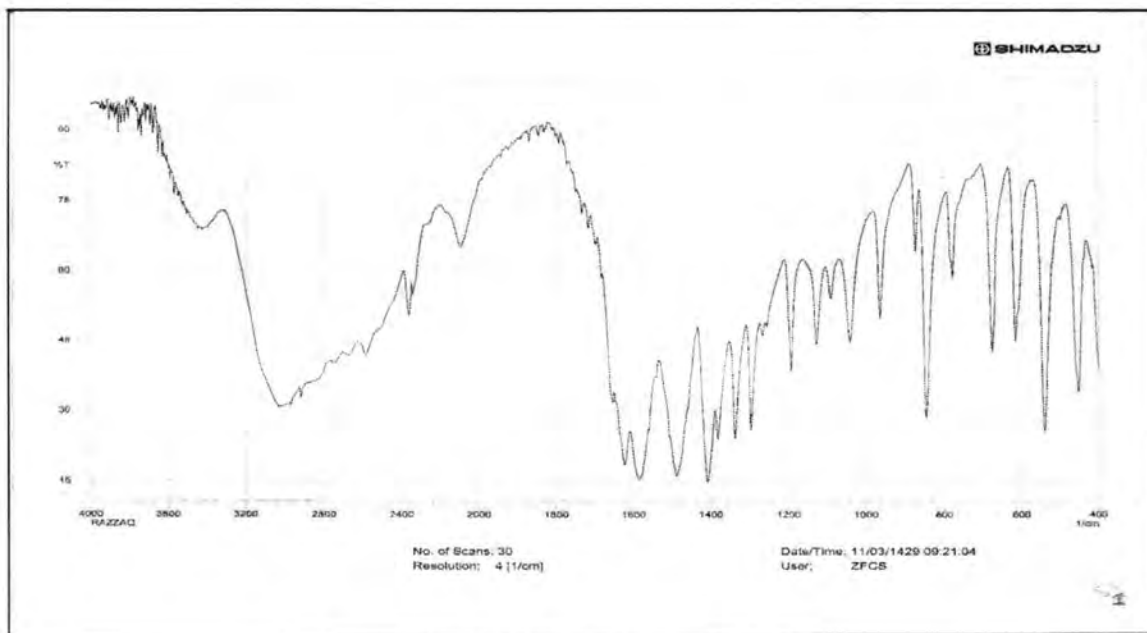
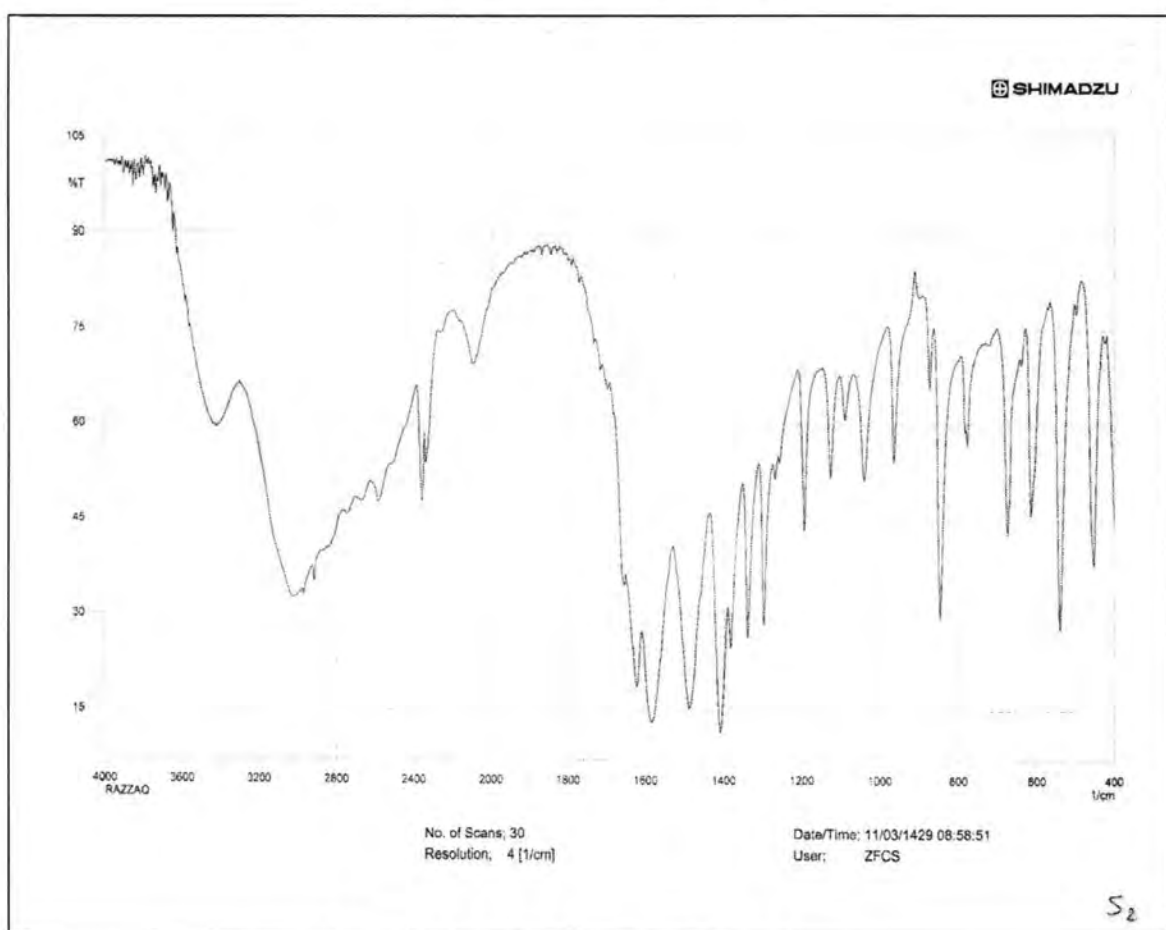
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Method Filename : EA-080.mth
 Summarize Result: Percent
 Configuration : CHNS
 Reference STD : BBOT
 Operator : Mohanad H.M.Masad
 Customer ID # : May Jalil



AL al-Bayt University

Sample Name	Sample ID#	C%	H%	N%	S%
S1		31.370	5.627	11.605	26.368
		31.025	5.662	11.636	26.441
Average		31.20	5.64	11.62	26.40
S2		31.795	5.566	9.767	19.690
		31.235	5.362	9.402	19.211
Average		31.52	5.46	9.58	19.45
S3		30.443	5.506	11.919	25.161
		30.110	5.424	12.303	24.923
Average		30.28	5.47	12.11	25.04
S4		30.282	5.526	12.908	27.287
		30.580	5.363	13.110	27.021
Avarege		30.43	5.44	13.01	27.15
S5		30.266	5.527	13.176	27.045
		30.562	5.558	13.333	26.410
Avarege		30.41	5.54	13.25	26.73
SCI		32.807	5.497	12.439	24.025
		31.023	5.478	12.692	23.628
Average		31.92	5.49	12.57	23.83
ST		74.437	8.112	14.492	2.438
		74.606	8.447	14.617	3.060
Average		74.52	8.28	14.55	2.75
SBr		47.677	3.812	8.926	10.859
Date : 15-9-2010		Signiture :			

**Figure 1: FTIR spectrum for S1****Figure 2: FTIR spectrum for S2**

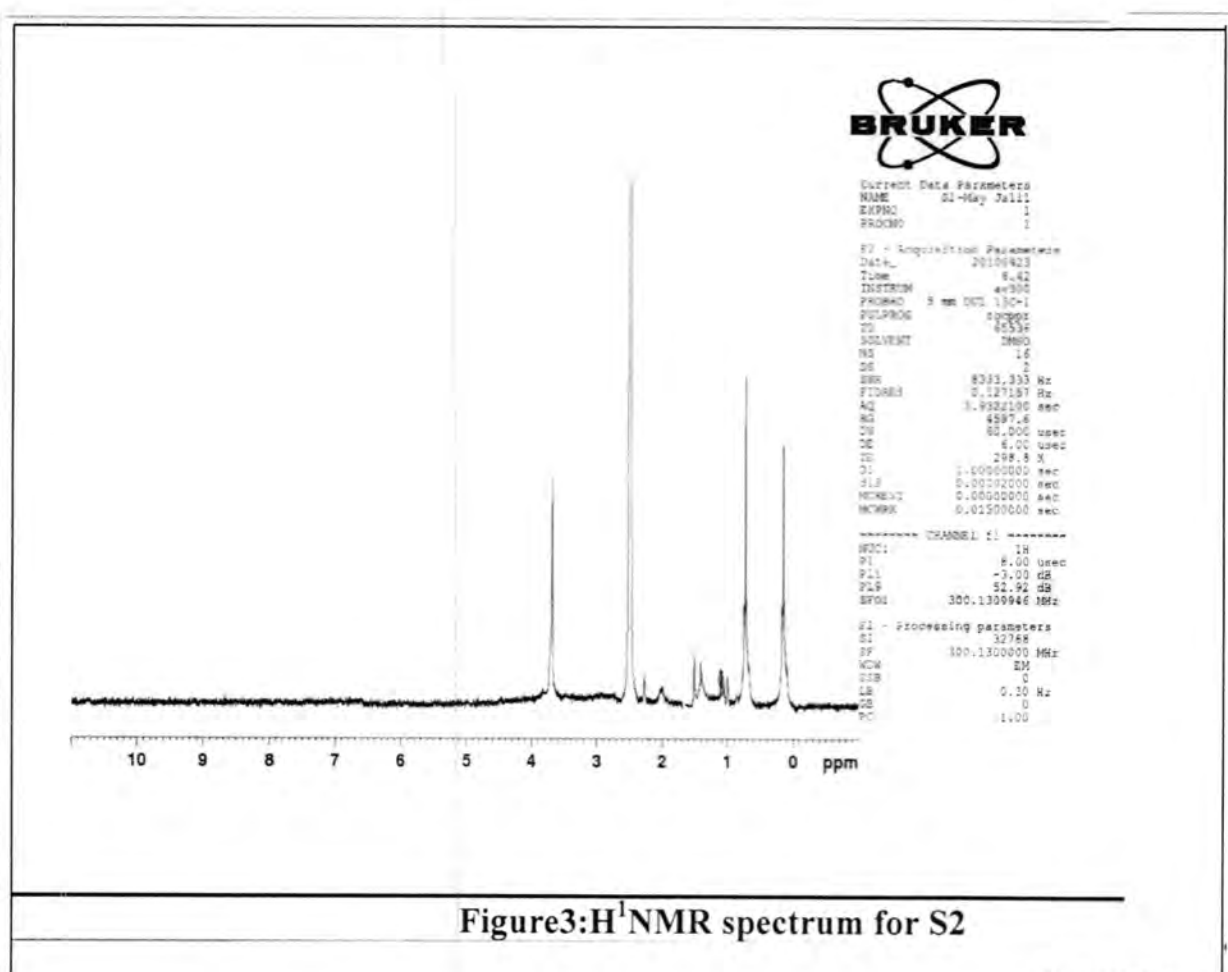


Figure3: ^1H NMR spectrum for S2

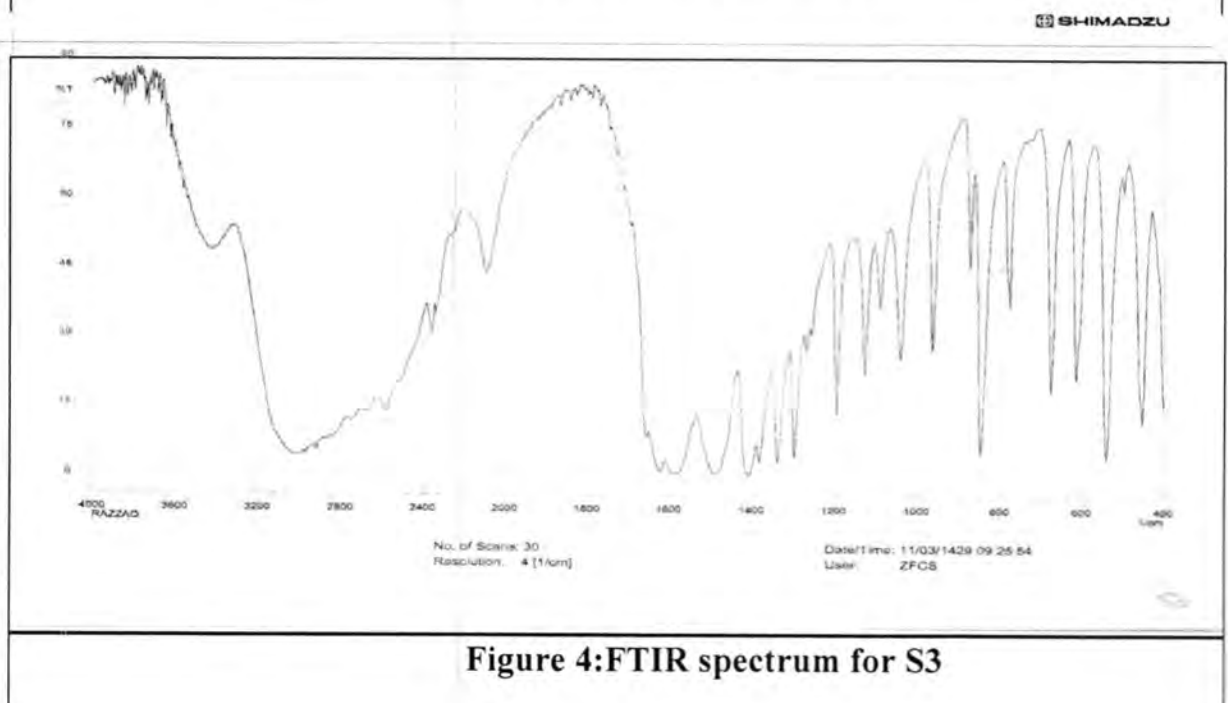


Figure 4: FTIR spectrum for S3

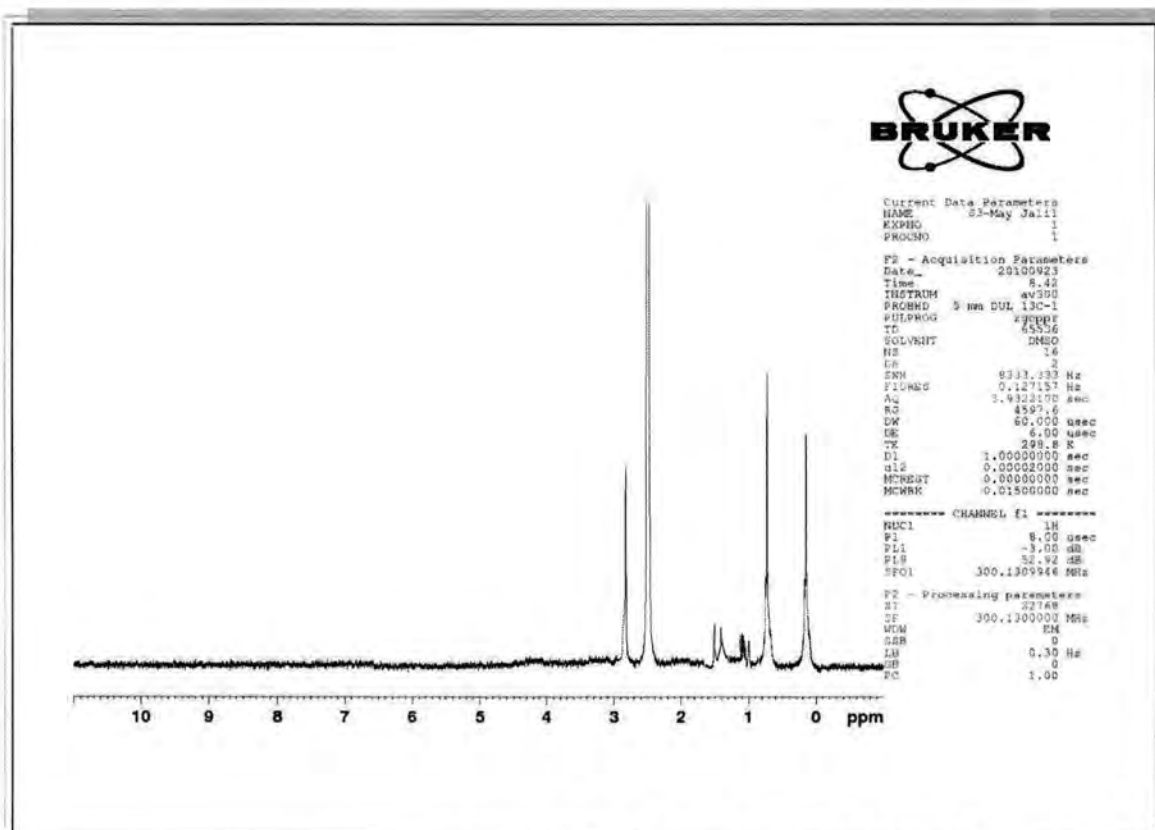
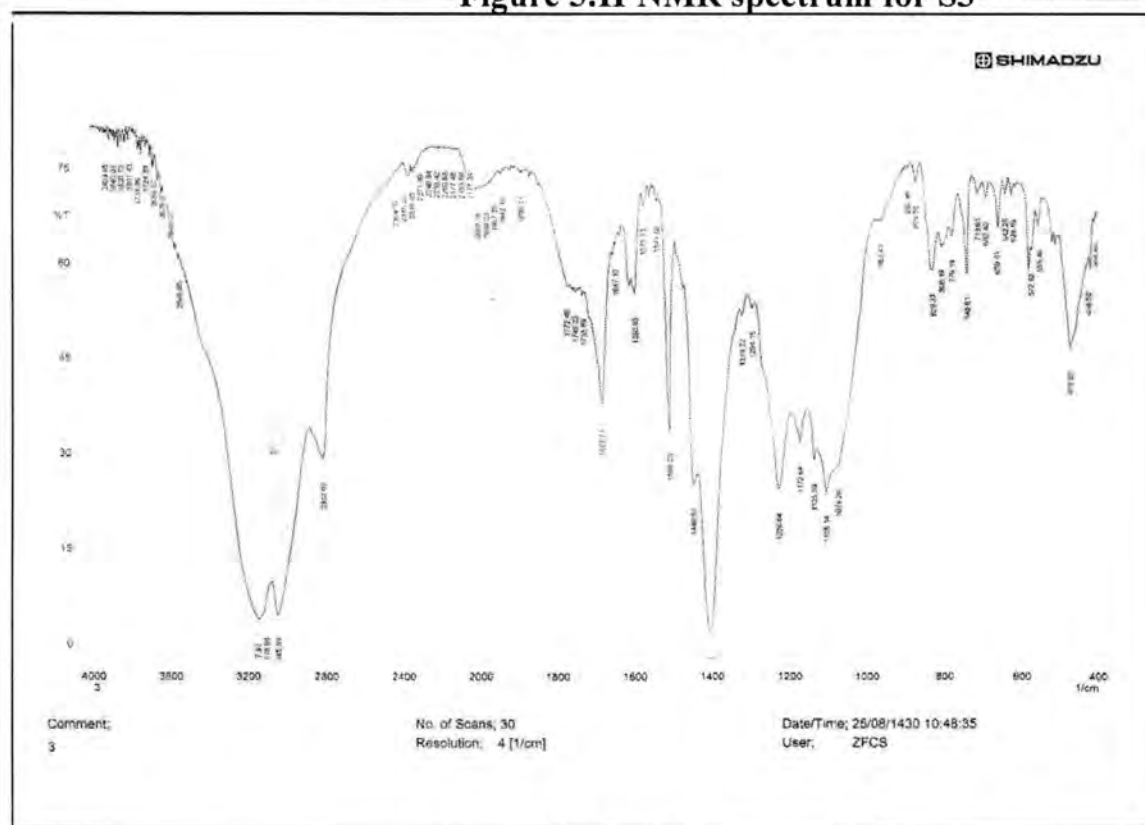
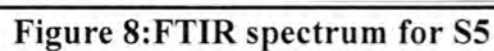
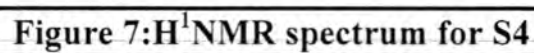
Figure 5: ^1H NMR spectrum for S3

Figure 6: FTIR spectrum for S4

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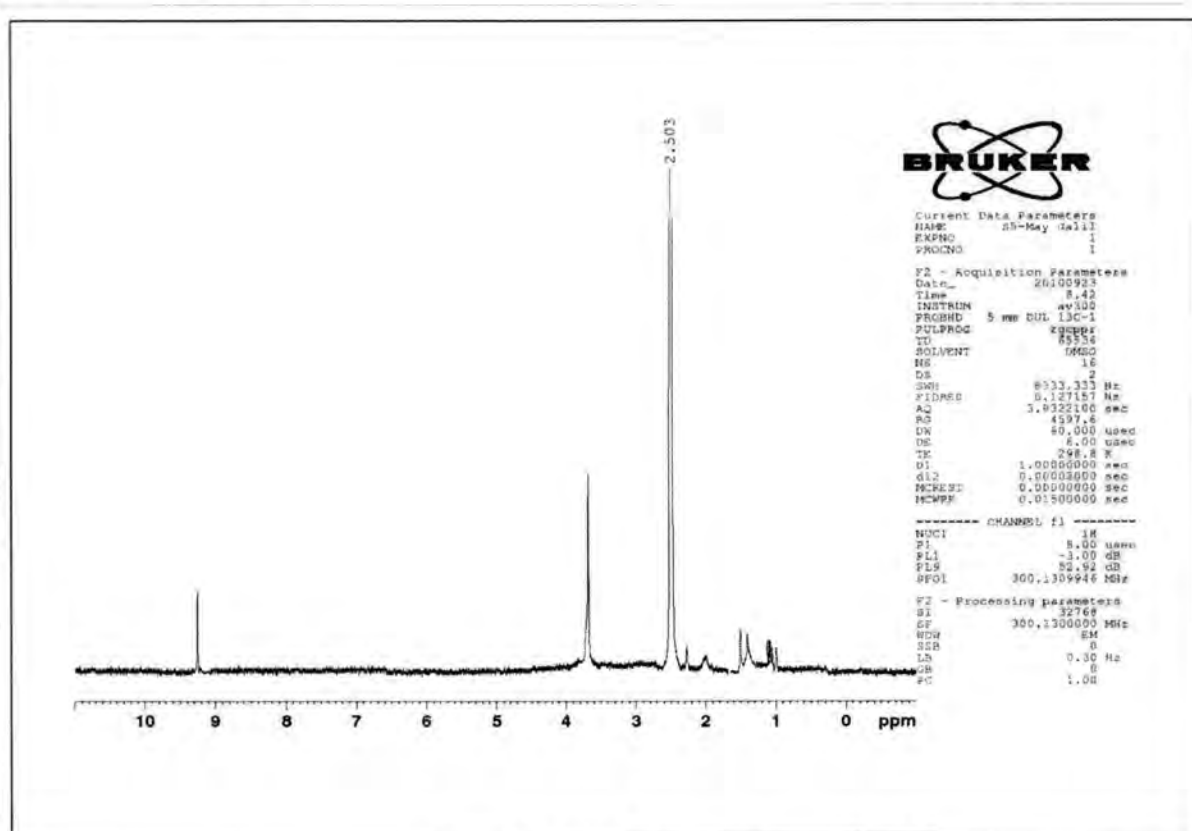
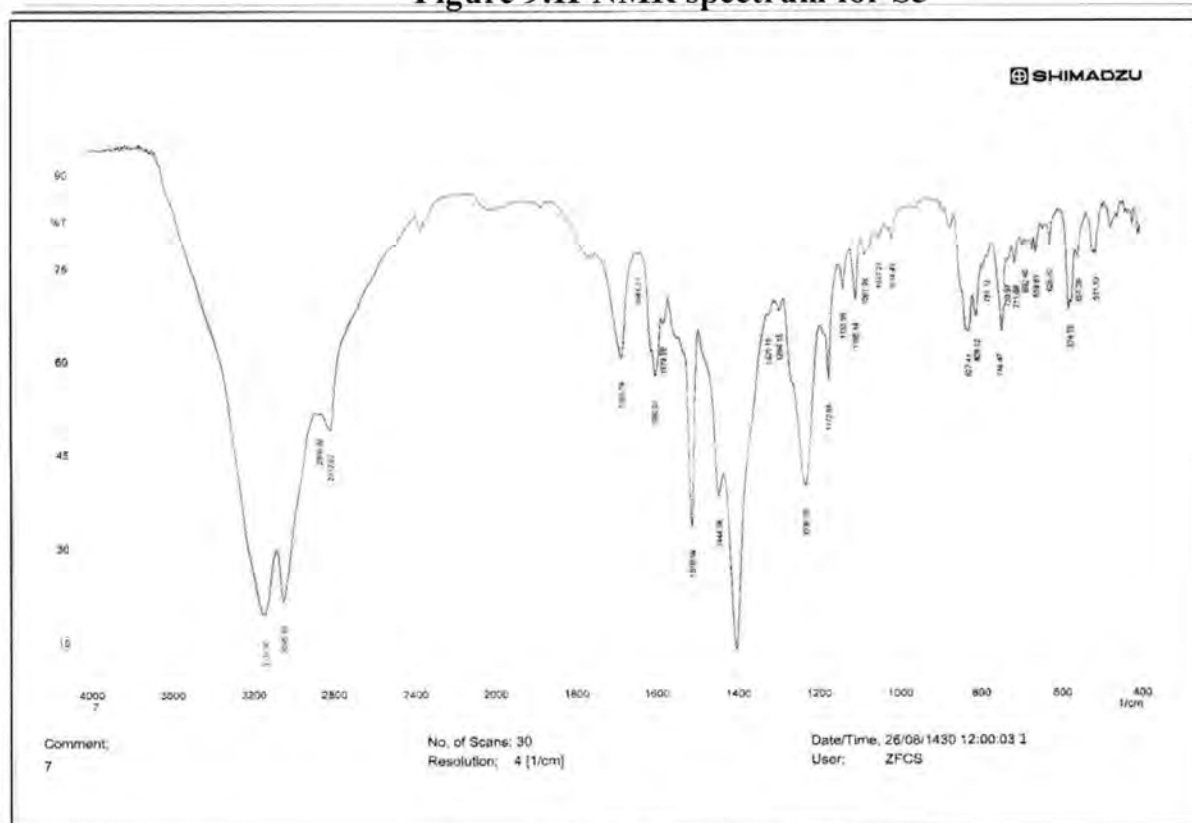
Figure 9: ^1H NMR spectrum for S5

Figure 10: FTIR spectrum for ST

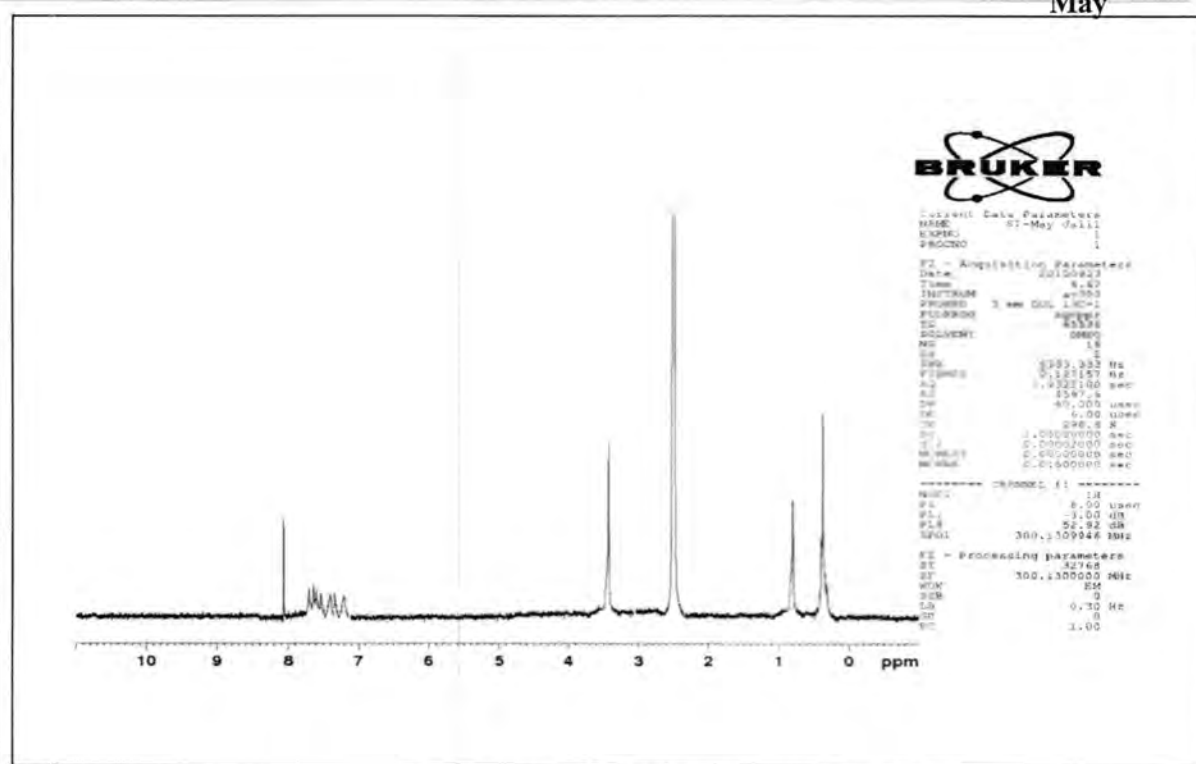


Figure 11: ^1H NMR spectrum for ST

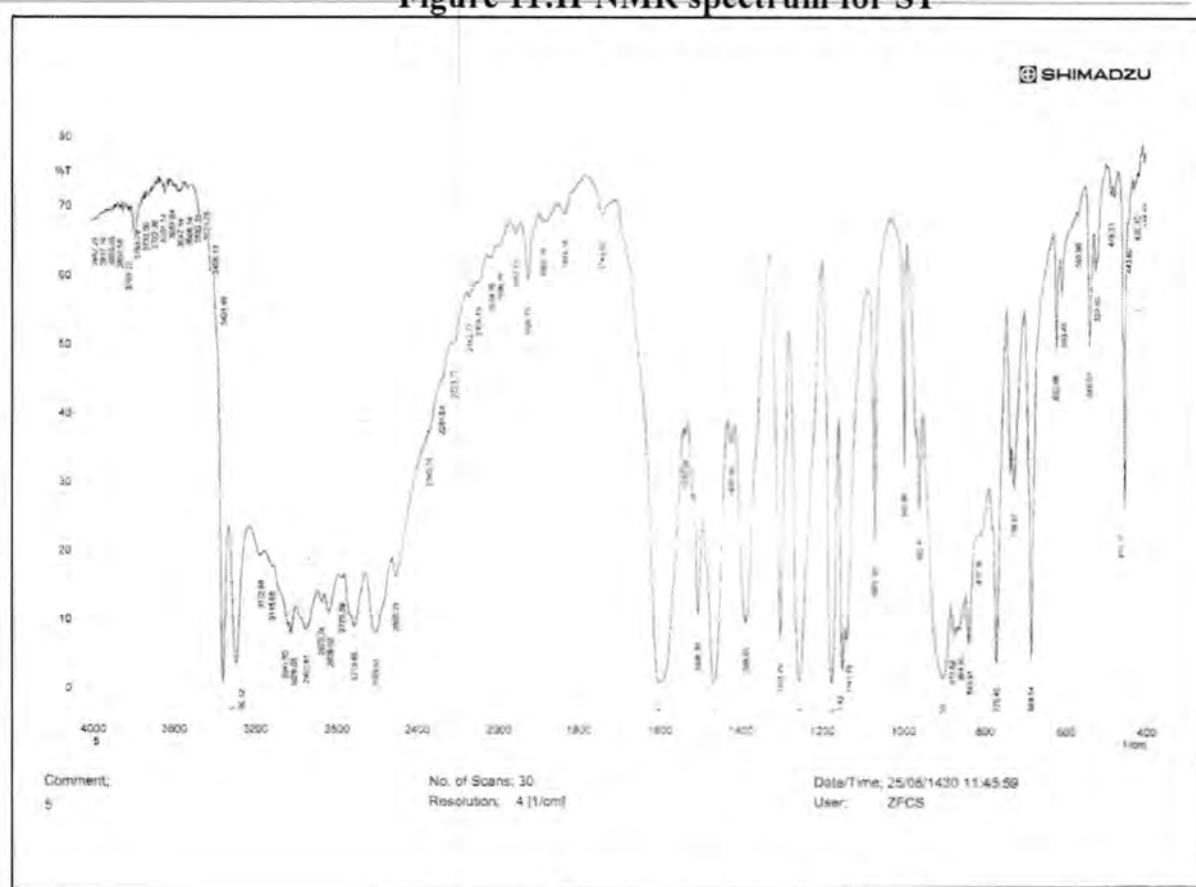


Figure 12: FTIR spectrum for SCI

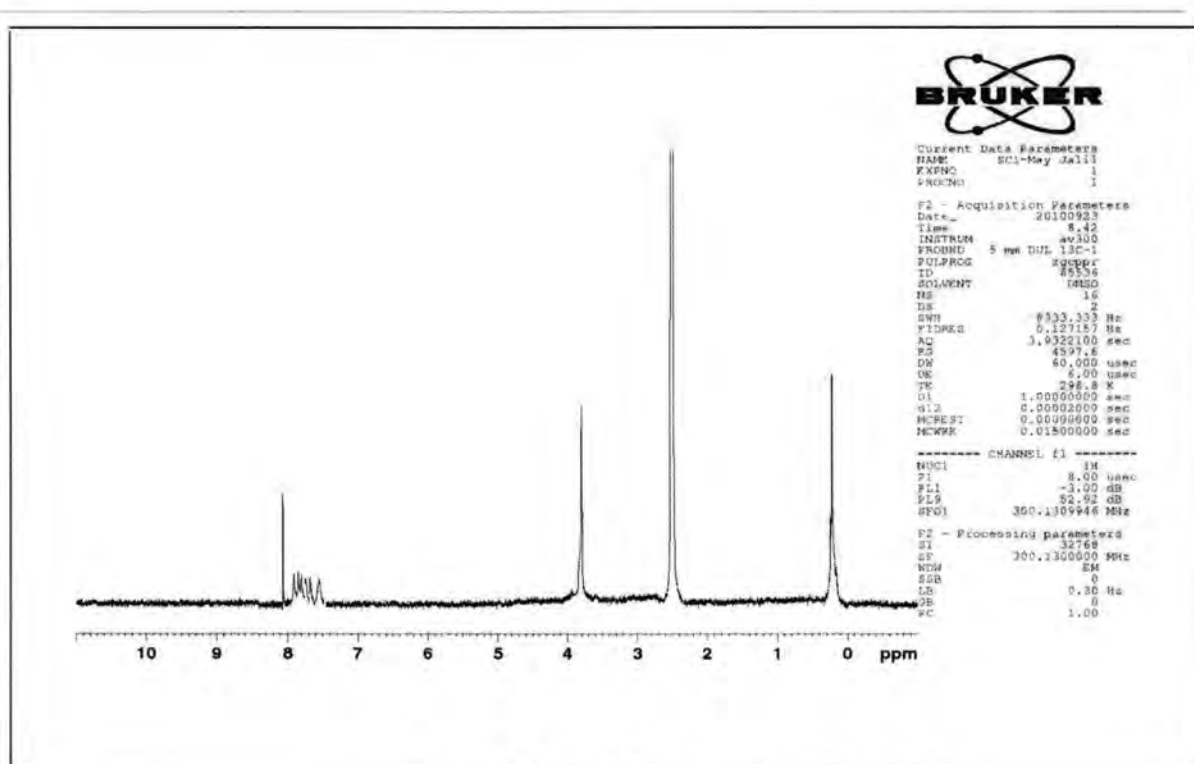


Figure 13: ^1H NMR spectrum for SCl

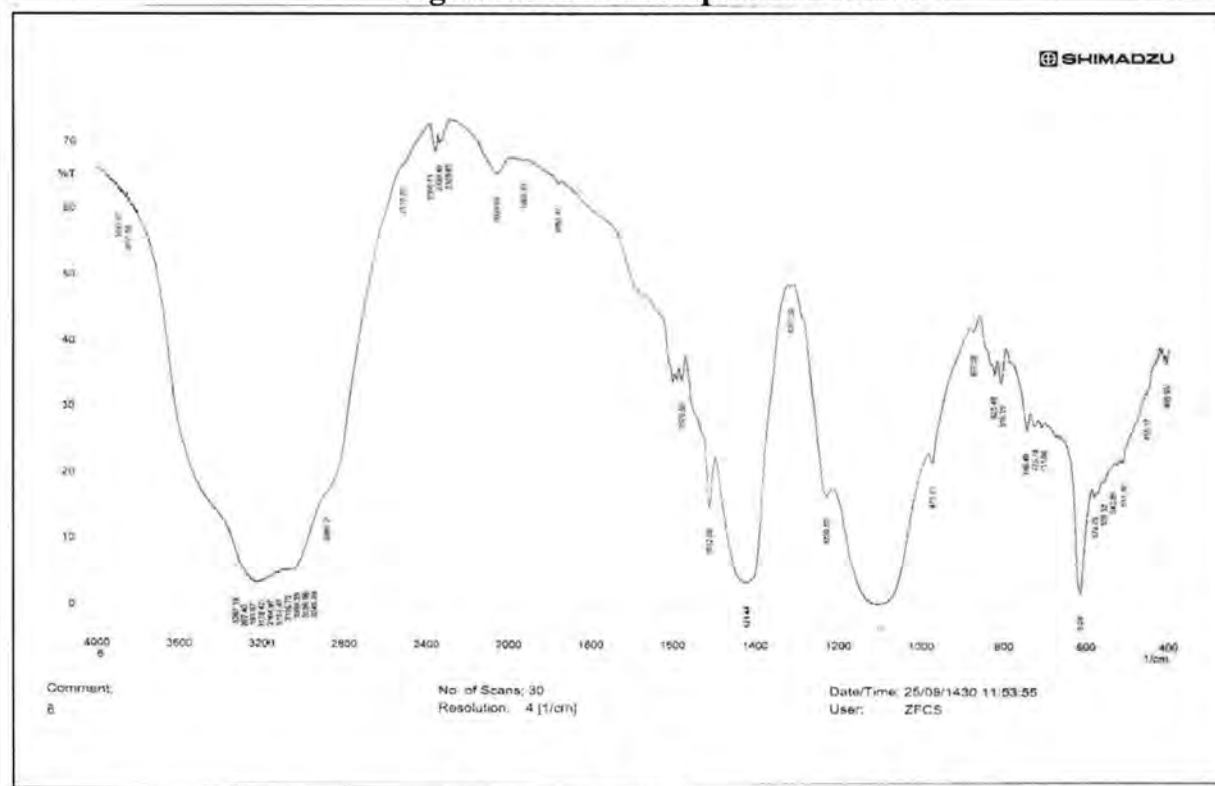


Figure 14:FTIR spectrum for SBr

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Kinetics Study of The Removal of Ni(II) ion from Aqueous Solution Using Poly Furfuryl Alcohol

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الخلاصة

حضر متعدد كحول الفورفريول واستخدم كمادة مازة لأزالة ايون النيكل الثنائي من محاليله المائية. استخدمت عددا من المعادلات لمعالجة البيانات وهي : pseudo first order , pseudo second order . intraparticle diffusion second order . اظهرت النتائج ان صيغة pseudo second order هي الصيغة الأمثل لوصف عمليتي الأمتزاز والأمتصاص (sorption) لأيون النيكل الثنائي على سطح متعدد كحول الفورفريول.

ABSTRACT

Poly(furfuryl alcohol) was prepared and used as new adsorbent for removal of Ni(II) from aqueous solution. Three kinetics model were applied to the experimental data .Pseudo-first order, Pseudo-second order, and Intraparticle Diffution. The results show that the pseudo-second order model is best describes the sorption of Ni(II) onto poly (furfural alcohol) .

INTRODUCTION

Heavy metal contamination is a main source of water pollution. The removal and recovery of heavy metals from wastewater are important in protecting the environmental and human health. A number of techniques such as chemical precipitation, solvent extraction, electrodialysis, evaporation, membrane separation, reverse osmosis, ion exchange, and sorption have been employed to remove heavy metals from wastewater(1). However, strict environmental protection legislation, public environmental concerns, and the expense of conventional disposal methods provide incentives for developing novel techniques for heavy metal wastewater treatment.

From the analytical point of view, it is known that solid phase extraction (adsorption) is an attractive technique based on the use of the sorbent that retains analytes . the adsorption process, proved it is advantage over the other process because of it's cost effectiveness and high quality of the treated effluent it products. Activated carbon is widely used as an adsorbent due to it is high adsorption capacity(2-4). Many types of low cost agricultural waste such as , Ram horn powder(5) , Blended periwinkle shell(6) , Sour sop seeds(7) , Potato peel(8), Groundnut hull(9) , White

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straw(10), Apple waste(11), Peanut hull pellet(12), olive stone(13), banana pith(14), saw dust(15), Wheat shell(16), Wheat bran(17), Carrot residue(18), oil palm fibre(19), besides that many chelating polymers have been used for this purpose(20-26)

Nickel is largely present in the wastewaters of electroplating, motor vehicle and aircraft industries(27). Acute nickel(II) poisoning causes dizziness, head ache, nausea and vomiting, chest pain, dry cough and shortness of breathe, rapid respiration, cyanosis and extreme weakness(28). World Health Organization, WHO has suggested that the maximum amount of nickel in drinking water should be 0.1 mg/L. But in many electroplating effluent water it is as high as 50 mg/L.

Poly (furfuryl alcohol) (PFA), is a common thermosetting resin that forms carbon with a rather high yield through polymerization of FA monomers when subjected to heating and/or with the presence of catalyst upon carboniation. The furfuryl alcohol (FA) monomers are of liquid state at room temperature. They dissolve easily in water and in many organic solvent, forming polymers and inorganic materials of various structures. In this regard, PFA is used not only as adhesives and binders, but is also used extensively in synthesis of functional material, such as nanoporous carbons and polymeric nanocomposites with applications ranging from adsorbents, separation membranes, catalyst, electrodes for fuel cells, lithium ion batteries, and electric double-layer capacitors, etc.(29)

No report on the utilization of poly furfuryl alcohol, for the adsorption of Nickel (II) has been found in literature. The present research was conducted to utilize (poly furfuryl alcohol) for the adsorption of Nickel(II) from wastewater. Influence of operating conditions like, temperature. The kinetics of adsorption process and their constants were investigated.

MATERIALS AND METHODS

Preparation of Poly (Furfuryl Alcohol)

Furfuryl alcohol (FA, $C_4H_3OCH_2OH$, molecular weight =98.1 purity more than 98%, sigma-Aldrich, Germany) was used as monomer for synthesis of poly(furfuryl alcohol). The FA was polymerized using hydrochloric acid (0.1 N) as a catalyst(29). After polymerization the black powdered products were formed, and the synthesized products were centrifuged and washed with deionized water repeatedly for three times until free of acid, followed then by drying at $70^\circ C$. Some of the synthesized powdered were then lightly ground by mortar for FTIR measurement. The remaining powdered was heated to $200^\circ C$, then put in screwed container and become ready to use.

Preparation of Nickel (II) Solution and Analysis

A stock solution of $\text{Ni}(\text{SO}_4) \cdot 2\text{H}_2\text{O}$, 500 ppm, was obtained by dissolving (1.624) g of $\text{Ni}(\text{SO}_4) \cdot 2\text{H}_2\text{O}$ in 1L of deionized water, this solution was used for further experimental solution preparation. pH of maximum adsorption was found to be 6, Analytical grade reagent were used through out this study. The residual $\text{Ni}(\text{II})$ in the sorption solution was determined by atomic absorption spectrophotometer type (phonex 986)

Batch Adsorption Studies

Effect of Time and initial concentration of Nickel (II)

The effect of initial of conc. of $\text{Ni}(\text{II})$ and time on adsorption of $\text{Ni}(\text{II})$ onto poly(furfuryl alcohol) were done at solution pH =6.0 by mixing 2g/l of poly(furfuryl alcohol) with 50 ml of $\text{Ni}(\text{II})$ solution of 20 ppm at 30°C and 120rpm the amount of $\text{Ni}(\text{II})$ adsorbed onto polymer q_e (mg/g) was calculated from the equation.

$$q_e = (C_i - C_e)V/M \text{ -----(1)}$$

Where q_e is the metal uptake at equilibrium, expressed as mg metal/g of the sorbent, V, the liquid volume, in L, C_i , the initial concentration of metal in the solution, in mg/L, C_e , the equilibrium concentration of the metal in the solution, in mg/L, and M the amount of the sorbent sample on dry basis in g.

RESULTS AND DISCUSSION

Preparation and characterization of PFA

Chemical structure

Figure (1) show FTIR spectra of the poly(furfuryl alcohol) After polymerization , the original functional groups of FA monomers diminish or even disappear while new functional groups related to PFA are formed at wavenumbers of $1708(\text{C}=\text{O})$, $1552(\text{C}=\text{C})$, 885 and 780 cm^{-1} ($\text{C}-\text{C}-\text{H}$) respectively(30). It is worth noting that two distinct characteristic peaks of C-H out-of-plane deformation in furan rings have been observed at 885 and 780 cm^{-1} for the PFA synthesized in the acidic solutions during polymerization. The $\nu_{\text{C}-\text{O}-\text{C}}$ band at 1040 cm^{-1} is ascribed to the FA/acids esterified groups, while the absorption band at 1552 cm^{-1} is attributable to the $\text{C}=\text{C}$ skeletal stretch vibration in the furan ring interconnected to the furan- CH_2 -furan group after formation of oligomers by a condensation reaction(31) . The occurrence of carbonyl signal at 1708 cm^{-1} is due to the acid- catalyzed ring opening of furan ring

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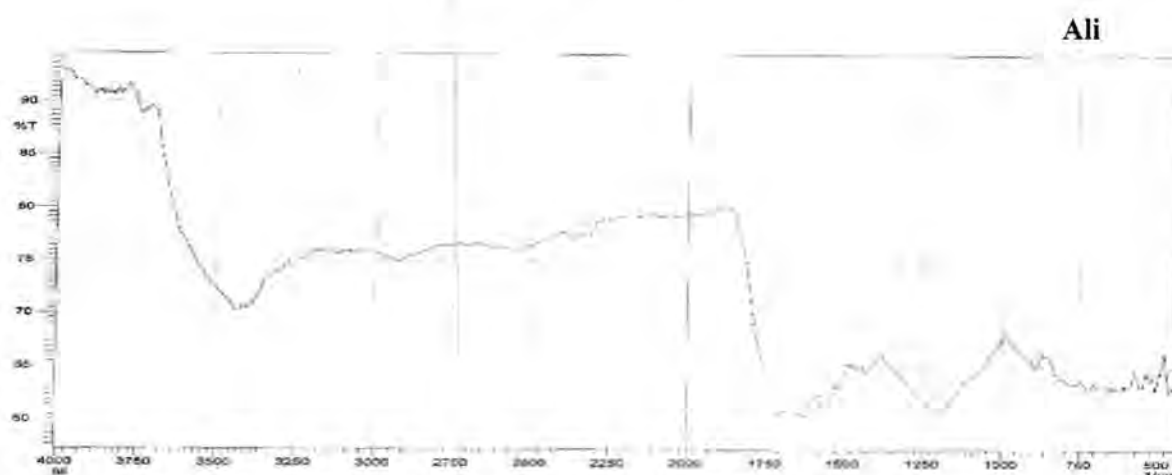


Figure 1: FTIR spectrum of poly (furfural-acetone)

Kinetics study

Three main kinetic models were used in this study :

The Pseudo First-Order model

The pseudo first-order equation(32) is generally expressed in its linear form as follow :

$$\text{Log}(q_e - q_t) = \text{log}q_e - (k_1/2.303)t \text{ -----(2)}$$

Where q_e and q_t are the sorption capacity at equilibrium and at any time, t , respectively, in mg/g, and k_1 is the pseudo-first order rate constant, in min^{-1} . By plotting the value of $\text{log}((q_e - q_t))$ versus t , the value of the rate constant k_1 can be obtained from the slope of graph, table (1) ,figure (4,5).

The Pseudo Second-Order model

The Pseudo-second order kinetics can be expressed in its linear form as follows(33)

$$t/q_t = (1/k_2 q_e^2) + (1/q_e)t \text{ -----(4)}$$

Where k_2 is the pseudo- second order rate constant, in g/mg.min .

By plotting t/q_t versus t , the value of q_e and k_2 can be obtained from the slope and the intercept, respectively, table (1) ,figure (6,7).

Intraparticle diffusion model

The Intraparticle Diffusion equation kinetics can be expressed in its linear form as follows(34)

$$q_t = K_{dif} t^{1/2} + B_L \text{(5)}$$

Where K_{dif} ($\text{mg g}^{-1} \text{min}^{-1/2}$) is the intra-particle diffusion rate constant, B_L represent the thinckness of the boundary layer.

By plotting of q_t versus $t^{1/2}$, the value of K_{dif} and B_L can be obtained from the slope and intercept respectively table (1), figure (8,9).

In this work, the influence of temperature on the kinetics of Ni(II) using poly(furfuryl alcohol) as sorbent was studied. the experimental tests were carried out in two temperatures 30 and 50 (keeping the initial metal concentration of 20mg/L). In figures (2 , 3) the sorption capacity values, q_e , was plotted against t for adsorption of Ni(II) onto PFA at 30 and 50C⁰ respectively.

The results were fitted by linear regression to the three kinetics models : pseudo-first order, pseudo-second order and intraparticle diffusion. Tables(1) report the parameter values obtained from the application of the kinetics models for Ni(II).

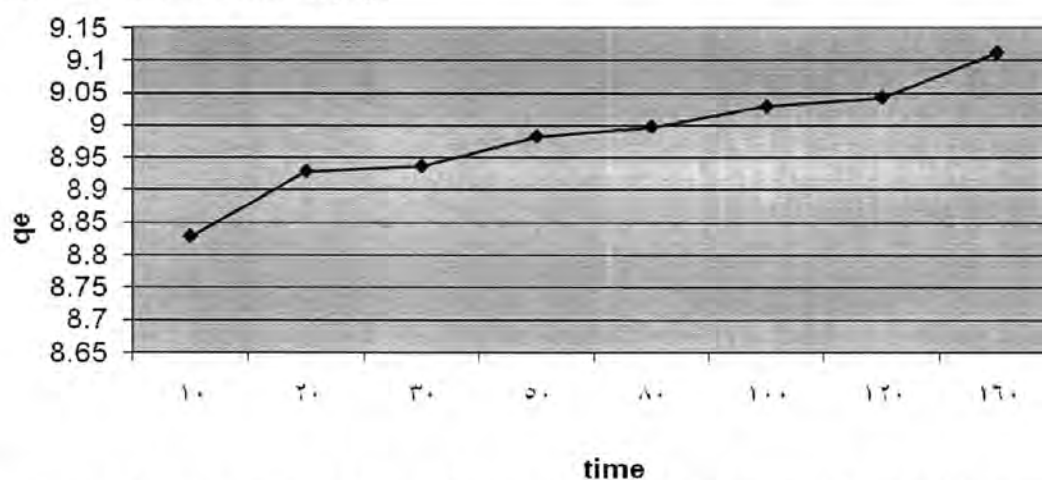


Figure 2: adsorption capacity of poly furfuryl alcohol for Ni(II) versus time at 30C⁰

Kinetics Study of The Removal of Ni(II) ion from Aqueous Solution Using Poly Furfuryl Alcohol

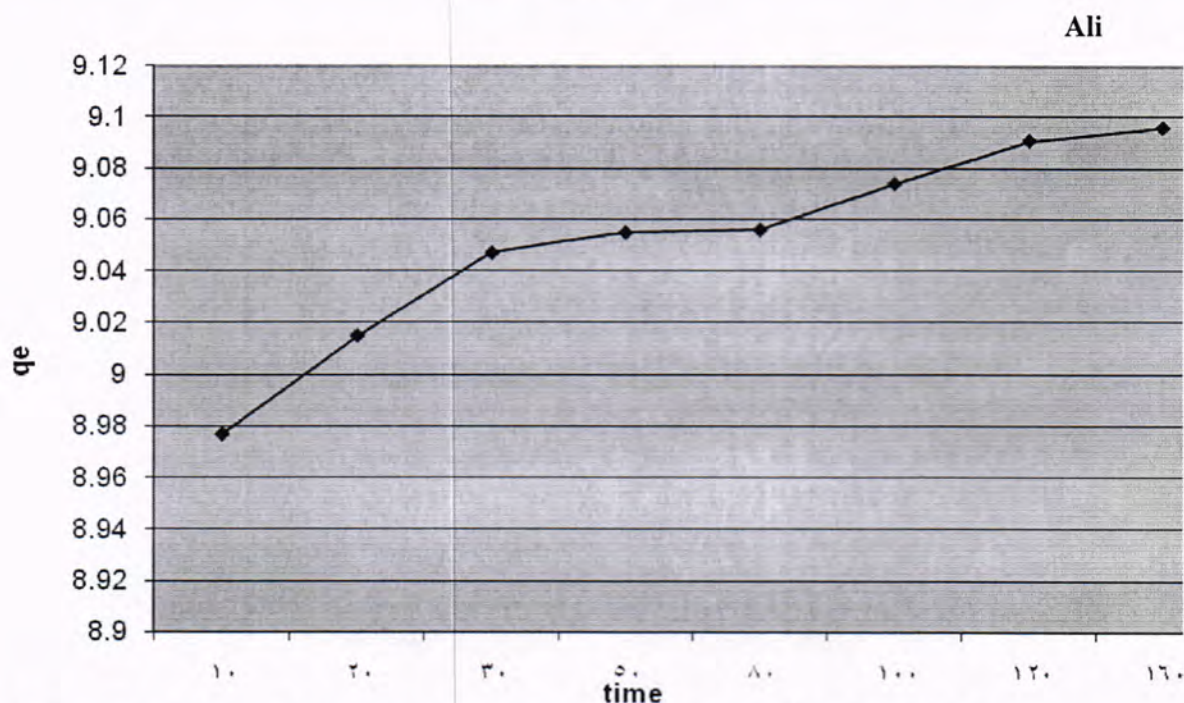


Figure 3: Adsorption capacity of poly furfuryl alcohol for Ni(II) versus time at 50C°

The correlation coefficient of plot of $\log(q_e - q_t)$ versus t was low, 0.8393, indicate that the first-order model did not describe the kinetic of Ni(II) adsorption. Beside that, the $q_e(\text{cal})$ did not agree with $q_e(\text{exp})$ figure (2, 3), table (1).

Correlation coefficients of the plot range between 0.899-0.8673 which indicate low linearity for the adsorption of Ni(II) by PFA.

As can be observed, the pseudo-second order model is the one that best describes the sorption of Ni(II) for all the range of experimental conditions investigated, The plot of t/q_e versus t gives straight line with $R^2=1$ and $q_e(\text{cal})$ agree very well with $q_e(\text{exp})$, table(1). h and k_2 increase, changing from 25.31 to 43.472 and 0.3085 to 0.596 when the temperature rises from 30c° to 50c°, respectively.

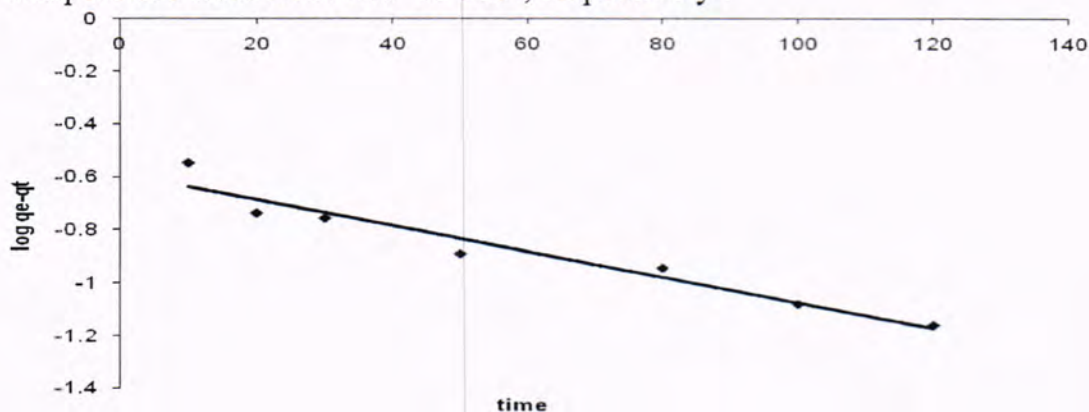


Figure 4: pseudo-first-order kinetics plot at 30C°

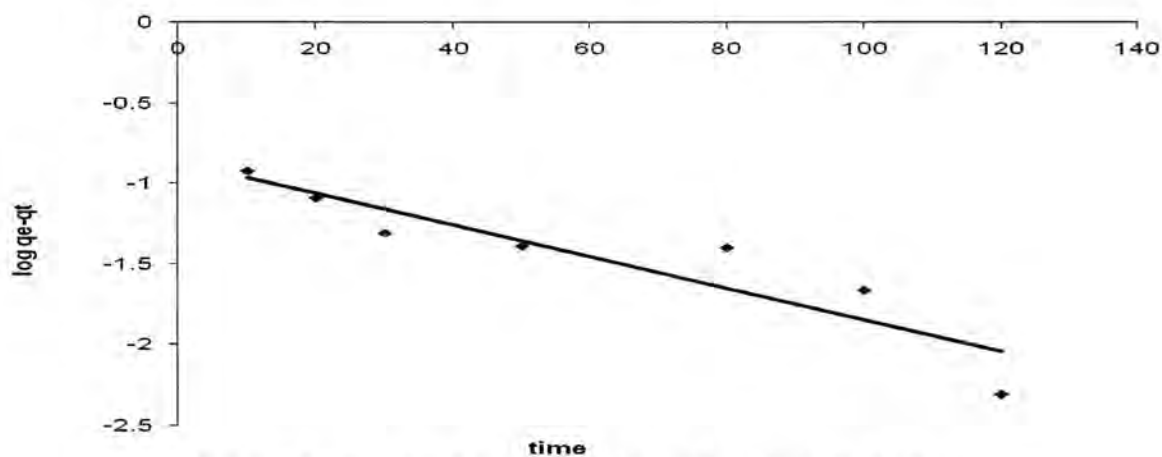


Figure 5: pseudo-first-order Kinetics plot at 50C°

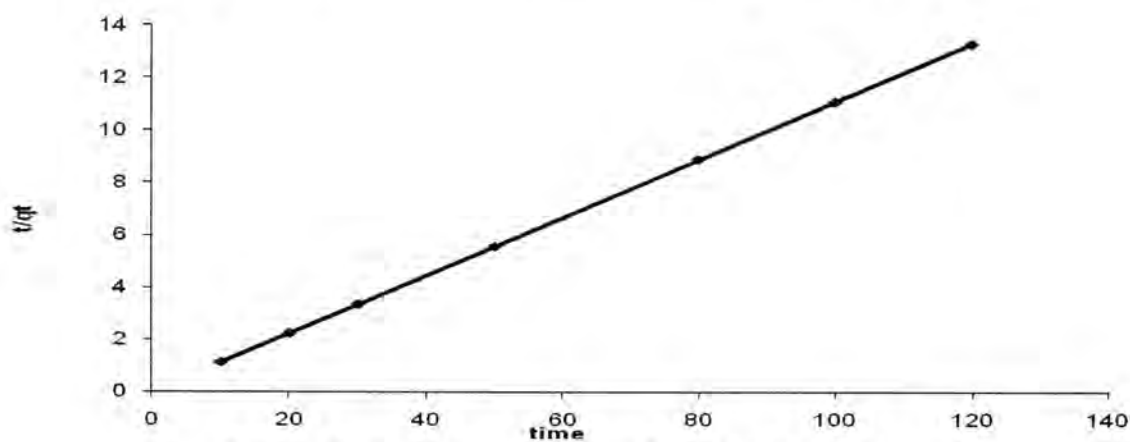


Figure 6: pseudo-second-order plot at 30C°

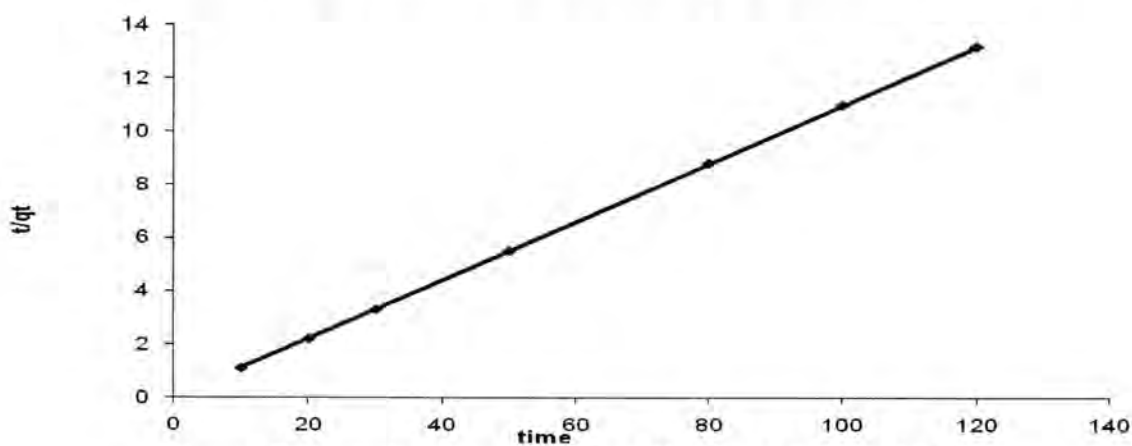


Figure 7: pseudo-second-order Kinetics plot at 50C°

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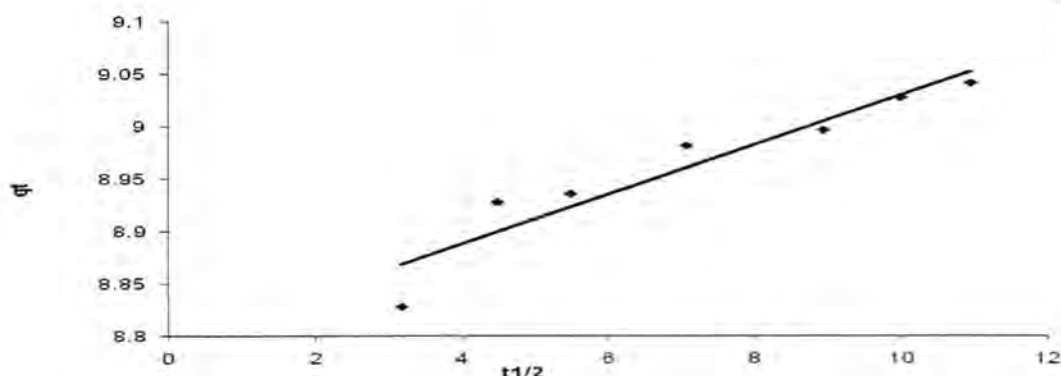


Figure 8: Intra-particle diffusion Kinetics plot at 30C°

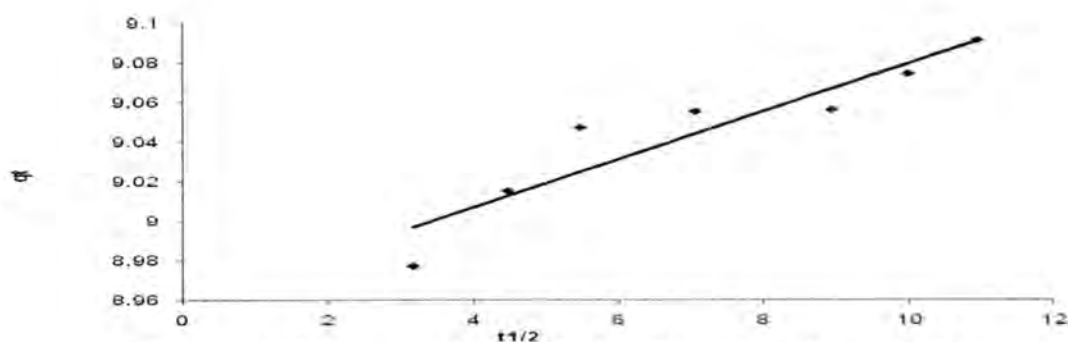


Figure 9: Intra-particle diffusion Kinetics plot at 50C°

The activation energy for Ni(II) metal ion sorption was calculated from the pseudo-second order constants by the Arrhenius equation. Its linear form for 30 and 50 C°(35).

$$\ln(k_1/k_2) = E_a/R(1/T_2 - 1/T_1) \quad \dots\dots\dots (6)$$

Where E_a is the activation energy, in KJ/mol, R is the gas constant, $8.314 \cdot 10^{-3}$ kJ/mol.k, k_1 , k_2 are the second- order constant at 30 and 50 C° respectively and T_1 , T_2 are the temperatures, in kelvin respectively . The activation energy was calculated and found to be 26.84 KJ mol⁻¹, which is in the range of physisorption mechanism

Table 1: The parameter of the three kinetics models of the adsorption of Ni(II) , onto PFA at 20ppm ,pH 6

1st-order

Temp	K_1	$q_e(\text{exp})$	$q_e(\text{cal})$	R^2
30	0.0113	9.111	0.2577	0.9413
50	0.0223	9.096	0.1348	0.8398

2nd-order

Temp	K ₂	q _e (exp)	q _e (cal)	h	R ²
30	0.3085	9.058	9.49	25.31	1
50	0.596	9.091	9.1	43.472	1

Intraparticle diffusion

Temp	K _{dif}	B _L	R ²
30	0.0236	8.798	0.899
50	0.0121	8.9585	0.8673

The present study indicates that the new adsorbent is effective for the removal of nickle from aqueous solution.

The adsorption process is highly dependent on pH, the maximum removal of nickle was obtained at pH 6. The experimental data fit well with the second-order kinetic.

The values of Ea was positive and lie in the range of physisorption.

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Synthesis and Studies of Some transition metals ions [M(II):Co, Ni, Cu, Zn and Cd] with 1,4- diphenylthiosimecarbazine (L)

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الخلاصة

حضرت معقدات جديدة للكاند (L) 4،1 ثنائي- فنيل ثايو سيمي كاربازيد مع أملاح كلوريدات ($M^{II} = \text{Ni, Co, Cu, Zn and Cd}$) شخّصت تراكيب المعقدات بواسطة استخدام التوصيلية المولارية، الاطياف (تحت الحمراء، فوق البنفسجية - المرئية) والنسبة المولارية مع التحليل الدقيق للفلز، أظهرت القياسات بأن سلوك الكاند (L) مع أيون الفلز ثنائي السن (N,S) معطيا شكل رباعي السطوح. تم دراسة الفعالية البايولوجية للكاند ومعقداته المختارة (Cu^{II} , Ni^{II} , Co^{II}) في تركيزين مختلفين (1 و 5 ملغم /مل) وقد اظهرت النتائج امتلاكها فعالية متباينة اتجاه البكتريا (*Staphylococcus aureus*) وليس لها تأثير على (*E. coli*).

ABSTRACT

Several new complexes of the title ligand 1,4-di-phenylthiosimecarbazine(L) with [$M^{II} = \text{Co, Ni, Cu, Zn and Cd}$] have been prepared. Structural assignments of the complexes have been made based on molar conductivity, spectral (IR, UV-Visible), molar ratio studies. It is proposed that (L) acts as a bidentate (S,N) donor in the present complexes and a tetrahedral structure is proposed. The antimicrobial activity of the ligand (L) and its complexes (Co^{II} , Ni^{II} and Cu^{II}) in two different concentration (1 and 5 mg/ml) have variety effect on *staphylococcus* and negative effect on *E. coli*.

INTRODUCTION

The study of compounds which contains (S,N) have been taken a wide area in an organic and inorganic field. An important type are those containing thioamide group-NCS. This group is also found in many basic structures of drug either as part of open chain e.g. thiocarbonate (R-NH- (S) NR_2) or involved in a hetero cyclic ring e.g thio derivatives and forming ability of above ligands with various metal ions have been also reported.(1-6). Prompted by the above observations, we thought it of interest to synthesis and characterize 1,4-diphenylthiosimecarbazine and its complexes with metal ion $M^{II} = \text{Co, Ni, Cu, Zn and Cd}$.

MATERIALS AND METHODS

A-Chemicals; All reagent used were anlar or chemically pure grade by companies British Drug Houses (BDH), Merk and Fuka.

- The chemical materials: Phenylhydrazine, Phenylthiocyanate, Potassium hydroxide, Cobaltchloridehexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), Copperchloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), Nickelchloridehexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$), Cadimium chloridehydrate ($\text{CdCl}_2 \cdot \text{H}_2\text{O}$) and Zincchloridemonohydrate ($\text{ZnCl}_2 \cdot \text{H}_2\text{O}$). Ethanol ($\text{CH}_3 \text{CH}_2 \text{OH}$), Dimethylformamide (DMF).

B-Instrument;

-Atomic Absorption (A.A) Emission spectro photometer (AA680) Shimadza.

-Melting points were determined by Gallen-Kamp apparatus.

-IR spectra were recorded as discs in the range ($4000\text{-}400 \text{ cm}^{-1}$) using shimadzu-FTIR 8000 series.

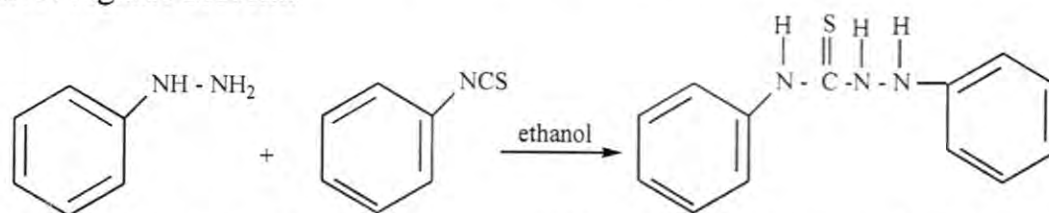
-UV-Visible spectra were recorded by SHIMDZU-UV-VIS-160A Ultra violent Spectro photometer at 25°C , using 1 cm quartz cell and examined at the range of (200-1100)nm at 10^{-13}M in DMF.

-Molar conductivity of the complexes were measure on pw 9526 digital conductivity at the concentration 10^{-3}M in dimethylformamide.

Preparation

Synthesis of the ligand 1,4di-phenylthiosimecarbaziid:

To a solution of 0.108 gm (0.001 mmol) of phenyl hydrazine in 10 ml absolute ethanol 0.135 gm (0.001 mmol) phenyl thiocyanate in 10 ml in solvente ethanol was added and the mixture was refluxed for one hour. A yellow precipited formed which separated out by filtration, crystallized from ethanol to give final product melt at 70°C with yield 80% soluble in most organic solvent.



phenylhydrazine phenyl thiocyanate 1,4- diphenylthiosimecarbazine

Synthesis of the metal complexes:

A stoichometric amount of the ligand (0.243 gm 0.001 mmol) in 10 ml of ethanol was added to a solution of potassium hydroxide(0.056 gm 0.001 mmol). The mixture was refluxed for half hour. An ethanolic solution 10ml of MCL_2 [$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.237gm 0.001mmol), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.237gm 0.001mmol), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.17gm 0.001mmol), $\text{ZnCl}_2 \cdot \text{H}_2\text{O}$ (0.154gm 0.001mmol), $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ (0.201gm 0.001mmol)]was added to it. The

mixture was refluxed for two hours. The solids obtained were filtered, washed repeatedly with hot distilled water, ethanol and dried in vacuo. Color, melting point, metal analysis and solubility of the ligand and its complexes are given in (Table 1).

Table 1: Physical properties of ligand (L) and its complexes.

No.	Compound	Color	m.pC°	M.wt	Metal analysis Found (calculated) M%	solubility
1	(L) $C_{13}H_{13}N_3S$	Yellowish	70 C°	243	-	DMF CH ₃ OH
2	L-CuCl \cdot H ₂ O	Green	128 C°	358	17.7 (17.32)	=
3	L-CoCl \cdot H ₂ O	Blue	135 C°	353.4	16.38 (16.99)	=
4	L-NiCl \cdot H ₂ O. 5(C ₂ H ₅ OH)	Green	139 C°	583.19	10.06 (10.98)	=
5	L-ZnCl \cdot H ₂ O	Dark brown	102 C°	359.89	18.16 (18.20)	=
6	L-CdCl \cdot H ₂ O	Dark brown	149 C°	406.91	27.62 (27.48)	=

DMF = Dimethylformamide

RESULTS AND DISCUSSION

The (L) was considered one of derivatives compound of thiourea. It was obtained by reaction of equi mole of phenyl thiocyanate and phenylhydrazine

1-The infrared of the ligand(L) and complexes:

Because of substituted thiourea consist of the SCN₂H group which may be available either the thion form (S=C-N-H) or the thio form (H-S-C=N). From the study of infrared spectroscopy as shown Fig.(1) indicated the ligand, the thione form in both free state and in complexes. This was disticted by the absence of the ν (S-H) bond in the region of 2600-2550 cm⁻¹ and the presence of ν (N-H) band in In the region of (3100) cm⁻¹. It is well known now that organic group compounds containing a thioamide group gives rise to four characteristic thioamide bands . Respectively thus, the strong bands at 1512 cm⁻¹ in the spectrum of the ligand may be the thioamide band I which has contribution from δ (N - H) + δ (C - H) mainly. This band shifts to 1492 cm⁻¹ due to coordination of nitrogen to metal ions. The thioamide band II appears at 1273 cm⁻¹ as strong band in the spectrum of the ligand which blue shifts to 1350-1307 cm⁻¹ in the spectra of all the complexes. Since this band has main contribution from ν (C = S) + ν

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(C = N), its blue shifting may be due to coordination through sulphur or through nitrogen of the ligand. The band III appears at 972 cm^{-1} in the spectrum of the ligand which is mixed band having contributions from $\nu(\text{C}\equiv\text{N}) + \nu(\text{C}\equiv\text{S})$ which red shifts to $891 - 914\text{ cm}^{-1}$ in the spectra of the complexes. This may be possible if coordination occur both through nitrogen as well as sulphur. The thioamide band (IV) appears at 779 cm^{-1} in the spectrum of the ligand which has main contribution from $\nu(\text{C}=\text{S})$. This band red shifts to $732 - 763\text{ cm}^{-1}$ in the spectra of all complexes. The $\nu(\text{C}=\text{S})$ band has been used as diagnostic of metal nitrogen or metal sulphur bonding and a red shift of $25 - 55\text{ cm}^{-1}$ in band IV indicates bonding through sulphur. A red shift of about $80 - 100\text{ cm}^{-1}$ indicates bridging sulphur ligand and a blue shift of $40 - 90\text{ cm}^{-1}$ indicates bonding through nitrogen. Thus, the red shift in the range $16 - 27\text{ cm}^{-1}$ of the band IV may be taken as the proof of bonds, through sulphur. It appears from above discussion the ligand acts as a bidentate ion ligand coordinating with metal ion with $\bar{\text{N}}$ nitrogen and thio carbonyl sulphur forming five member ring (7-8). The IR spectra of all complexes shows new bands at $(3414-3213)\text{cm}^{-1}$. This may have contribution from OH due to water and ethanol. The mode of coordinated water gave band $914-826\text{ cm}^{-1}$ and new bonds at $(520-540)\text{cm}^{-1}$ and $(455-447)\text{cm}^{-1}$ are due to metal-nitrogen and metal-sulphur bands (9-10).

Table 2: Selected IR peaks of (1,4di-phenylthiosimecarbazine) bands and its complexes

No.	Compound	$\nu(\text{N-H})$ $+ (\text{OH})\text{ cm}^{-1}$	Band I	Band II	Band III	Band IV	Band Δ	$\nu(\text{O-H}_2)$ $\text{cm}^{-1}\text{equ.}$	M-N	M-S
1	(L) $\text{C}_{13}\text{H}_{13}\text{N}_3\text{S}$	3167.12 3213.41	1512	1273	972	779	-	-	-	-
2	L-CuCl.H ₂ O	3236.55. 3414.00	1492	1307.7 4	914.26	763	16	914.20	540.07	447.49
3	L-CoCl.H ₂ O	3194.12 3363.86	1492	1323.1 7	910.40	752.24	27.76	837.11	540.01	455.20
4	L-NiCl.H ₂ O. 5(C ₂ H ₅ OH)	3132.46 3414.00	1492	1350.1 7	902.69	752.24	27.76	817.82	520.78	447.49
5	L-ZnCl.H ₂ O	3275.13 3360.00	1492	1315.4 5	891.11	756.10	22.9	837.11	536.21	447.49
6	L-CdCl.H ₂ O	3350.64 3264.16	1492	1317.2 4	912.56	755.01	23.99	826.92	539.99	449.98

OH = Due to either water and ethanol

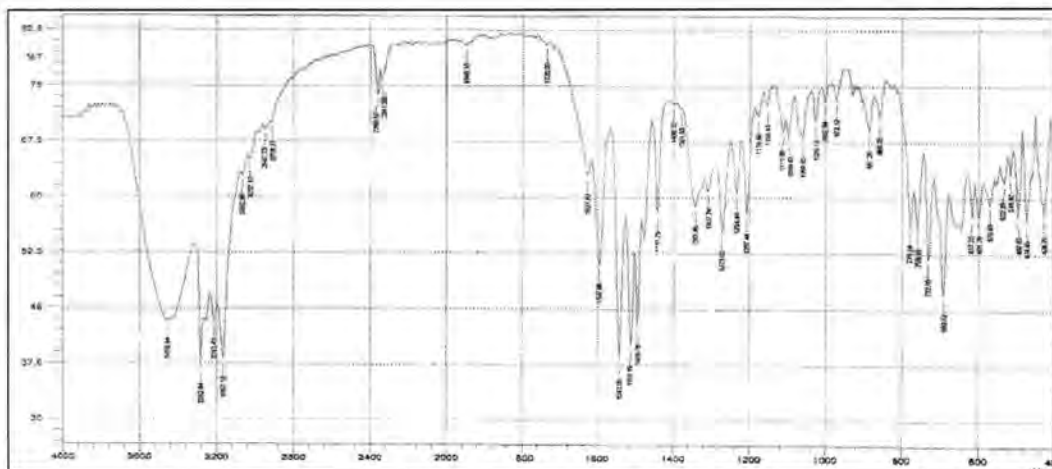


Figure 1 (a): Infrared Spectra of (L)

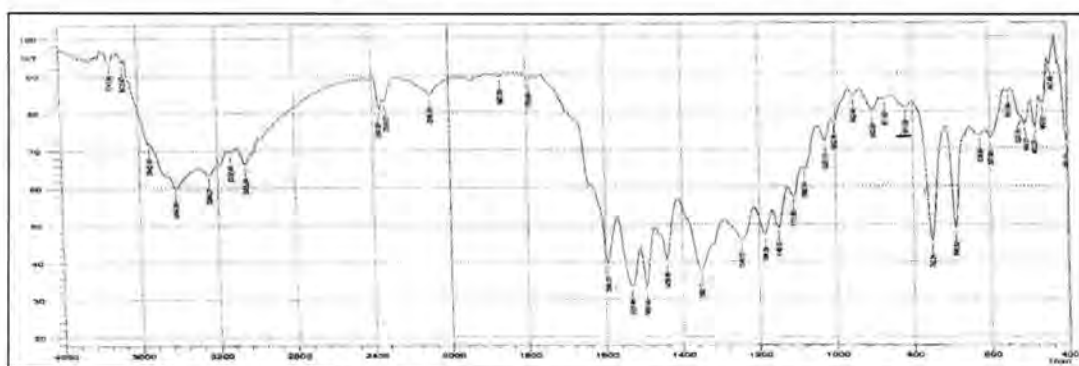


Figure 1 (b): Infrared Spectra of L.Ni Complex

2-The UV-Visible spectra of the ligand and its complexes:

The UV-Visible spectrum of the ligand in Dimethylformamide solution exhibited strong absorption band at 240 nm (41666 cm^{-1}) and shoulder at 275 nm (36363 cm^{-1}). This may attributed to the $\pi\text{-}\pi^*$ and $n\text{-}\pi^*$ transition (9). The green colored Copper complex showed abroad at 698 nm (14321 cm^{-1}) expected for tetrahedral due to the transion ${}^2T_2 \rightarrow {}^2E$. (10, 11). The tetrahedral cobalt (II) complex is commonly intense blue color, the electronic spectrum of Co-complex showed broad absorption band at 495 nm (20202 cm^{-1}) which is agreement with tetrahedral structure (T_d stereochemistry). The Ni (II) forms green colored complex. The electronic spectra of Ni-complex showed one broad absorption band in the region 569 nm (17609 cm^{-1}) ${}^3T_{1(P)} \leftarrow {}^3T_1$ is absorption typical of tetrahedral complex. The absorption spectra of ,Zinc(II) and Cadmium(II) complexes showed tail in ($340,366\text{ cm}^{-1}$) may be due to partially interaction between the ligand and metal ions(12). The molar conductance of all complexes in Dimethylformamide were found to be low which suggested that they are non-electrolytes(13). Electronicspectra, conductance in dimethylformamide), of the ligand and its complexes are give in Table (3).

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**Table 3: Electronic spectra (DMF), conductance in DMF, of the ligand
(L) and its complexes**

No.	Compound	λ (nm) cm^{-1}	Assignment Bands	$\Lambda \text{ S. cm}^{-1}$ DMF (10^{-3} M)
1	(L) $\text{C}_{13}\text{H}_{13}\text{N}_3\text{S}$	(240) 41666	$\pi \rightarrow \pi^*$	-
2	L-CoCl.H ₂ O	(495) 20202	T_d Sterechemistry	1.68
3	NiCl.H ₂ O 5(C ₂ H ₅ OH)	(569) 17609	${}^3T_{1(p)} \leftarrow {}^3T_1$	1.18
4	L-CuCl.H ₂ O	(698) 14321	${}^2T_2 \rightarrow {}^2E$	2.18
5	L-ZnCl.H ₂ O	(340) 29411	Charge-Transfer	1.59
6	L-CdCl.H ₂ O	(366) 27322	Charge-Transfer	2.63

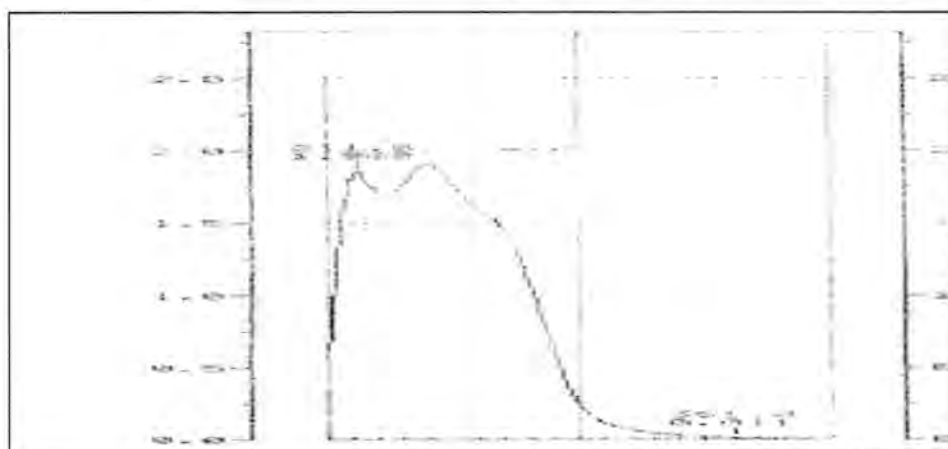


Figure 2(a): U.V Visible Spectra of(a)L

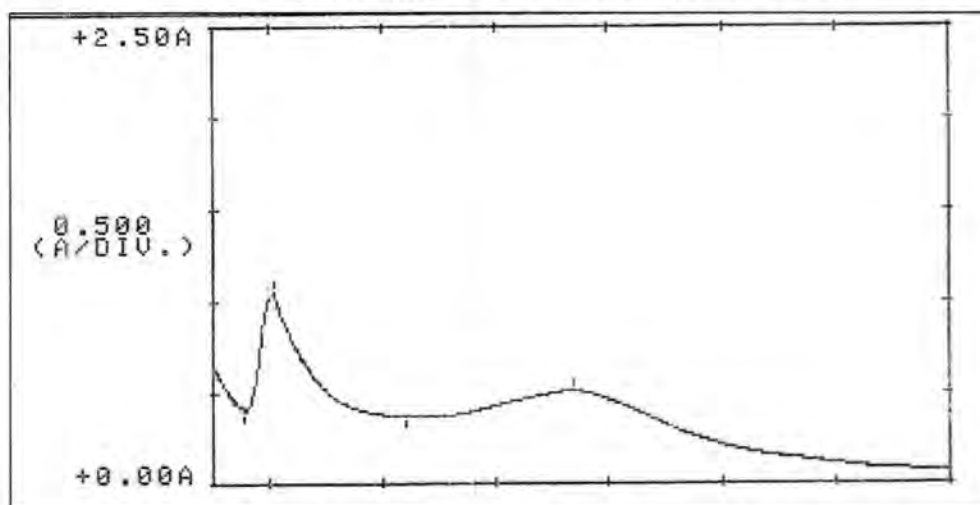


Figure 2(b):U.V Visible Spectra of L.Ni Comple

Molar ratio**Study of ligand complexes formation in solution:**

The complexes of this ligand with metal ion (II) (Co, Ni, Cu, Zn, Cd) were studied in solution using ethanol as solvent, in order to determine (M:L) ratio in the prepared complexes, following molar ratio method (14). A series of solutions were prepared having a constant concentration (C) 10^{-3} M of hydrated metal salts and the ligand. The (M:L) ratio was determined from the relationship between the absorption of absorbed light and molar ratio (M:L) found to be 1:1 for the all complexes Fig.3 (a),(b),(c),(d),(e). The result of complexes formation in solution are shown in Table (4).

VM = volume of metal in ml

VL = volume of ligand in ml

Table 4 : Results of Complexes Formation in Solution

L – CdCl . H ₂ O		
VM	VL	Abs
1 ml	0.25	0.04
1	0.50	0.19
1	0.75	0.175
1	1	0.23
1	1.25	0.23
1	1.50	0.23

L – CoCl . H ₂ O		
VM	VL	Abs
1 ml	0.25	0.34
1	0.50	1.23
1	0.75	1.28
1	1	1.62
1	1.25	1.84
1	1.50	1.84

L – CuCl . H ₂ O		
VM	VL	Abs
1 ml	0.25	0.32
1	0.75	1.04
1	1	1.40
1	1.75	1.40
1	2	1.40

L – NiCl . H ₂ O 5(C ₂ H ₅ OH)		
VM	VL	Abs
1 ml	0.25	0.035
1	0.50	0.090
1	0.75	0.096
1	1	0.139
1	1.25	0.139

L – ZnCl . H ₂ O		
VM	VL	Abs
1 ml	0.25	0.60
1	0.75	2.42
1	1	2.34
1	1.25	2.42
1	1.50	2.43
1	1.75	2.43

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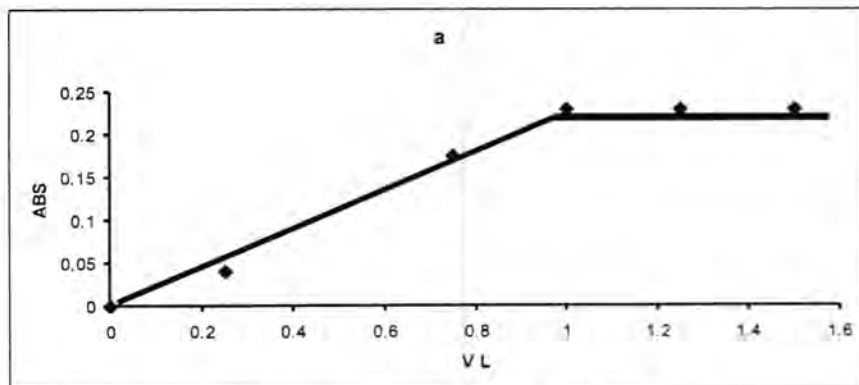


Figure 3 (a) : Mole-ratio plots for Cd^{+2} ion $\lambda(420)$

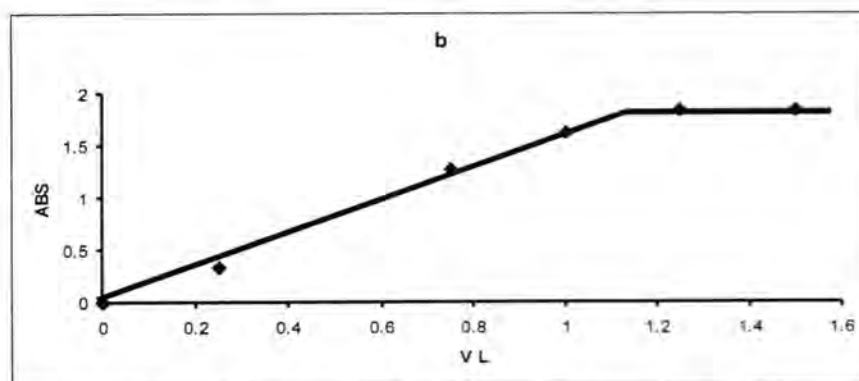


Figure 3(b): Mole-ratio plots for Co^{+2} ion $\lambda(350)$

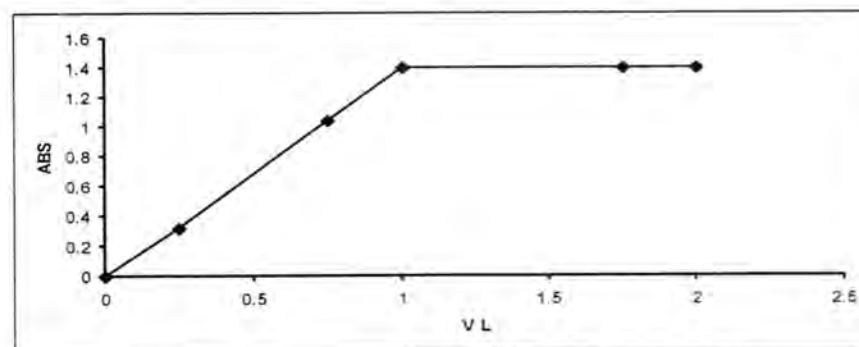


Figure 3 (c): Mole-ratio plots for Cu^{+2} ion $\lambda(678)$

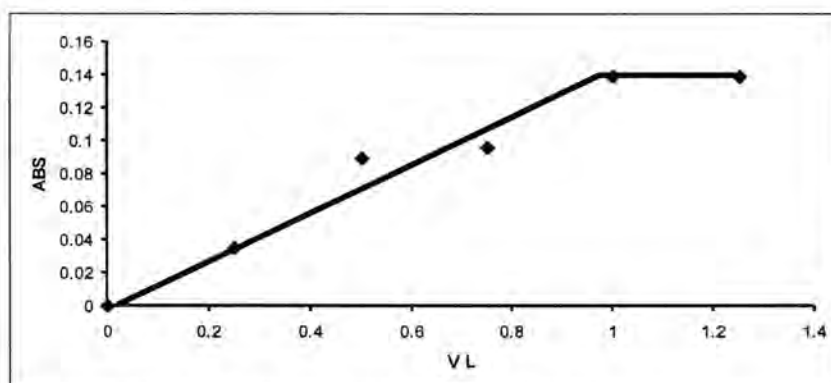


Figure 3 (d): Mole-ratio plots for Ni^{+2} ion $\lambda(380)$

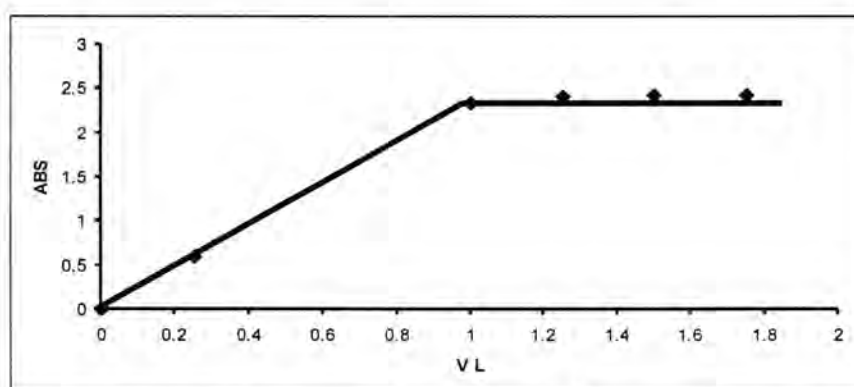


Figure 3 (e): Mole-ratio plots for Zn^{+2} ion $\lambda(245)$

Study of biological activity

The biological of the prepared new ligand and its complexes were studied against selected types of microorganisms which include gram positive bacteria like *staphylococcus aureus* and gram Negative bacteria like *E-Coli*, in agar diffusion method, which is used Dimethylformamide as a solvent, and were used these Antibiotics disc which include Cephalosporin Amoxicillin and Nystatin as control. Agar diffusion method involves the exposure of the Zone of inhibition toward the diffusion of microorganisms on agar plate. The plates were incubated for (24) hours at (37°C). The Zone of inhibition of bacterial growth around the disc was observed. The biological effect of the ligand and its complexes showed variety effect on *staphylococcus aureus* and no effect on *E.coli* given in Table (5). Biological effects of new ligand and its complexes (Co, Ni, Cu) indicated variety of antibacterial activities in different concentration against *staphylococcus aureus* except Copper complex didn't show any effect. The ligand and its complexes (Co, Ni, Cu) did not show any effect on *E.coli* (Fig.4).

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Table 5: The biological effect of ligand and its complexes:

Compounds	(Gram positive) <i>staph</i>		(Gram positive) <i>E.coli</i>	
	1 mg	5 mg	1 mg	5 mg
(L)C ₁₃ H ₁₃ N ₃ S	11	20	no	no
L-NiCl.H ₂ O.5(C ₂ H ₅ OH)	16	12	no	no
L-CoCl.H ₂ O	12	24	no	no
L-CuCl.H ₂ O	no	no	no	no

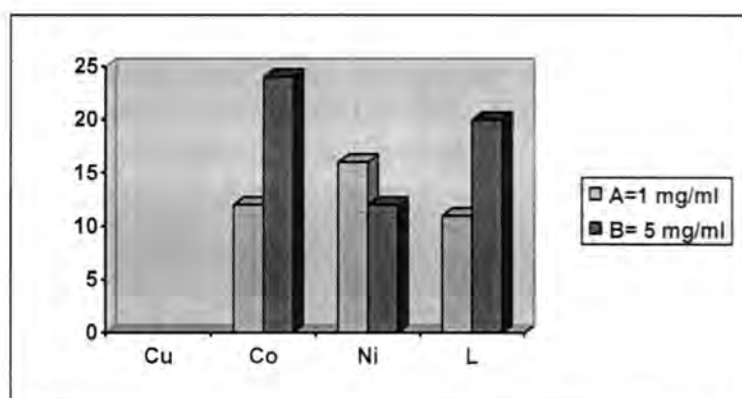
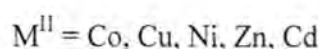
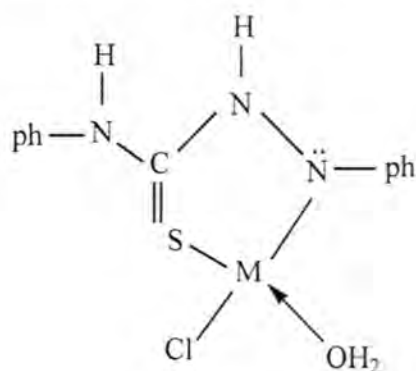


Figure 4: Effect of ligand and its complexes on *staphylococcusaureus*.

A series of complexes of bivalent metal ion (Co, Ni, Cu, Zn, Cd) with 1,4-Diphenylthiosimecarbazid have been prepared and characterized. The ligand is behaving as anionic bidentate ligand (S, N) and binding metal ions forming tetrahedral structure as follow;



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Synthesis of New Compounds Derived from 3,5-Dinitrobenzoyl Chloride

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الخلاصة

المركب رقم (2) ينتج من عملية أسيلة مركب 2-أمينو حامض الخليك (الكلايسين) مع 3، 5-ثنائي نايتروبنزويل كلورايد، 1، 3 - اوكسازول (4H)5 اون يخلق من عملية الغلق الحلقي للمركب (2). المركبات (4a-i) حولت الى المشتقات الاخرى في البحث. شخّصت المركبات المحضرة بواسطة الطرائق الطيفية $^1\text{H NMR}$, FTIR, UV.

ABSTRACT

Starting compound (2) was readily obtained by acylation of 2-amino acetic acid (**Glycine**) with 3,5-dinitrobenzoyl chloride. 1,3-oxazol-5(4H)-one (3a-c) was synthesized by cyclization of [3,5-dinitrophenyl-carbonyl) amino] acetic acid (2). Compounds (4a - i) were converted into a variety of derivatives. All new compounds were characterized by $^1\text{H NMR}$, FTIR and UV spectroscopy.

INTRODUCTION

The imidazole nucleus appears in a number of naturally occurring products like the amino acids, histidine and purines which comprise many of the most important bases in nucleic acids. Imidazole derivatives possess a broad spectrum of pharmacological activities such as anticonvulsant(1)anti-parkinson (2)and monoamineoxidase (MAO) inhibitory(3) activity. The imidazole-containing DNA enzyme, one of the smallest known nucleic acid enzymes, combines the substrate-recognition properties of nucleic acid enzymes and the chemical functionality of protein enzymes in a molecule that is small, yet versatile and catalytically efficient (4) 1-methyl imidazole as a co-catalyst should play a dual role in the reaction: by coordinating at the zinc center it should help solubilizing the zinc carboxylate into the epoxide/ CO_2 reaction mixture and, on the other hand, it might activate the epoxide due to its highnucleophilicity.(5). (2,4-Dioxoimidazolidin-1-yl) alanine derivatives have been formed via the corresponding ureidoalanine intermediate in the course of investigations of the synthesis of quisqualic acid analogues(6). On the other hand, relatively little is known about 1H-imidazol-1-yl substituted α,β -didehydroaminoacid derivatives. The most

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frequently investigated derivatives of this type were obtained by the Michael addition of imidazole or protected histidine to *N*-(*tert*-butoxycarbonyl)-*N*-(*p*-toluenesulfonyl)- α,β -didehydro- α -amino acid esters followed by spontaneous detosylation of the Michael products.(7),(8). Metronidazole (MTZ) is a synthetic compound that is used in the treatment of infection caused by Gram negative anaerobic bacteria like *Helicobacter pylori* and Protozoan such as *Giardia*, *Lambli*a, *Eutomoeba hostolytica*(9).

MATERIALS AND METHODS

Melting point were determined in capillary tubes on a Galen Kamp melting point apparatus and are uncorrected. The IR Spectra were recorded by KBr discs using a Perkin-Elmer 1600 series FTIR spectrometer. UV. Spectra were recorded on Hitachi 2000 spectrophotometer using absolute ethanol as solvent ¹HNMR Spectra were recorded on a Varian-Mercury 200 MHZ Spectrometer.

Synthesis of [(3,5-dinitrophenyl-carbonyl amino)acetic acid (2)

To a stirring solution of Glycine (0.75 g, 0.01 mole) and sodium hydroxide (10 ml, 10% solution), 3,5-dinitrobenzoyl chloride (1.41 g, 0.01 mole) was added. Then, the reaction mixture was shaken vigorously for 1h. ,a few grams of crushed ice was added with stirring. After that, the solution was acidified with conc. HCl and the product was collected and recrystallized from ethanol. (yield 67 %), (m.p, C°)(250-252), (IR. (KBr) (ν , Cm^{-1}) 3115 (NH), 3329 (acid OH), 2910-2799 (C-H alph.) ,1726 (acid C=O),1657 (amide C=O); ¹HNMR (DMSO-*d*₆) δ (ppm) 2.96 (s, NH), 3.28 (s, CO-CH₂-NH), 7.02-8.11 (m, Aromatic proton); U.V (EtOH) 267 nm , 381 nm.

Synthesis of 4-(arylidene)-2-(3,5-dinitrophenyl)-1,3-oxazol-5(4H)-one(3a- c)

To a stirring mixture of compound 2 (1.8 g, 0.01 mole) acetic acid (5 ml) acetic anhydride (20 ml), aromatic aldehyde (0.01 mole) was added. The temperature of reaction was reached to 70 C° for 10 min., then the mixture was poured in to crushed ice and stirred for 30 min. the product was collected and recrystallized from ethanol to afforded the desired compound.

3a. (yield 45 %), (m.p, C°)(132 -134), IR. (KBr) (ν , Cm^{-1}) 3066 (C-H Ar), 3164 (C-H olefene.), 1773g (oxazole C=O), 1600 - 1500 (C=C Ar), ¹HNMR (DMSO-*d*₆) δ (ppm) 8.90 (s, C=CH-), 6.91 – 8.1 (m, Aromatic proton); U.V (EtOH) 227 nm , 359 nm

3b. (yield 41 %), (m.p, C°)(118 - 120), IR. (KBr) (ν , Cm^{-1}) 3082 (C-H Ar), 3143 (C-H olefene.), 1769 (oxazole C=O), 1603 - 1517 (C=C Ar); U.V (EtOH) 228 nm , 361 nm

3c. (yield 45 %), (m.p, C°)(156 - 158), IR. (KBr) (ν , Cm^{-1}) 3053 (C-H Ar), 3141 (C-H olefene.), 1752g (oxazole C=O), 1592 - 1487 (C=C Ar); U.V (EtOH) 211 nm , 339 nm.

Synthesis of 3-amino-5-(arylidene)-2-([3,5-dinitrophenyl]-3,5-dihydro-4H-imidazol-4-one (4a – c)

To a mixture of compound (3a – c) (0.01 mole) in dry benzene (5ml) hydrazine hydrate (99%) (10ml) was added. The reaction mixture was refluxed for 7 hrs. Then, the mixture was allowed to cool to room temperature and benzene was removed. The product was recrystallized from ethanol to afford the desired compound.

4a. (yield 61 %), (m.p, C°)(231 -233), IR. (KBr) (ν , Cm^{-1}) 3361-3220 (NH₂), 3032 (C-H Ar), 3140 (C-H olefene.), 1657 (imidazole C=O), 1591 - 1486 (C=C Ar); U.V (EtOH) 223 nm , 310 nm

4b. (yield 35 %), (m.p, C°)(252 -254), IR. (KBr) (ν , Cm^{-1}) 3320-3239 (NH₂), 3091 (C-H Ar), 3176 (C-H olefene.), 1636 (imidazole C=O), 1601 - 1522 (C=C Ar), ¹HNMR (DMSO-d₆) δ (ppm) 8.77 (s, C=CH-), 8.19 (s, NH₂), 7.13 – 8.09 (m, Aromatic proton); U.V (EtOH) 255 nm , 396 nm.

4c. (yield 38 %), (m.p, C°)(221 - 223), IR. (KBr) (ν , Cm^{-1}) 3321-3280 (NH₂), 3065 (C-H Ar), 3161 (C-H olefene.), 1690 (imidazole C=O), 1600 - 1497 (C=C Ar); U.V (EtOH) 236 nm , 371 nm

Synthesis of 5-(arylidene)-3-[(arylidene)amino]-2-(3,5-dinitrophenyl)-3,5-dihydro-4H-imidazol-4-one (5a – i)

The corresponding aryl aldehyde (0.01 mole) was added to a stirred solution of compound (4a – c) (0.01 mole) in absolute ethanol (20ml) and the mixture was refluxed for 2h. After cooling, the mixture was filtered and the solid recrystallized from ethanol to afford the desired compound.

5a. (yield 68 %), (m.p, C°)(292 - 294), IR. (KBr) (ν , Cm^{-1}) 3084 (C-H Ar), 3173 (C-H olefene.), 1645 (imidazole C=O), 1667 (C=N, Schiff's base) 1600 - 1517 (C=C Ar), 1210 (C-N); ¹HNMR (DMSO-d₆) δ (ppm) 8.45 (s, C=CH-), 8.72 (s, CH=N), 7.02 – 8.21 (m, Aromatic proton); U.V (EtOH) 246 nm , 365 nm.

5b. (yield 65 %), (m.p, C°)(261 - 263), IR. (KBr) (ν , Cm^{-1}) 3059 (C-H Ar), 3134 (C-H olefene.), 1661 (imidazole C=O), 1653 (C=N, Schiff's base) 1600 - 1501 (C=C Ar), 1232 (C-N); U.V (EtOH) 241 nm , 390 nm

5c. (yield 78 %), (m.p, C°)(211 - 213), IR. (KBr) (ν , Cm^{-1}) 3065 (C-H Ar), 3146 (C-H olefene.), 1666 (imidazole C=O), 1675 (C=N, Schiff's base) 1602 - 1509 (C=C Ar), 1252 (C-N); ¹HNMR (DMSO-d₆) δ (ppm) 8.42 (s, C=CH), 8.65 (s, CH=N), 7.11 – 8.23 (m, Aromatic proton); U.V (EtOH) 253 nm , 379 nm

5d. (yield 88 %), (m.p, C°)(263 - 265), IR. (KBr) (ν , Cm^{-1}) 3046 (C-H Ar), 3129 (C-H olefene.), 1638 (imidazole C=O), 1645 (C=N, Schiff's base) 1589-1486 (C=C Ar), 1221 (C-N); ¹HNMR (DMSO-d₆) δ (ppm) 8.52 (s,

C=CH-), 8.68 (s, CH=N), 6.98 – 8.31 (m, Aromatic proton); U.V (EtOH) 211 nm , 386 nm

5e. (yield 83 %), (224 - 226) (m.p, C°), IR. (KBr) (ν , Cm^{-1}) 3067 (C-H Ar), 3201 (C-H olefene.), 1627 (imidazole C=O), 1651 (C=N, Schiff's base) 1609 - 1489 (C=C Ar), 1210 (C-N); $^1\text{HNMR}$ (DMSO- d_6) ζ (ppm) 8.49 (s, C=CH), 8.56 (s, CH=N), 7.11 – 8.27 (m, Aromatic proton); U.V (EtOH) 229 nm , 356 nm

5f. (yield 63 %), (263 - 265) (m.p, C°), IR. (KBr) (ν , Cm^{-1}) 3043 (C-H Ar), 3128 (C-H olefene.), 1635 (imidazole C=O), 1656 (C=N, Schiff's base) 1600 - 1500 (C=C Ar), 1230 (C-N); U.V (EtOH) 256 nm , 330 nm

5g. (yield 75 %), (m.p, C°) (275 - 277), IR. (KBr) (ν , Cm^{-1}) 3074 (C-H Ar), 3206 (C-H olefene.), 1631 (imidazole C=O), 1656 (C=N, Schiff's base) 1603 - 1499 (C=C Ar), 1249 (C-N); $^1\text{HNMR}$ (DMSO- d_6) ζ (ppm) 8.47 (s, C=CH-), 8.79 (s, CH=N), 7.00 – 8.11 (m, Aromatic proton); U.V (EtOH) 234 nm , 372 nm.

5h. (yield 81 %), (244 - 246) (m.p, C°), IR. (KBr) (ν , Cm^{-1}) 3066 (C-H Ar), 3191 (C-H olefene.), 1656 (imidazole C=O), 1664 (C=N, Schiff's base) 1591 - 1507 (C=C Ar), 1235 (C-N); $^1\text{HNMR}$ (DMSO- d_6) ζ (ppm) 8.25 (s, C=CH-), 8.71 (s, CH=N), 7.04 – 8.23 (m, Aromatic proton); U.V (EtOH) 225 nm , 317 nm.

5i. (yield 86 %), (242 - 245) (m.p, C°), IR. (KBr) (ν , Cm^{-1}) 3071 (C-H Ar), 3229 (C-H olefene.), 1621 (imidazole C=O), 1654 (C=N, Schiff's base) 1600 - 1487 (C=C Ar), 1249 (C-N); U.V (EtOH) 210 nm , 359 nm.

Synthesis of *N*-[chloro(aryl)methyl]-*N*-[arylidene-5-oxo-2-(3,5-dinitrophenyl)-4,5-dihydro-1*H*-imidazol-1-yl]benzamide (6a - i)

To a stirring solution of compound (5a - i) (0.003 mole) in dry benzene (15 ml), benzoyl chloride (0.003 mole, 0.35 gm) in benzene (10 ml) was added drop wise, then the mixture was refluxed for (4 hrs.) with stirring. After cooling, the precipitate crystals was filtered and recrystallized from ethanol .

6a. (yield 58 %), (m.p, C°) (198 - 200), IR. (KBr) (ν , Cm^{-1}) 3063 (C-H Ar), 3161 (C-H olefene.), 1659 (imidazole C=O), 1667 (C=O, amide) 1591 - 1499 (C=C Ar), 1239 (C-N) ; $^1\text{HNMR}$ (DMSO- d_6) δ (ppm) 8.91 (s, C=CH-), 4.39 (s, N-CH-Cl), 6.79 – 8.42 (m, Aromatic proton); U.V (EtOH) 221 nm , 359 nm.

6b. (yield 76 %), (m.p, C°) (201 - 203), IR. (KBr) (ν , Cm^{-1}) 3065 (C-H Ar), 3138 (C-H olefene.), 1643 (imidazole C=O), 1676 (C=O, amide) 1600 - 1503 (C=C Ar), 1250 (C-N) ; $^1\text{HNMR}$ (DMSO- d_6) δ (ppm) 8.94 (s, C=CH-), 4.03 (s, N-CH-Cl), 7.00 - 8.01 (m, Aromatic proton); U.V (EtOH) 238 nm , 376 nm.

6c. (yield 56 %), (m.p, C°) (231 - 233), IR. (KBr) (ν , Cm^{-1}) 3059 (C-H Ar), 3145 (C-H olefene.), 1625 (imidazole C=O), 1661 (C=O, amide) 1579 - 1487 (C=C Ar), 1220 (C-N); U.V (EtOH) 231 nm , 398 nm

6d. (yield 69 %), (m.p, C°)(185- 187), IR. (KBr) (v, Cm^{-1}) 3080 (C-H Ar), 3121 (C-H olefene.), 1625 (imidazole C=O), 1653 (C=O, amide) 1602 - 1513 (C=C Ar), 1236 (C-N); U.V (EtOH) 267 nm , 334 nm.

6e. (yield 78 %), (m.p, C°)(173 - 175), IR. (KBr) (v, Cm^{-1}) 3084 (C-H Ar), 3205 (C-H olefene.), 1632 (imidazole C=O), 1648 (C=O, amide) 1603 - 1511 (C=C Ar), 1250 (C-N); U.V (EtOH) 246 nm , 375 nm.

6f. (yield 58 %), (m.p, C°)(264 -266), IR. (KBr) (v, Cm^{-1}) 3080 (C-H Ar), 3134 (C-H olefene.), 1638 (imidazole C=O), 1690 (C=O, amide) 1581 - 1479 (C=C Ar), 1218 (C-N) ; $^1\text{HNMR}$ (DMSO- d_6) δ (ppm) 8.69 (s, C=CH-), 4.21 (s, N-CH-Cl), 6.61 – 8.23 (m, Aromatic proton); U.V (EtOH) 263 nm , 371 nm

6g. (yield 75 %), (m.p, C°)(242 - 244), IR. (KBr) (v, Cm^{-1}) 3032 (C-H Ar), 3125 (C-H olefene.), 1632 (imidazole C=O), 1653 (C=O, amide) 1600 - 1508 (C=C Ar), 1256 (C-N) ; U.V (EtOH) 223 nm , 378 nm

6h. (yield 82%), (m.p, C°)(179 181), IR. (KBr) (v, Cm^{-1}) 3029 (C-H Ar), 3231 (C-H olefene.), 1642 (imidazole C=O), 1656 (C=O, amide) 1597 - 1501 (C=C Ar), 1261 (C-N); U.V (EtOH) 212 nm , 386 nm

6i. (yield 73 %), (m.p, C°)(265 -267), IR. (KBr) (v, Cm^{-1}) 3084 (C-H Ar), 3173 (C-H olefene.), 1624 (imidazole C=O), 1647 (C=O, amide) 1604 - 1491 (C=C Ar), 125 (1C-N) ; $^1\text{HNMR}$ (DMSO- d_6) δ (ppm) 8.90 (s, C=CH-), 3.92 (s, N-CH-Cl), 6.39 -7.86 (m, Aromatic proton); U.V (EtOH) 242 nm , 389 nm.

Synthesis of aryl{[4-arylidene-5-oxo-2-(pyridin-3-yl)-4,5-dihydro-1H-imidazol-1-yl](benzoyl)amino}methyl carbamimidothioate (7a - i)

A mixture of compounds (6a - i) (0.005 mole) thiourea (0.005mole, 0.44 gm) and anhydrous sodium carbonate (0.005 mole) in absolute ethanol (20 ml) was refluxed for 5 hrs. The mixture was filtrated then cooling and the precipitated crystals was filtered and recrystallized from appropriate solvent.

7a. (yield 63 %), (m.p, C°)(165 – 158), IR. (KBr) (v, Cm^{-1}) 3324-3221 (NH₂), 3161 (NH) 3060 (C-H Ar), 3111 (C-H olefene.), 1630 (imidazole C=O), 1665 (C=O, amide) 1600 - 1502 (C=C Ar), 1235 (C-N); U.V (EtOH) 256 nm , 334 nm.

7b. (yield 76 %), (m.p, C°)(234 -236), IR. (KBr) (v, Cm^{-1}) 3298-3233 (NH₂), 3136 (NH) 3079 (C-H Ar), 3123 (C-H olefene.), 1647 (imidazole C=O), 1675 (C=O, amide) 1600 - 1486 (C=C Ar), 1253 (C-N); $^1\text{HNMR}$ (DMSO- d_6) δ (ppm) 8.57 (s, NH₂), 8.34 (s, C=CH-), 4.49 (s, N-CH-S), 6.35 – 7.97 (m, Aromatic proton); U.V (EtOH) 231 nm , 378 nm.

7c. (yield 73 %), (m.p, C°)(187 -189), IR. (KBr) (v, Cm^{-1}) 3321-3287 (NH₂), 3147 (NH) 3092 (C-H Ar), 3111 (C-H olefene.), 1620 (imidazole C=O), 1649 (C=O, amide) 1602 - 1500 (C=C Ar), 1258 (C-N); $^1\text{HNMR}$ (DMSO- d_6) δ (ppm) 8.68 (s, NH₂), 8.25 (s, C=CH-), 4.27 (s, N-CH-S), 6.21 – 7.93 (m, Aromatic proton) U.V (EtOH) 242 nm , 387 nm.

Synthesis of New Compounds Derived from 3,5-Dinitrobenzoyl Chloride

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7d. (yield 81 %), (m.p, C°)(161 -163), IR. (KBr) (ν , Cm^{-1}) 3336-3273 (NH_2), 3134 (NH) 3064 (C-H Ar), 3110 (C-H olefene.), 1640 (imidazole C=O), 1672 (C=O, amide) 1582 - 1511 (C=C Ar), 1229 (C-N); $^1\text{HNMR}$ (DMSO-d_6) δ (ppm) 8.72 (s, NH_2), 8.41 (s, C=CH-), 3.87 (s, N-CH-S), 6.09 – 7.77 (m, Aromatic proton); U.V (EtOH) 229 nm, 364 nm.

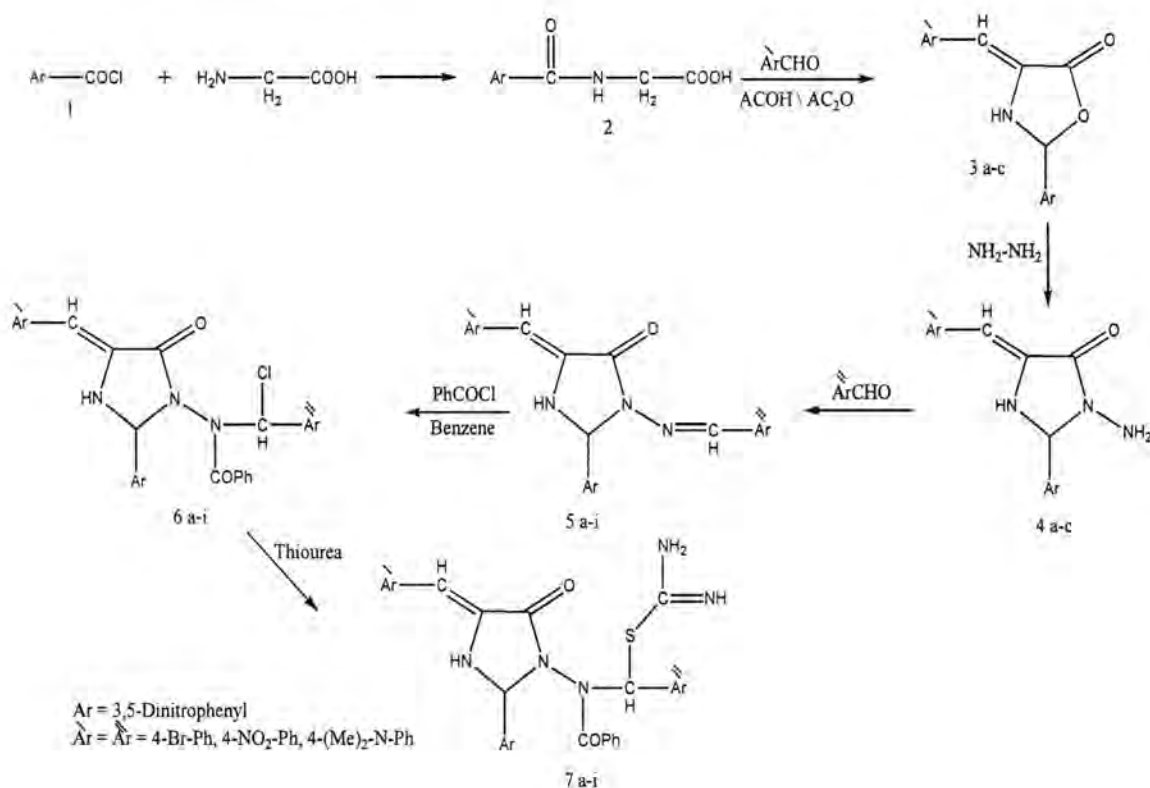
7e. (yield 74 %), (m.p, C°)(231 -233), IR. (KBr) (ν , Cm^{-1}) 3334-3259 (NH_2), 3146 (NH) 3052 (C-H Ar), 3121 (C-H olefene.), 1650 (imidazole C=O), 1659 (C=O, amide) 1579 - 1474 (C=C Ar), 1255 (C-N); U.V (EtOH) 254 nm, 369 nm.

7f. (yield 77 %), (m.p, C°)(157 -159), IR. (KBr) (ν , Cm^{-1}) 3332-3199 (NH_2), 3138 (NH) 3060 (C-H Ar), 3101 (C-H olefene.), 1643 (imidazole C=O), 1657 (C=O, amide) 1600 - 1500 (C=C Ar), 1242 (C-N); $^1\text{HNMR}$ (DMSO-d_6) δ (ppm) 8.75 (s, NH_2), 8.31 (s, C=CH-), 4.53 (s, N-CH-S), 7.02 – 7.93 (m, Aromatic proton); U.V (EtOH) 237 nm, 391 nm.

7g. (yield 72 %), (m.p, C°)(264 - 266), IR. (KBr) (ν , Cm^{-1}) 3344-3211 (NH_2), 3158 (NH) 3060 (C-H Ar), 3119 (C-H olefene.), 1651 (imidazole C=O), 1649 (C=O, amide) 1587 - 1500 (C=C Ar), 1238 (C-N); U.V (EtOH) 258 nm, 368 nm.

7h. (yield 69 %), (m.p, C°)(259 - 261), IR. (KBr) (ν , Cm^{-1}) 3389-3299 (NH_2), 3188 (NH) 3061 (C-H Ar), 3121 (C-H olefene.), 1652 (imidazole C=O), 1668 (C=O, amide) 1603 - 1476 (C=C Ar), 1250 (C-N); U.V (EtOH) 253 nm, 378 nm.

7i. (yield 70 %), (m.p, C°)(141 -143), IR. (KBr) (ν , Cm^{-1}) 3331-3262 (NH_2), 3172 (NH) 3070 (C-H Ar), 3127 (C-H olefene.), 1643 (imidazole C=O), 1671 (C=O, amide) 1600 - 1500 (C=C Ar), 1235 (C-N); $^1\text{HNMR}$ (DMSO-d_6) δ (ppm) 8.54 (s, NH_2), 8.92 (s, C=CH-), 4.39 (s, N-CH-S), 6.02 – 7.97 (m, Aromatic proton); U.V (EtOH) 234 nm, 310 nm



Scheme 1

RESULTS AND DISCUSSION

Schemes (1) was summarized the synthesis of different derivatives of 3,5-dinitrobenzoyl chloride. [(3,5-dinitrophenyl-carbonyl amino)acetic acid (2) was synthesized by treatment of 3,5-dinitrobenzoyl chloride with Glycine. The reaction is followed by the appearance of ($\nu_{C=O}$) absorption bands at 1726 cm^{-1} (acid and at 1657 cm^{-1} (amide C=O) in their spectra. Compounds 4-(arylidene)-2-(3,5-dinitrophenyl)-1,3-oxazol-5(4H)-one (3a-b) was obtained by reaction of compound (2) with different aldehydes in present of acetic acid and acetic anhydride. Compounds was confirmed by the appearance of ($\nu_{C=O}$) absorption bands at $1752 - 1773\text{ cm}^{-1}$. The ^1H NMR for compound 3a shows signal at (ppm) 8.90 (s, C=CH-), 6.91 – 8.1 (m, Aromatic proton). Hydrazine hydrate was added to compounds (3a – c) to gave compounds (4a – c) The reaction is followed by decreasing of absorption band for ($\nu_{C=O}$) at $1752 - 1773\text{ cm}^{-1}$ to $1630 - 1690$ and appearance of new absorption band at $3361 - 3220\text{ cm}^{-1}$ due to (ν_{NH_2}). In the ^1H NMR spectra for compound 4b shows the proton signals (ppm) 8.77 (s, C=CH-), 8.19 (s, NH₂), 7.13 – 8.09 (m, Aromatic proton). The treatment of compound (4a -c) with aryl aldehyde in ethanol absolute led to the formation of Schiff's bases 5a – i), Schiff's bases was confirmed by the absence of absorption bands near $3361 - 3220\text{ cm}^{-1}$ for (ν_{NH_2}) and

presence of absorption bands at $1645 - 1675 \text{ cm}^{-1}$ due to ($\nu_{\text{C=N}}$) stretching. ^1H NMR spectra of compound (5a,b,d,e,g,h) show the new signals observed at 8.61–8.79 ppm integrating for (CH=N) When the Schiff's bases (5a-i) were treated with benzoyl chloride (scheme 1) in boiling benzene, derivative (6a-i) was obtained Scheme (1). The IR spectrum indicated the presence of a (ν_{CON}) function ($1647\text{-}1690 \text{ cm}^{-1}$) ^1H NMR spectra for compounds (6a,b,f,i) showed signals at 3.92 -4.39 ppm which belonged to for (N-CH-Cl).

On the other hand, when the derivatives (6a - i) was treated with thiourea, derivatives (7a - i) was obtained in good yield. The IR spectra indicated the presence of a doublet absorption bands near ($3389\text{-}3199 \text{ cm}^{-1}$) for (ν_{NH_2}). ^1H NMR spectra showed signals at 8.54-8.75 ppm due to (NH_2).

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Study on the Activation of Qara Tappah Iraqi Bentonite and Its Test as Gelling Agent

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الخلاصة

يهدف البحث الى دراسة تنشيط بنتونايت منطقة قرّة تبة لتحويل الطين الى مادة جل واستخدام هذه المادة في التطبيقات الصناعية المختلفة. تم استخدام مادة كاربونات الصوديوم ونسب مختلفة (2.5%, 5%, 7.5%) حيث اعطت النسبة (7.5%) افضل النتائج عند اختبارها في معامل تكون الجل ومثانة الجل.

ABSTRACT

The aim of this research is to study the activation conditions of Qara Tappah bentonite at various ratios for converting it to the gelling form. Soda ash is used in the activation process with ratios (2.5%, 5%, 7.5%). The best result for obtaining the gelling form was found at the activation ratio (7.5%).

INTRUDUCTION

Bentonite is a smectite clay, the major mineral in it is montmorillonite with exchangeable cations (sodium and calcium), which imparts bentonite the property of high exchange capacity and good swelling property (1, 2, 3).

Because of differences in structure and rheological properties between calcium bentonite and sodium bentonite, Na-bentonite is preferred for most of the industrial applications(4) , therefore the Ca-bentonites are treated with some inorganic chemicals like Na_2CO_3 to develop the rheological properties (5).

A clay gel is a transitional hydrous (saturated) phase that exists between the plastic phase and fluid phase (6). The property of gel is present when the main exchangeable cat ion is Na^+ in suspension with a low solid content, since the particles orientate themselves negative to positive and form a gel (7,8) , which seems to consist of polymeric chains of individual montmorillonite layers (9) .

Because of this property, bentonite is sometimes used in clarifying turbid liquids, and used as carrier for a number of cosmetic preparations, tooth pastes, creams and other pharmaceutical industry (10).

Our study concern on Iraqi bentonite to be prepared as a gel and study their properties.

MATERIALS AND METHODS

Fractions smaller than $38\mu\text{m}$ of Iraqi Qara Tappah Ca-bentonite were used . the chemical analysis of this bentonite is given in table(1) . The X-ray

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powder diagrams of the original and activated bentonite were obtained with XRD unit model (7000) , target cu, (λ) = 1.5405 $^{\circ}$ A , 40 (kv) ,30 (mA) .

Table 1: Chemical analysis of ca-Bentonite sample

Material oxide	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	Na ₂ O	MgO	SO ₃	L.O.I
Bentonite (wt%)	58.58	15.8	2.5	2.77	0.7	6.1	0.1	12.48

Qara Tappah bentonite was activated with Na₂CO₃ at various mass ratios(soda ratio: 2.5,5,7.5%) labeled (Q2.5,Q5,Q7.5). Bentonite and Na₂CO₃ were add to distilled water until we get a slurry , the slurry was heated and mixed for 60 min by using mechanical stirrer ,then cooled with water quickly ,left for 24h, they mixed with a suitable amount of Ethanol(1:4 Ethanol: Water), and centrifuged (6000 rpm, 3 min) by using (LABOFUGE-HERAEUSE) , and dried in an oven at 100 C . Then the dried samples were ground by ball mill to reduce the particle size. The samples as defined above after these process of preparation, were tested by adding a distilled water at 5% (w/v), this test for samples Q5 and Q7.5 shows a clear structure gel formation. It was found that the time is an important parameter for the formation.

Determination of gel strength:

Gel strength is a measure of the ability of a colloid to form gels and is related to inter particle forces of the mud. it is measured under static conditions. Gel strength measurements are normally taken as initial gel strength (zero quiescent time) and final gel strength (ten-minute quiescent time).

The following procedure was employed to determine two values- the initial gel-strength (g_0) and the 10 minute gel- strength (g_{10})(by using U.S.A viscometer, model 800, Ofite).

- 1) The mud sample (22.5 g of bentonite: 350 ml distilled water) was stirred at(6000 rpm)for 10 sec. and then allowed to stand undisturbed for 10 sec. followed by rotating the instrument at (3 rpm) and the maximum reading attained after the start of the rotation was recorded. this maximum reading was the initial gel strength in lb /100ft².
- 2) The mud was re-stirred at high speed (i.e. 600 rpm) for ten second and then allowed to stand undisturbed for ten minutes, followed by rotating the instrument at 3 (rpm) and the maximum reading was recorded , this maximum reading was the ten- minute gel in lb/100ft. Fig.(2) shows the behavior of gel strength as a function of activation conditions.

Determination of gel formation index.

By mixing 6g of prepared samples with 0.3g of light magnesium oxide, then this mixture was added in step wise of addition to 200ml of

water contained in a 500-ml stoppered measuring cylinder, agitated thoroughly for one hour, then transferred 100 ml to a 100-ml measuring cylinder and allowed to stand for 24 hours, and the supernatant liquid was measured.

RESULTS AND DISCUSSION

X-ray diffraction patterns of original and Na_2CO_3 activated samples are illustrated in figure(1). The main montmorillonite hkl diffraction reflections are present in all samples. The lower $d(001)$ values were found for the Na-Bentonite obtained by sod activation at (7.5%), which is about (11.84°A) than in the original Ca-B (14.8°A). These results show that the original Qara-Tappah bentonite was converted to Na-bentonite. In addition, maximum rheological properties were observed for Na-bentonite (Q7.5) which show the maximum value of gel strength, as shown in the figure (2), and gel formation index as shown in the figure (3). This means that the repulsive force between the sodium bentonite plates surfaces is high enough to prevent the aggregation of the plates, so the plates intercept free amount of water from the suspension between them, and then they were oriented positive edge to negative surface ((flocculation) to form the card-house structure(2). In addition, Na^+ ions which are adsorbed onto one clay surface, pass through into the solution when they interact with water and easily leave out the clay minerals, so the water molecules easily moved into the layers of clay which caused an increasing in the viscosity and leads to form the flocculation process (edge to edge or edge to face)(11).

The conclusion behind this study shows the Q.T. bentonite have an ability to activation at 7.5 % as an excellent result and shows a gel behavior which is an important results for industrial applications.

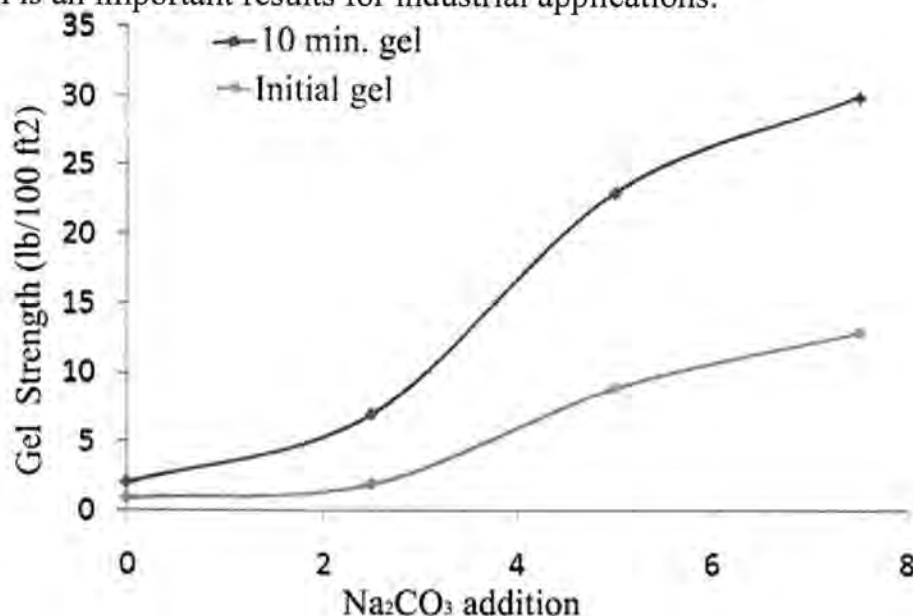


Figure 1: XRD patterns of the original and activated bentonite

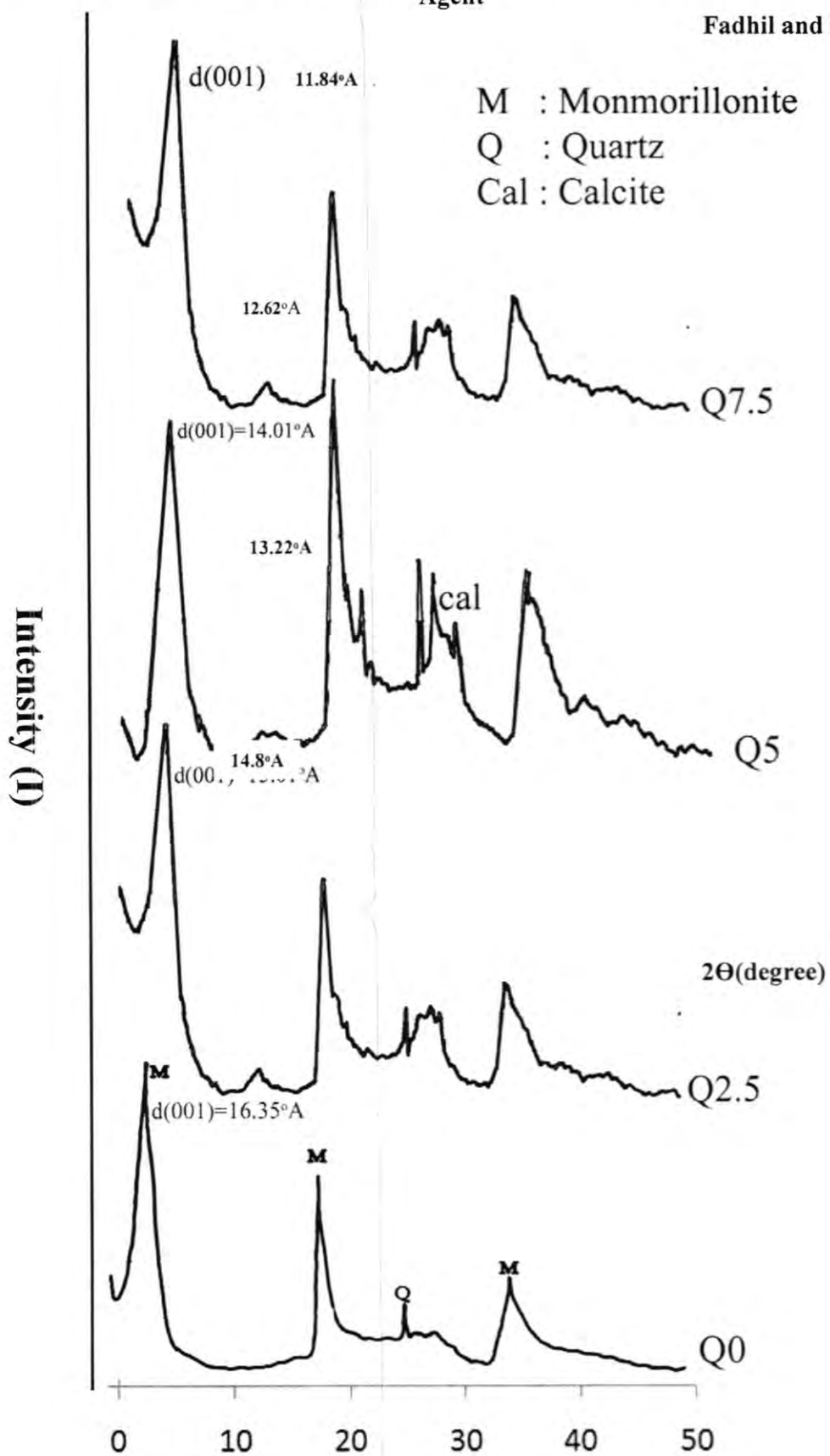


Figure 2: Gel strength at various ratios of soda addition

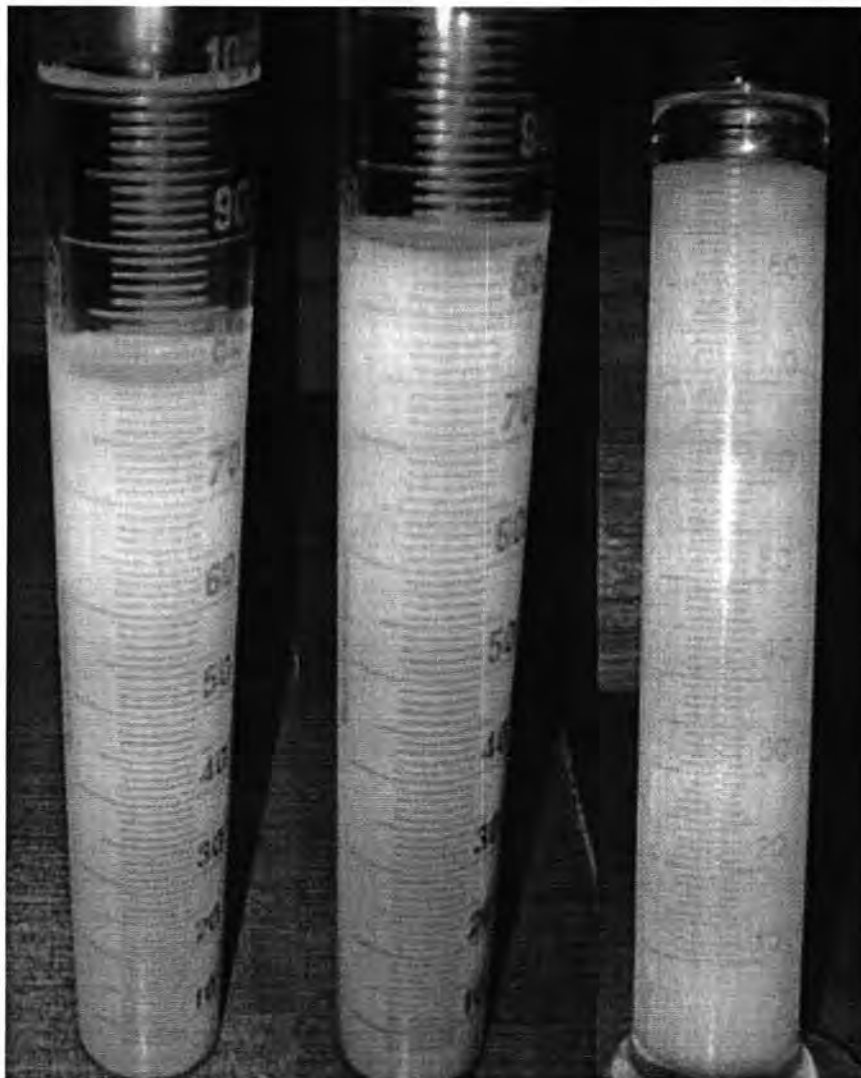


Figure 3: Gel formation index for the activated samples

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Effect of Doping Ni(etx)₂ on Optical Properties of Poly styrene

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الخلاصة

تم حساب طيف الامتصاصية والنفاذية للمنطقة المرئية للطيف (200-900nm) لأفلام تم تحضيرها بنسب وزنيه مختلفة من Ps و Ps-Ni(etx)₂، إن فجوة الطاقة (E_{opt}) ومعامل الانكسار ومعامل الخمود وثابت العزل الحقيقي والخيالي تم حسابها ومناقشة تأثير نسبة التشويب من Ni(etx)₂ إلى Ps حيث أن قيم فجوة الطاقة تم حسابها من الانتقال المباشر المسموح في فضاء-K.

ABSTRACT

The optical transmission and UV-VIS absorption spectra have been measured in the wave length range (200-900)nm for different concentration of Ps and Ni(etx)₂ composite thin films. Energy gap(E_{opt}), refractive index(n), extinction coefficient (K), real and imaginary part of dielectric constant(ϵ_r, ϵ_i) have been evaluated. The effects of doping percentage of Ni(etx)₂ on these parameters have been discussed the values of the optical energy band gap(E_{opt}) have been obtained from indirect allowed transition in K-space.

INTRODUCTION

Polymers are present in our daily life from the wrappings around the food we eat to the sacks used for the garbage, polymers are practically everywhere [1]. polymers are macromolecules built up by small molecules are termed "monomers" and reactions by which they combine are termed polymerization. The number of these repeated units are called degree of polymerization[2].

May be hundred, thousand, tens of thousands or more monomer molecules linked together in a polymer molecule. There are three main structural shapes in which polymer molecules are produced, which can be classified as; linear, branched, or crosslink polymers depending on the structural shape of the polymer molecules[3].

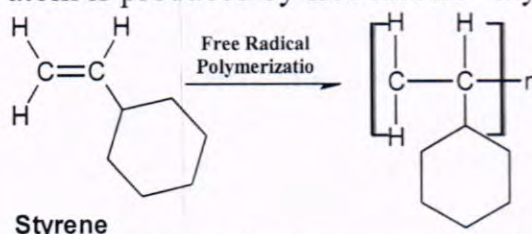
Composite is combined material created by the synthetic assembly of two or more components-a selected filler or reinforcing agent and compatible matrix binder in order to obtain specific properties [4]. The components of a composite do not dissolve or otherwise merge completely into each other, but they do act in concert.

There are three fields of producing composite materials namely:-

- a. Metal-matrix composites.
- b. Ceramic-matrix composites.
- c. Polymers-matrix composites.

For the interest of this work only the third type of composite will be considered.

The polymer used in this work are polystyrene. The polystyrene is an inexpensive and hard plastic and is more common used in our everyday life[5]. The body of computers we are using now is probably made of polystyrene, and is also used in toys, and the housing of things like hairdryers and kitchen appliances[6]. polystyrene is vinyl polymer. structurally, it is a long hydrocarbon chain, with a phenyl group attached to every other carbon atom is produced by free radical vinyl polymerization:-



Polystyrene is perfect for optical measurements[7] and immunological assays. It is soluble in aromatic hydrocarbon solvents, cyclohexane and chlorinated hydrocarbons.

In the last two decades, many scientists have studied the electrical behavior of modified polymeric materials. These polymers are important for modern technology applications. Thus, the present work is focused to modify the electrical and optical properties of polystyrene thermoplastic insulating polymer into semiconductor polymer by adding ethyl xanthate complexes with different concentration as a conductive additive to the PVC. This complex are named Bis(ethyl xanthato)Nickel(II); Ni(etx)₂.

The absorbance(A) of a sample is defiend by[8]

$$A = \log I / I_0 \dots \dots (1)$$

Where, I_0 is the intensity of incident light. I is the intensity of incident light at distant(x). the absorption coefficient (α) can be expressed by Lambert Beer's Law[9]:-

$$\alpha = \log A / x \dots \dots (2)$$

where, (x) is a sample thickness.

The relation between the optical band gap, absorption coefficient and energy(hv) of the incident photon is given by [10,11]:-

$$\alpha h\nu = B(h\nu - E_g)^r \dots \dots (3)$$

where E_g the optical energy gap, B is a constant and r is an index which can be assumed to have values of 1/2, 3/2, 2 and 3, depending on the nature of the electronic transition responsible for the absorption $r = 1/2$ for allowed direct transition $r = 3/2$ for forbidden direct transition and $r = 3$ for forbidden indirect

transition, with $r = 2$ refers to indirect allowed transitions [12]. Polymers, in general, are transparent and colorless the existence of conductive additive raising the transition wavelength into visible region and the optioned lighter structure is very useful in some specific advanced technology such as elect chromic displays, Optical switching and rechargeable batteries [12].

MATERIALS AND METHODS

Polystyrene supplied by ICI with purity 99.995, was used as matrix. Chloroform (CHCl_3) of purity 99.998 used as solvent was supplied by (BDH) company Chemicals (Ltd. Poole. England). complexes were prepared by method described by Yousif [13]. To 25ml of ethanolic solution of 0.01mol, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ was added, with constant stirring. After that 0.02mol of Potassium, ethyl xanthate dissolved in 25ml of water was added. This mixture was then stirred until Brown crystalline solid was optioned. The product was recrystallized from a mixture of Petroleum ether and acetone to yield white crystals of $\text{Ni}(\text{etx})_2$.

Polymer films and polymer ethyl xanthate metal complexes composite prepare by dissolved the PS in chloroform. the desired salt %wt additive [bis(ethylxanthato) Nickel (II); $\text{Ni}(\text{etx})_2$, was added and the mixture was cast into a glass- sheet of dimensions ($5 \times 5 \text{ cm}^2$) and kept in a dry atmosphere at (40°C) for (24) hours. The thickness of the polymer films was (150 ± 5 Micron).

RESULTS AND DISCUSSION

Optical Energy Gap:-

Undoped and doped PS films obeys the role of indirect allowed transition and the various energy gap of pure polystyrene while absorption of doped $\text{Ni}(\text{etx})_2$ with various concentrations are determined from straight line fitting the plot for allowed and forbidden $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^{1/3}$ as a function of photon energy are shown in Fig(1) and Fig(2).

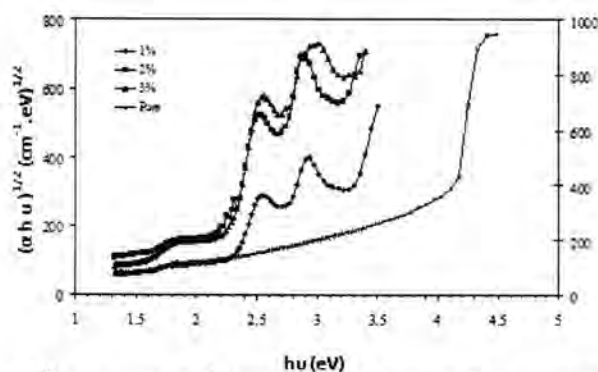


Figure 1: $(\alpha h\nu)^{1/2}$ Vs. photon energy (allowed direct transition) for pure and doped Ps

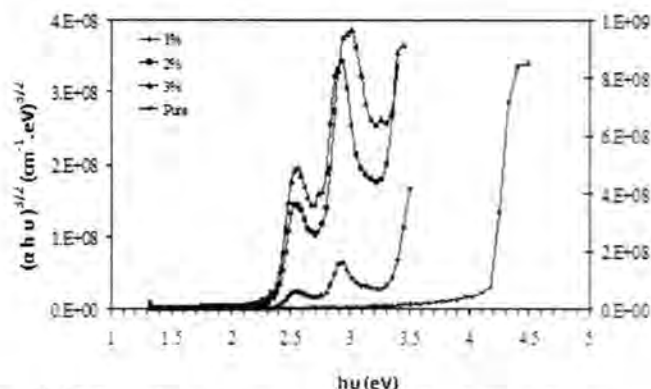


Figure 2: $(\alpha h\nu)^{3/2}$ Vs. photon energy (forbidden direct transition) for pure and doped Ps.

The present results were found to obey equation(3) with $r=2$ to indirect allowed transition and $r=3$ for indirect forbidden transitions for all films. From figure(1) the calculation of optical energy gap of doped PS sample with Ni(etx)₂ for different concentration showed which decrease with increasing of Ni(etx)₂ concentration. The optical energy gap, E_g decreased from 4.2 eV for pure PS films to 2.6 eV for PS+3% Ni(etx)₂ as shown in table (1), this is ascribed to increase in absorption coefficient as a result of introducing dopant atoms and hence E_g will be decreasing, it is clear that Ni(etx)₂ has greater effect on optical energy gap of Polystyrene polymer and that result will agreement with rana(14) that she found that energy gap of PVC will decreased when she doped by Ni(etx)₂ with different concentrations.

Table 1: The calculated values of E_{opt} obtained from optical mechanism for Ps+Ni(etx)₂ composite.

Dopping Concentration	E_{opt}
Ps+0.0 Ni(etx) ₂	4.2eV
Ps+1% Ni(etx) ₂	2.8eV
Ps+2% Ni(etx) ₂	2.7eV
Ps+3% Ni(etx) ₂	2.6eV

The optical constant:-

The extinction coefficient can be calculated by the relation[1]:-

$$K = \alpha\lambda/4\pi \dots (4)$$

Where (λ) is the wave length, (α) is the absorption coefficient.

The variation of (K) with pure (PS) various filler constant as a function of the wave length (λ) is shown in fig(3), which give an indication that extinction coefficient (K) increased with increasing salt content, this behaviour can be attributed to the increasing of the packing density as result

of salt content[15].this result agreement to what have been found by other workers[16,17].

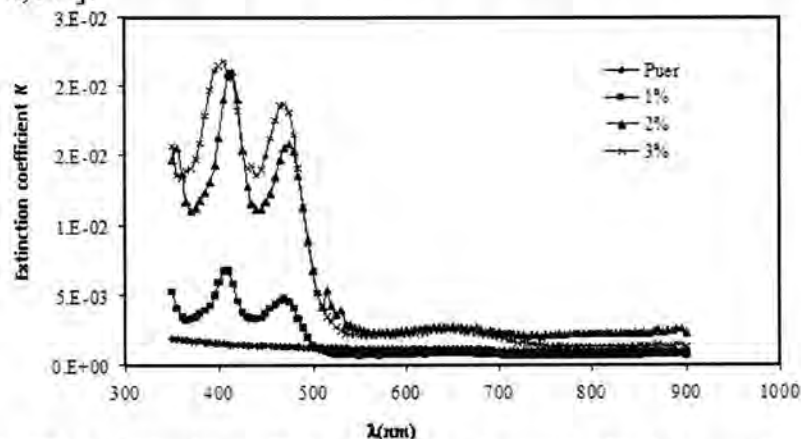


Figure 3: The variation of K with wave length (λ) for pure and doped films

The refractive index(n) can be measured (when the reflectance (R) and (K) are known) by using the equation(5):-

$$n = \sqrt{\frac{4R(R+1)}{(R-1)^2 - K^2(R-1)}} \quad \text{.....(5)}$$

The refractive index (n) for pure and doped Ps with Ni(etx)_2 were determined using equ(5).Fig(4) shows variation of (n) as a function of wavelength(λ).this figure showed that the (n) systematic increase with increasing Ni(etx)_2 concentration(18,19).

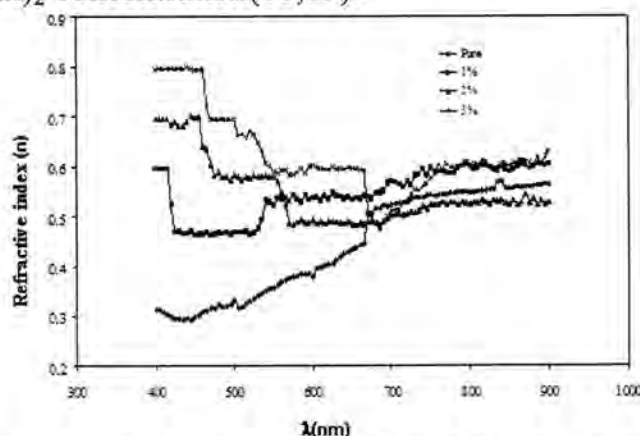


Figure4: The variation of refractive index with pure Ps and doped films

The complex index (N) is given by (20):-

$$\overline{N} = n - iK = \sqrt{\epsilon} \quad \text{... (4)}$$

Where (ϵ_2) is the complex dielectric constant, given by:-

$$\epsilon = \epsilon_1 - i\epsilon_2 \quad \text{... (5)}$$

The parameter (ϵ_1)is the real part of dielectric constant, (ϵ_2) is the imaginary part of dielectric constant.

From equs (4) and (5) one can obtain:-

$$\epsilon_1 = n^2 - K^2 \dots (6)$$

$$\epsilon_2 = 2nK \dots (7)$$

The dependence of (ϵ_1) and (ϵ_2) on λ are shown in fig (5,6).it is concluded that the variation of (ϵ) mainly depends on the (n^2) because of small values of (K^2), while (ϵ_2) mainly depends on the (K) values which are related to the variation of absorption coefficients.

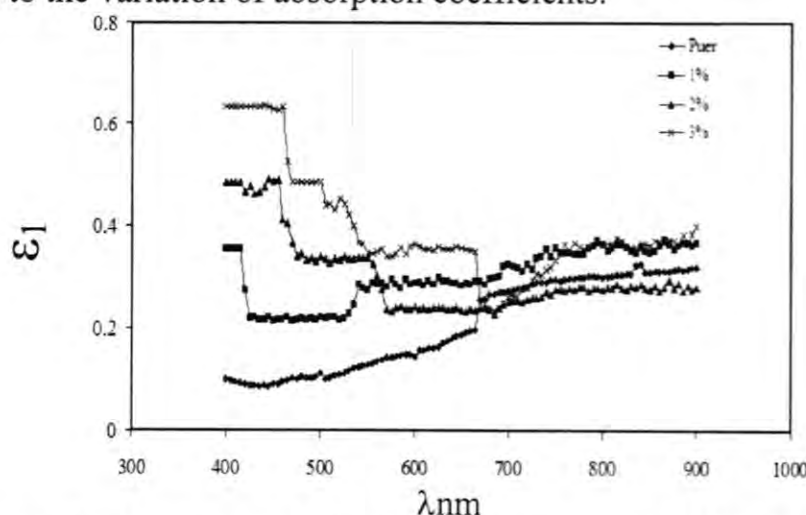


Figure 5: The variation of real part of dielectric constant (ϵ_1) as a function of wavelength of pure and doped Ps with Ni(etx)₂ with different concentrations

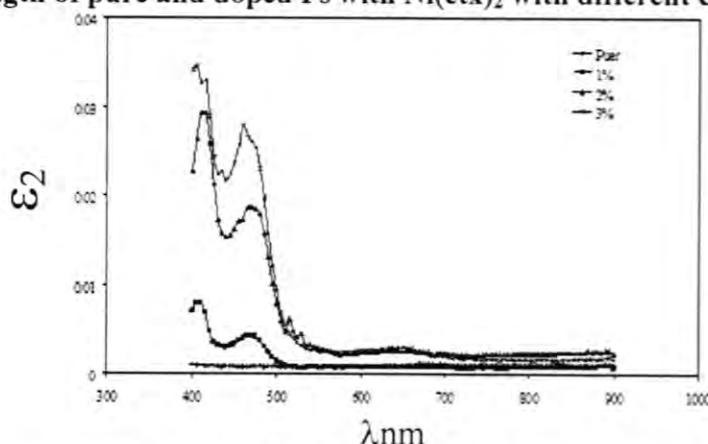


Figure 6:-the variation in imaginary part of dielectric constant(ϵ_2) as a function of wavelength for pure and doped ps with Ni(etx)₂ with different concentration

Polystyrene Polymer modification with Ni(etx)₂ with different concentration have been successfully prepared which were used for measurement of optical properties. The main conclusion could be drawn from this work are:-

1. The ethyl xanthate metal complex are effectively modifying the optical properties(i.e. energy gap)of Ps films. The band gap is decrease with increase filler concentration.

2. The refractive index in the optical region has been found to be increases with the increasing filler content .
3. We noticed also that the extinction coefficient (K) increase with increasing doping concentration.
4. The real and imaginary parts of dielectric constants (ϵ_1) and (ϵ_2) is found to be increase with increasing Ni(etx)₂ concentration.

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الخلاصة

في هذا البحث اقترحنا طريقتين للتصنيف المرشد لسحابة ماجلان الصغرى. التصنيف المرشد يعتمد على المعلومات المسبقة للمنطقة التي تضم لاصناف المختلفة في الصورة. هذا انجز في مجال عملنا حقل معالجة الصور الفلكية (سحابة ماجلان الصغرى). صنفت هذه الصورة باستخدام طريقتين للتصنيف المرشده ومن تحليل النتائج. الطريقة الاولى تعتمد على معيار اقل مسافة لتصنيف المناطق المختلفة في الصورة. بينما الطريقة الثانية تعتمد على تصنيف نسيج الصورة التي تستخدم باستخلاص ملامح من مصفوفة الحدث لتمييز بين مناطق الصورة.

ABSTRACT

In this paper we suggested to classify the small Magellan cloud by two methods of supervised classification. Supervised classification relies on the prior knowledge of the location and identity of land cover types that are in the image. This can be achieved through field our work, study of Astronomical image "Small Magellan cloud". In this paper was devoted to classify the image by using two methods of supervised classification and analysis. The first, named supervised classifier, based on minimum distance criterion, to classify different regions in an image. While the Second method, named Texture classifier, utilizes the features extracted from the co-occurrence matrices to discriminate between image regions.

INTRODUCTION

Small Magellan cloud (SMC) is a dwarf galaxy. It has diameter about 7000 light years. Contains several hundred million stars. It has total mass of approximately 7 billion times of the mass of our Sun. The SMC was once a barred spiral galaxy that is once disrupted by the Milky way to be, somehow shown irregular. The nearest neighbor of Milky way is at a distance of about 200000 light years, it can be seen with naked eye. If we come to analysis the visible light image of the small Magellan cloud we shall see. [1]

1. White and blue of x-ray image referred to distribution of the young stars.
2. Ultra violet ray is emitte by new born (massive stars).
3. Pinky nebula is created by ionizing Hydrogen gas.

4. The glowing red is because of the heating up of the embedded dust grains.
5. Grey luminosity is produced heating of the synchrotron emission resulted from supernova explosions.

Supervised Classification

Supervised classification always classifies pixels of unknown identity by samples of known identity located within training areas. The analyst defines training areas by identifying regions on the image that can be clearly matched to areas of known identity on the image. Such areas should typify spectral properties of the categories they represent, and, of course, must be homogeneous in respect to the informational category to be classified. Clearly, traditional supervised algorithms are based on probability distribution models for the class of interest. The selection of these training data is a key step in supervised classification. Differences in the selection of training data were more important influences on accuracy than those among other four different classification procedures. Two methods have been devised to implement the basic strategy of supervised classification as follows: minimum distance classification and texture classification. [2]

MINIMUM DISTANCE CLASSIFICATION METHOD

The minimum distance decision rule compare the spectral distance between the measured mean value and those mean values stored in the predefined vector. The image pixel is then classified as to belong to that predefined class in which minimum difference is achieved . [3]

$$SD = |m_c - m| \dots\dots\dots(1)$$

Where m_c , m represent the mean values of predefined class c , and of unclassified sample, respectively.

The mean of a set of values represents some times their statistical average for example if x_1, x_2, \dots, x_k are elements of a set of k values then their mean is given by ;

$$m = (x_1 + x_2 + \dots + x_k) / k \dots\dots\dots(2)$$

This is, however, true if the test values have normal distribution.

Fig. (1) and table (1) demonstrate the results of applying the above mentioned classification rule on Magellanic cloud image. As it is clear, each image point assigned a color of the closest predefined class.

TEXTURE CLASSIFICATION METHOD

Texture describes the spatial distribution of tonal values and thus provides a very useful tool for performing automatic interpretation and recognition for the image regions by computer. One of the most important and powerful statistical texture analysis algorithm is the co-occurrence

matrices which is defined as a two-dimensional histogram of the number of times that pairs of image intensity values occur in a given spatial relationship.[4]

The co-occurrence matrix can be presented in the form of relative frequencies as $P(I,j,d, \theta)$; where "I" and "j" representing two gray points separated by distance "d", with an angular direction " θ ". It can be presented by; [5]

$$P(I,j,d,\theta) = \# \{ (x1,y1), (x2,y2) | i=f(x1,y1), j=f(x2,y2), d=|(x1,y1)-(x2,y2)| \} \dots\dots(3)$$

Here, # denotzes the number of elements in the set, (x,y) are the coordinates of a given element, and "d" is the distance between points (x1,y1) and (x2,y2).

RESULTS AND DISCUSSION

The two methods of classified (Minimum distance and Texture) are performs by visual basic the results show as following:

Figure (1) Represent the original image and its Histogram.

Table (1) Represent the Statistical properties of original image.

Figure (2) Represent the classified image by minimum distance and its histogram.

Figure (3) represent The Classified image by Texture and its histogram.

Table (2) show the results when we apply classification methods on small Magellan cloud.

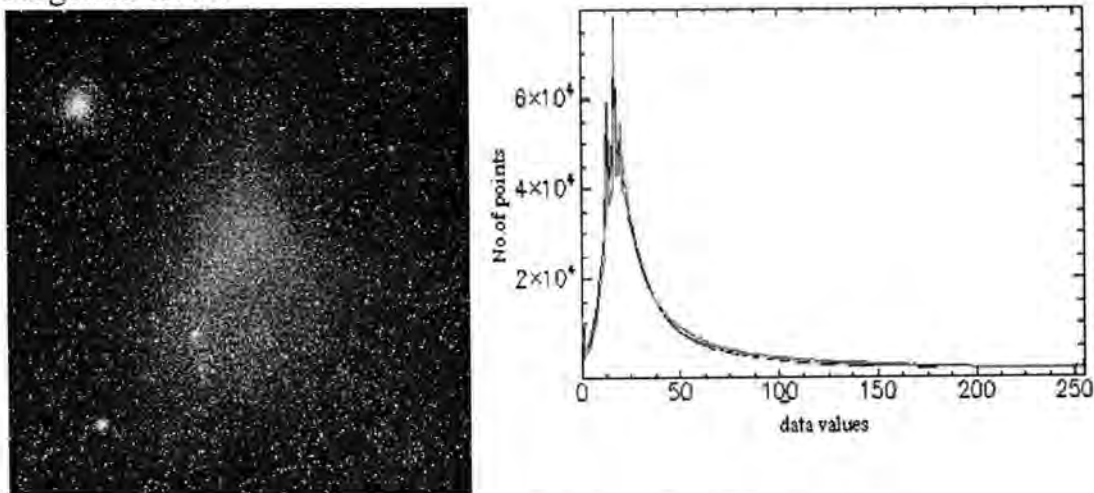


Figure 1 : Original Image and its Histogram

Table 1: Statistical properties of original image

No. of bands	Band1	Band2	Band3
min	0	0	0
Max	255	255	255
mean	35.764402	38.543467	41.841507
Stdev.	33.909056	35.303241	39.861691

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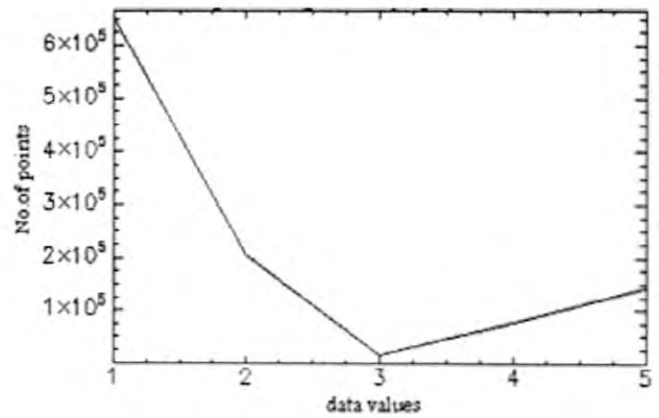
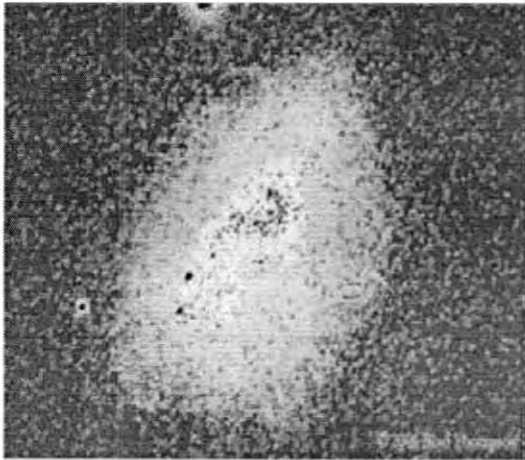


Figure 2: Classified image by minimum distance and its histogram

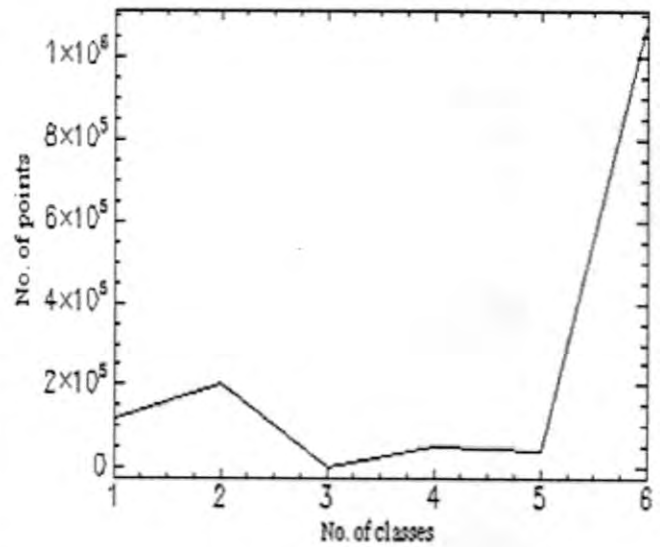


Figure 3: Classified image by Texture method and its histogram

Table 2: Result of classified images

Classified images	classes	NO. of points
Minimum distance classification	1	650795
	2	203940
	3	14631
	4	76772
	5	145702
Texture Classification	1	116967
	2	202426
	3	0
	4	53201
	5	40043
	6	1086163

The process of classifying this image wasn't easy because of interfering of the regions with each other. So there was a difficulty to point out the area of the test, and also because of the farina of the picked image by the telescope, we found the follows:-

1. The most of areas were for the young stars and massive stars. That makes a clue that the galaxy (SMC) is the vessel of the small stars or at the primmer forming.
2. The results were much for concerning the pinky color because of the area of dust cloud.
3. We show from original image and Classified Images There are many Pieces of evidence indications between the magellanic clouds(the small Magellan cloud and large Magellan cloud) and our Galaxy .The existence of the eastern wing of SMC,extending out in the direction of the LMC.
4. From the Experimental result we fond The Texture classified gave best result than the minimum distance Classified.

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Study of Grains Volume Average of $\text{SnO}_2\text{:Sb}$ Films Using Image Processing Techniques

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الخلاصة

حضرت أغشية رقيقة من اوكسيد القصدير المشوب بالانتيمون باستخدام تقنية التحلل الكيميائي الحراري، ودرست الخصائص التركيبية من خلال دراسة نتائج الصور الرقمية الممتلئة للأغشية المحضرة التي تم الحصول عليها باستخدام مجهر ضوئي وكاميرا رقمية مربوطة بالحاسوب، تبين وجود تغير في معدل الحجم الحبيبي للأغشية بسبب عملية التشويب، وقد تم ملاحظة ذلك من خلال استخدام وتطبيق عدد من تقنيات معالجة الصور الرقمية.

ABSTRACT

Antimony doped tin oxide have been prepared by chemical spray pyrolysis technique. The structural properties of these thin films were investigated through the study of digital images, which could obtain using optical microscope and digital camera connected to computer. It has been found that there is a variation in the average grain size due to doping process; this could be noticed by using and applying many image processing techniques.

INTRODUCTION

Transparent conductive oxides like tin oxide are particularly attractive due to its unique properties such as it has a wide band gap $E_g=3.5\text{-}4.1$ eV, high transparency in the visible region, high exaction binding energy of 130 meV the resistivity of undoped SnO_2 films dependent upon oxygen vacancies whose concentration is usually difficult to control and too much oxygen vacancies can also deteriorate the quality of the films [1-3]. There for the challenge is to prepare non- stoichiometric tin oxide films is supposed to be due to doubly ionized vacancies serving as donors [4].

Antimony is commonly used as a dopant to substitute for Sn^{+4} ions in the SnO_2 host lattice by Sn^{+5} ions. The antimony doped SnO_2 thin film can have higher carrier concentration, but often involves an enrichment of Sb^{+3} and Sb^{+5} species in the particles and Sb^{+3} is supposed to act as an electron trap [5].

A large variety of techniques have been developed for TCO_3 thin film deposition, DC magnetron sputtering [6], R. F. magnetron sputtering [7], sol-gel [8], pulsed laser deposition [9] and spray pyrolysis [10].

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The field of digital image processing has grown rapidly and now, where techniques are used and different methods and the multiple purposes of improving the information image for interpretation and analysis, given the importance of these images and its widespread use in many areas of daily life for humans, for example in the field of medicine using these technologies for improved picture X-Ray images and ultrasound in the military to improve the thermal images and X-Rays, infrared and radar images, also used to improve the space and aerial images and pictures of fingerprints and photographs used in the process of mineral exploration using seismic waves [11].

The goal of this research is to obtain a digital image of these thin films and study the structural properties using many image processing techniques in order to study the change in the color of the film, the change of size, shape and number of grains.

MATERIALS AND METHODS

Thin films of antimony doped tin oxide was prepared by chemical spray pyrolysis technique at a substrate temperature of 500°C , the Sb doping was varied from (1%-9%) volume concentration. An economic stannous chloride ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$) was used as a source of tin where as antimony chloride (SbCl_3) for Sb doping. The spray solution was 50 ml and the predetermined solution was sprayed to achieve $0.5\ \mu\text{m}$ thickness.

SnO_2 and $\text{SnO}_2\text{:Sb}$ thin films were selected with different Sb concentration and were magnified by 400x using light microscope with a digital camera (N-200m) linked directly to computer which allow us to see the image on the screen directly. The study of these images has entered many steps as follows.

Unification the image size (NXM) where N and M are the dimension of image the current image are of bmp kind in (256x256) dimensions.

Number of techniques were applied to the images that concern image processing by *Matlab* program like:

Technology Stained Glass:

The application of this technology to have an impact in the photos appear in nature's glass, stained or spotted in color [12].

• Technology Smudge Stick:

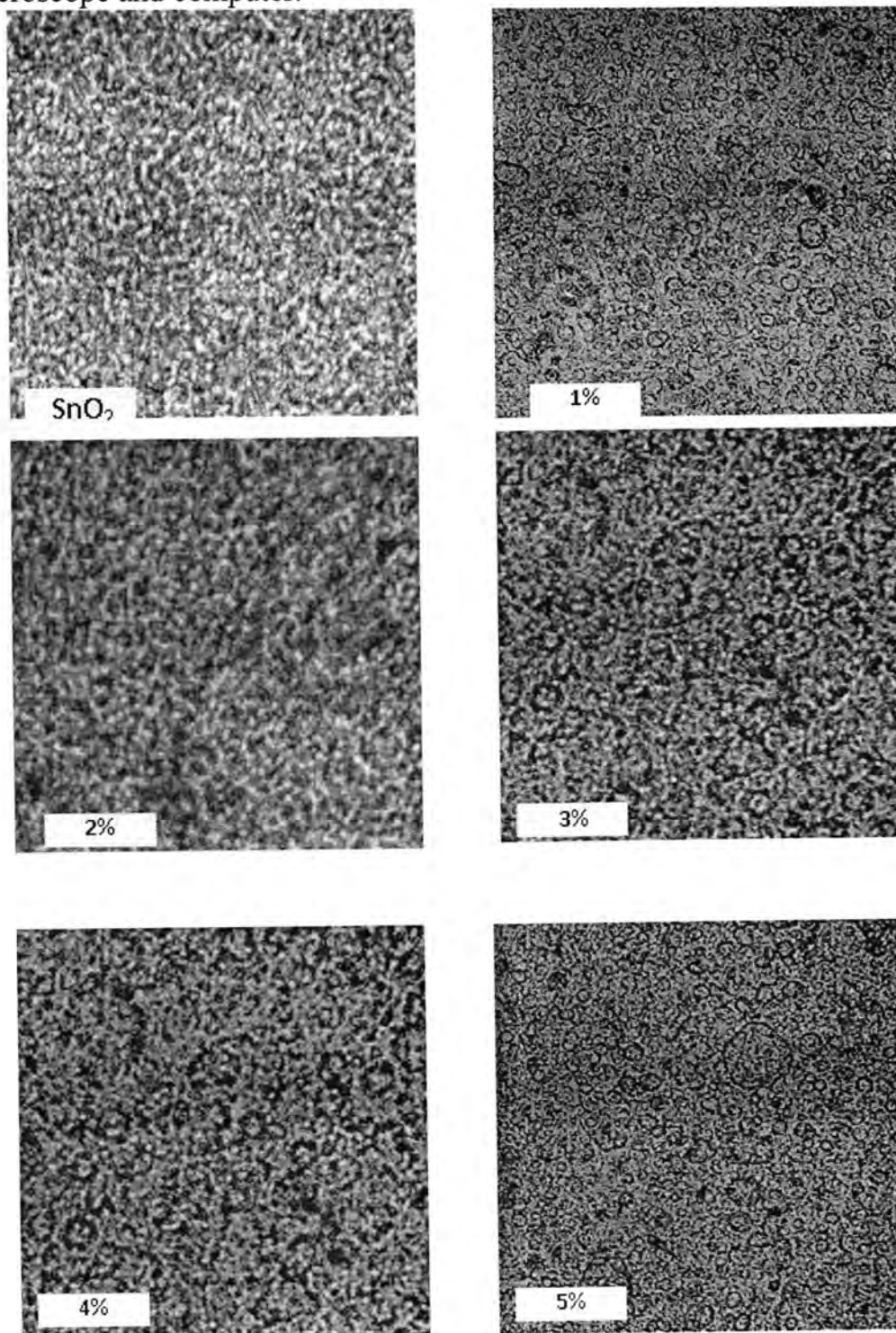
Effect is added to real images so as to give the final product impression as if the picture painted wooden coloring pencils [12].

• Technology Pixel-Pointillist paintings:

The installation is a candidate pixel with a color common to cells creator impression if we look at the images displayed circular grains with different diameters [12].

RESULTS AND DISCUSSION

Fig. (1) Illustrates a number of representative image samples for the study, which was obtained using a digital camera tethered between optical microscope and computer.



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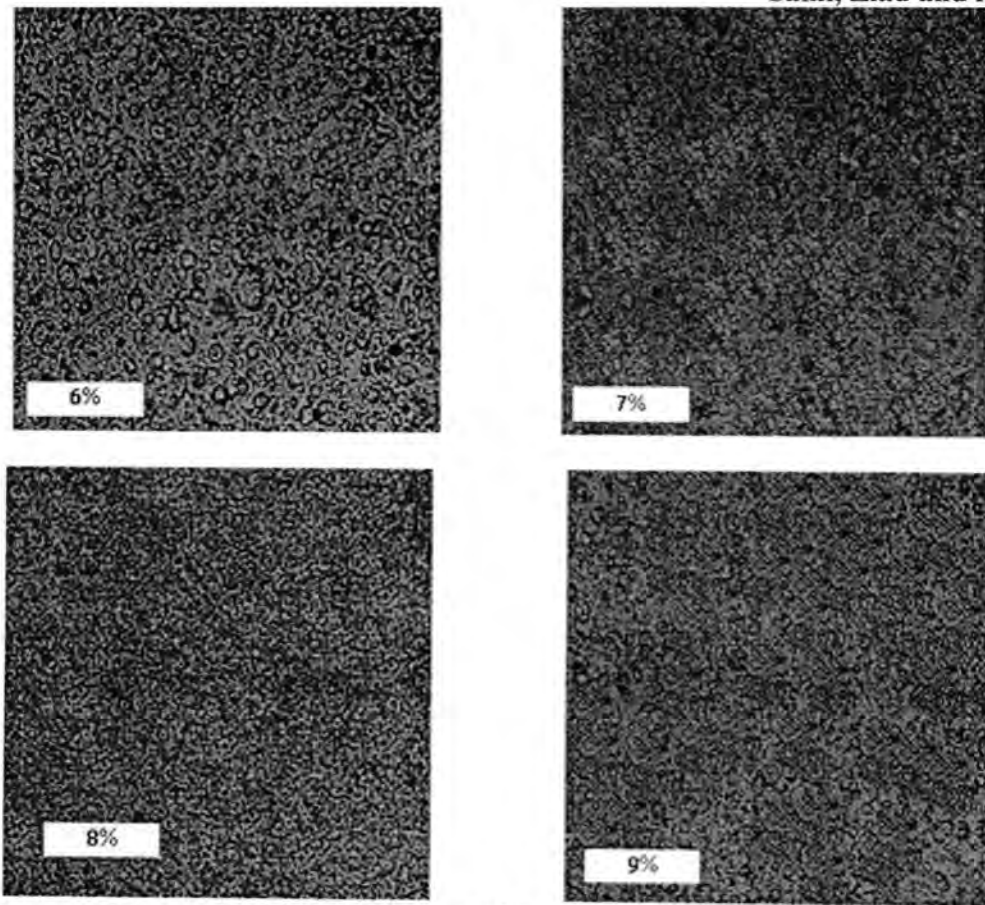


Figure 1: digital images of $\text{SnO}_2\text{:Sb}$ thin films (400x)

A number of techniques have been applied to the images in Fig. (1) to study and calculate the change in particle size. By the techniques applied which were taken from Fig.(1).

a- Stained Glass technology:-

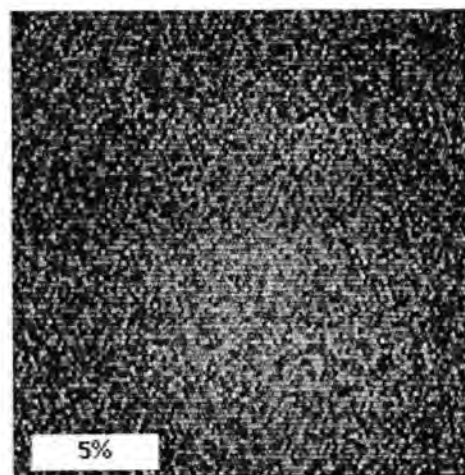
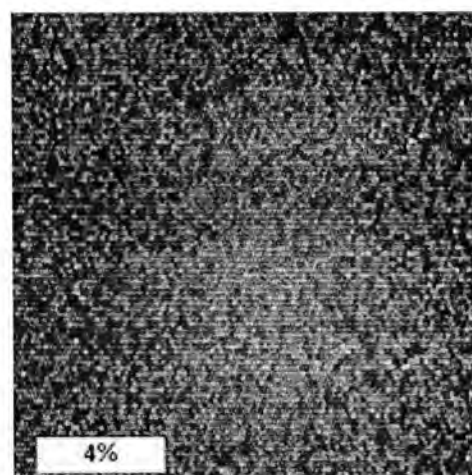
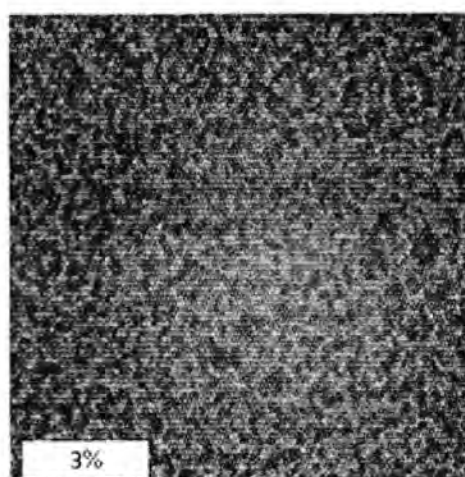
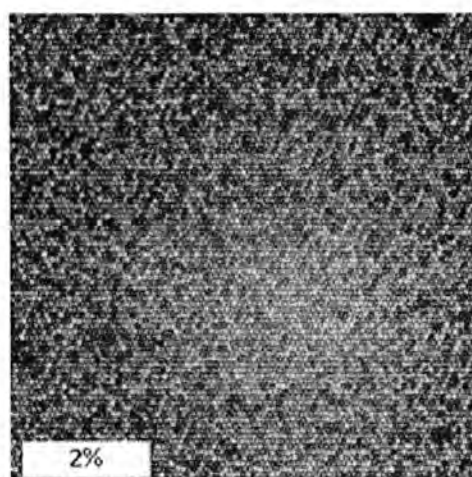
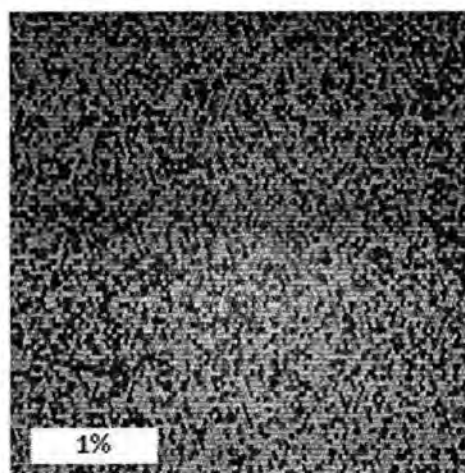
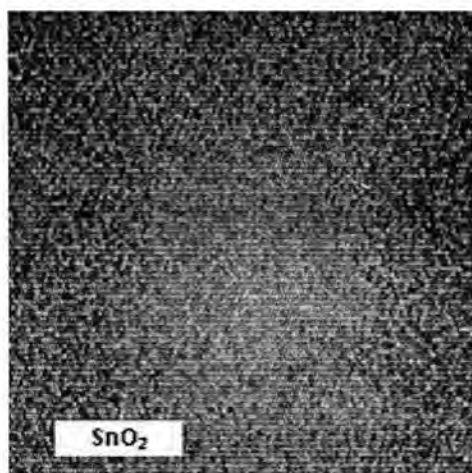
Fig. (2) the application of Stained Glass technique in images.

b- Smudge Stick technique:-

Fig. (3) the application of Smudge Stick technique to the images.

c- Pixel-Pointillist technique:-

Fig. (4) the application of Pixel-Pointillist technique images.



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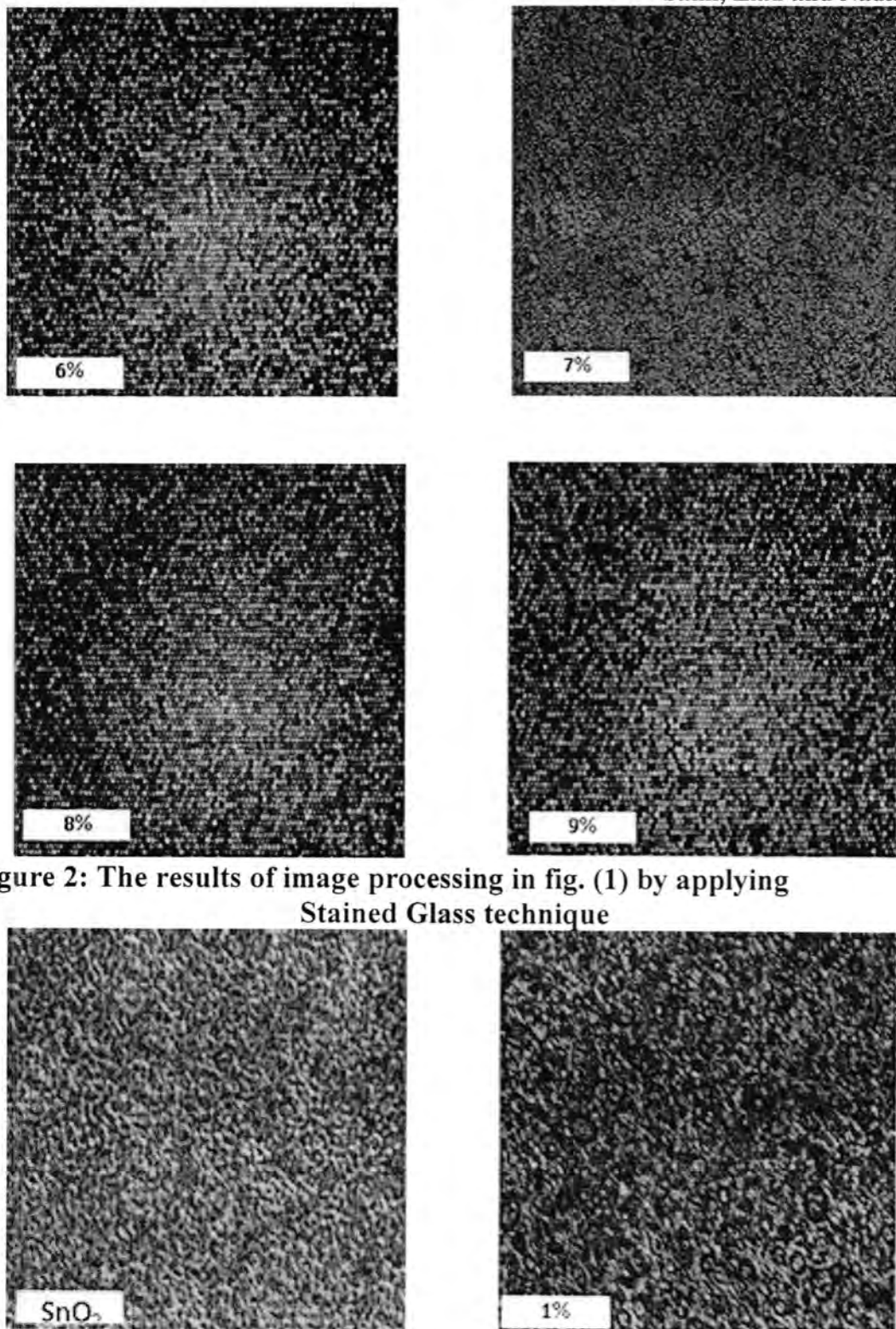


Figure 2: The results of image processing in fig. (1) by applying Stained Glass technique

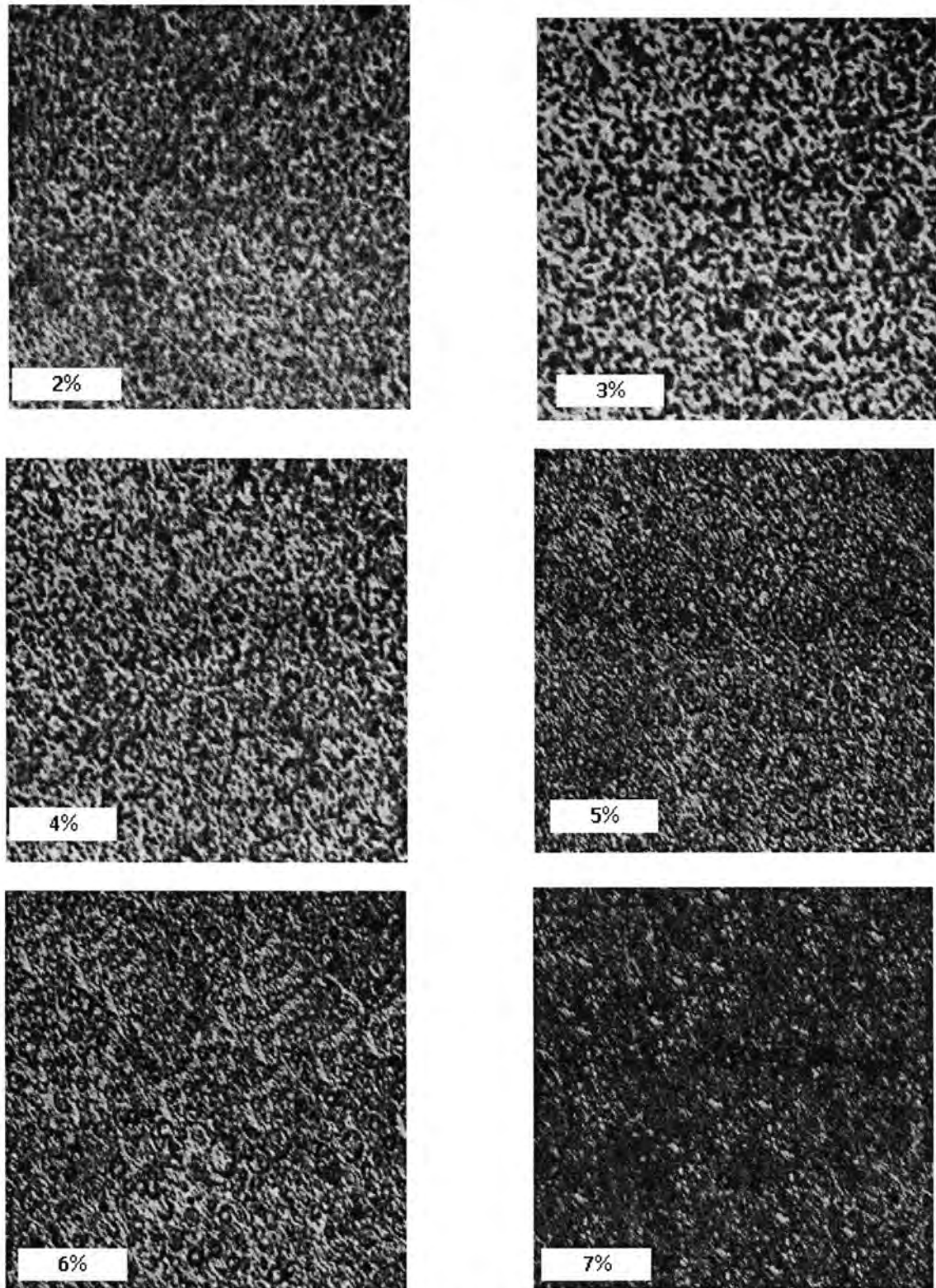
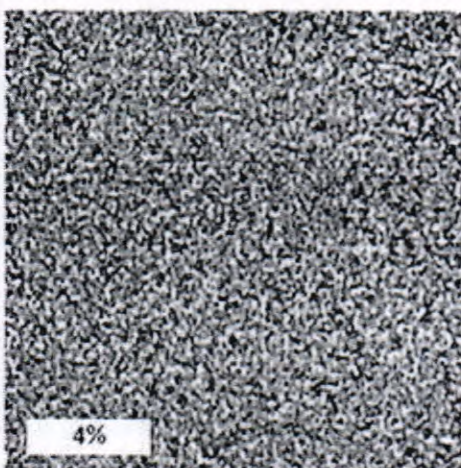
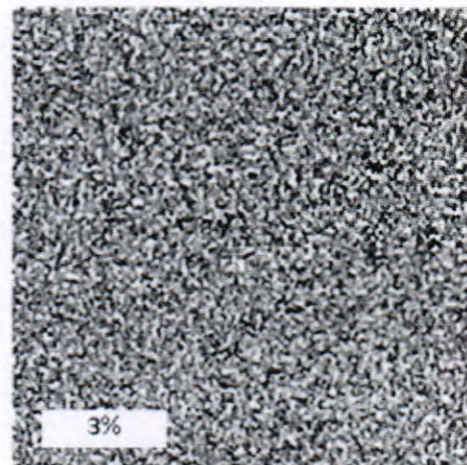
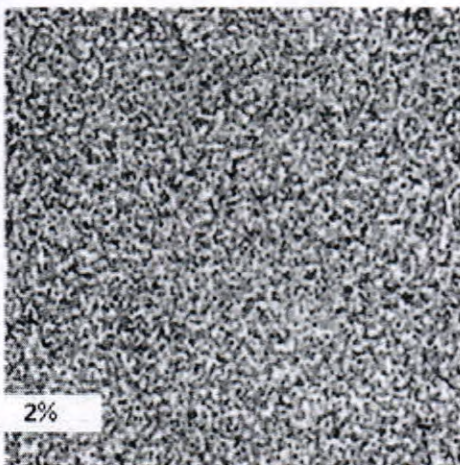
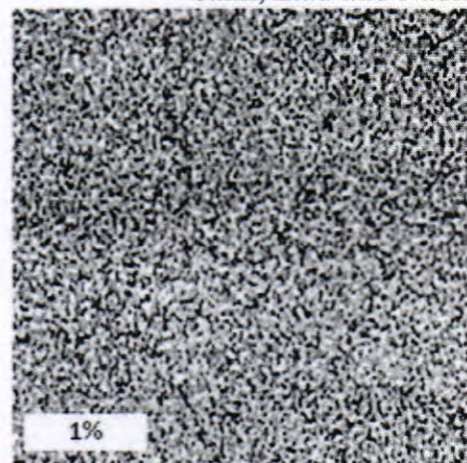
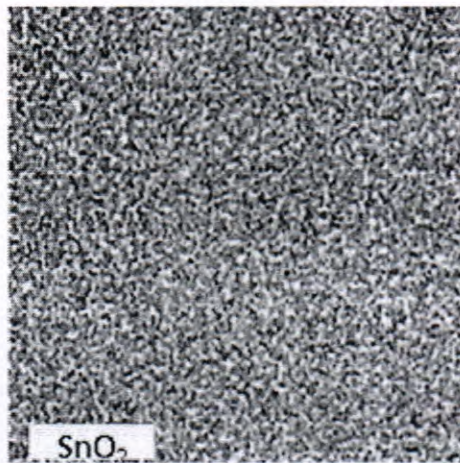


Figure 3: The results of image processing in fig. (1) by applying Smudge Stick technique

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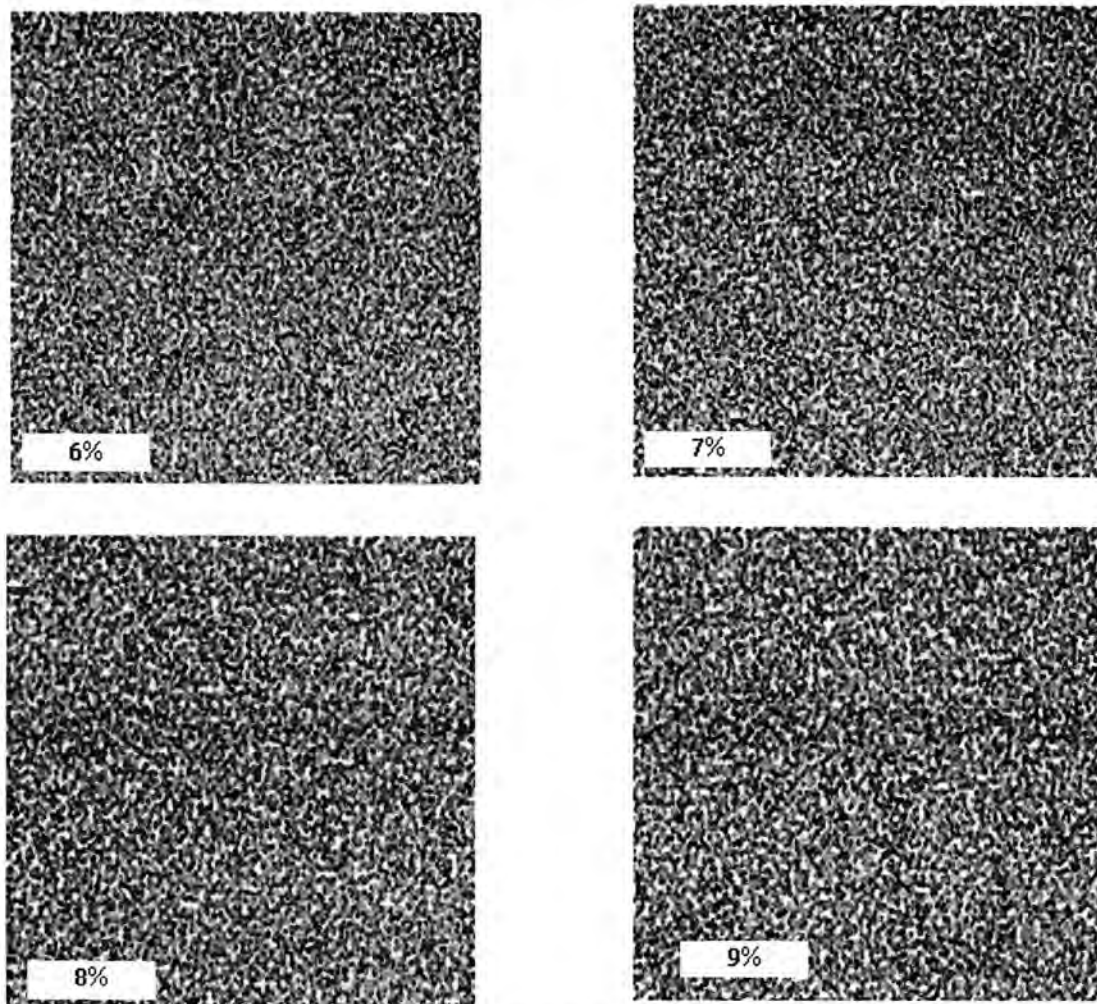


Figure 4: the results of image processing in Fig. (1) by applying Pixel-Pointillist technique

Using Visual Basic (VB) language to calculate the average grain size of samples and non-vestiges. This program has been applied to the previous three techniques. Fig. (5) shows VB program interface using some statistics, we taken for each nucleus window's position, the mean value and standard deviation for red, green, and blue colors bands of the image by:

- The mean (\bar{x}) is calculated from:

$$\bar{x} = \frac{\sum_{i=1}^N x_i}{N}$$

where x_i represents pixels with location (i) and N the total number of pixel.

- The standard deviation is calculated from:

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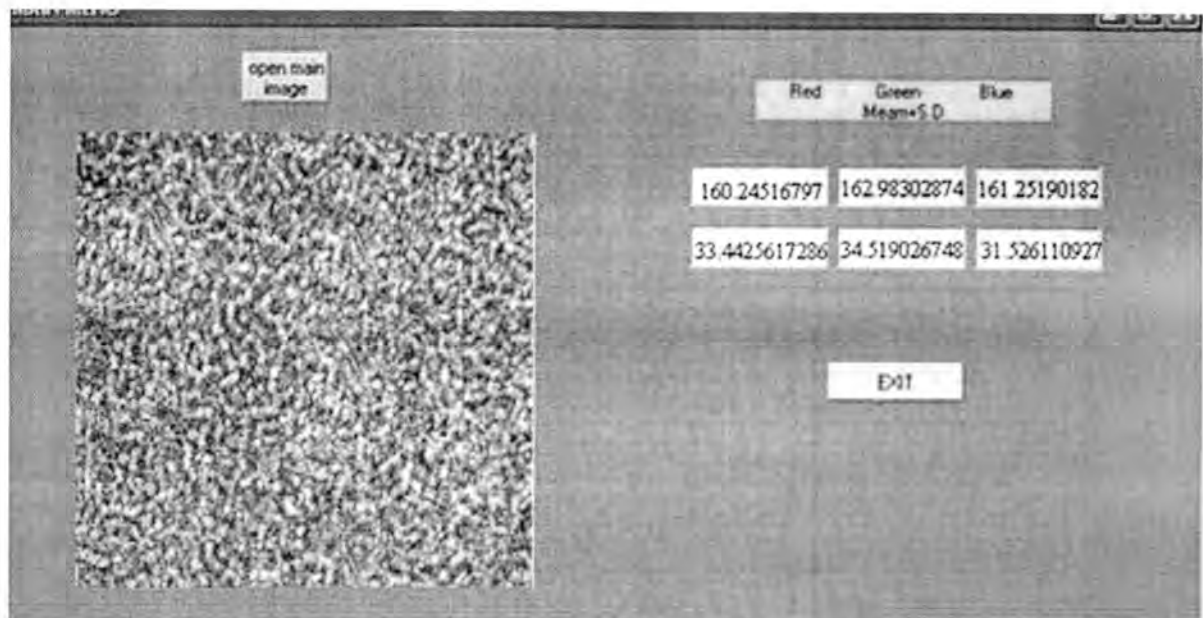
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$$s = \sqrt{\frac{\sum_{i=1}^N (x_i - \bar{x})^2}{N-1}}$$

To calculate the average grain size after a number of separate grains and calculate the average area of the unity of our beloved (Pixel), as well as the shape of each case study of the three cases mentioned above.

Table 1: the rate of grain size unit pixel of the membranes prepared

Applied techniques	Pixel- Pointillist	Smudge Stick	Stained Glass
Prepared film	Average grain size (pixel)		
0%	42.8	38.0	44.5
1%	42.2	38.1	44.9
2%	42.4	39.5	45.1
3%	43.8	38.7	46.1
4%	45.1	39.1	46.2
5%	44.2	37.8	45.9
6%	43.8	38.4	46.6
7%	43.3	39.8	45.7
8%	42.8	40.2	46.1
9%	43.9	40.3	47.1
average	43.37	38.84	45.67
shape	circle	elliptical	ribbed



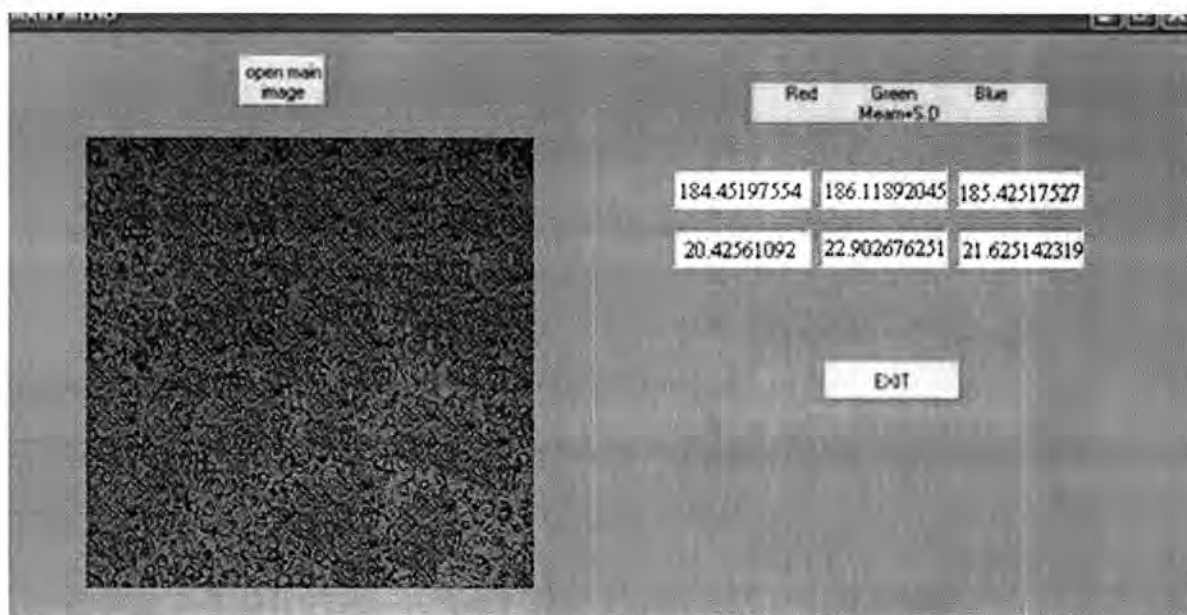


Figure 5: the program interface by V.B. to calculate the average and the standard deviation for undoped film and doped with 9% Sb

We can conclude

- There is differentiation of color and a clear distinction between membranes due doping.
- The rate equal to the size of grain 40 Pixel.
- Improvement in the standard deviation of the color of the membrane with the increase in the proportion of doping to 9%.

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Investigation of Creep Behavior of Polyester Resin Composted with Different Volume Fractions of Fiber E-Glass and Aluminum Powder Particles

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الخلاصة

تم حساب سلوك الزحف لراتنج البولي استر المتراكب المحضر بكسور حجميه مختلفه من الياف E-الزجاجيه (woven roving) , ودقائق (مسحوق الالمنيوم) وتحت اختبار انحناء النقاط الاربعه عند درجة حرارة المحيط . اظهرت قوة الانحناء لمتراكبات (woven roving) احسن القيم بالمقارنه مع متراكبات الالمنيوم الدقائقيه او متراكبات woven roving/Al المختلطه . ان انفعال الزحف المحسوب لمدة 10^3 ساعه لثلاثة اجهادات مختلفه اي 15, 30, 45 MPa اظهر بان متراكبات WR تتحمل اقل انفعال بالنسبة لجميع العينات الاخرى . أظهر معامل الزحف ازاء الزمن خصائص السلوك لانفعال الزحف ولكن بصورة عكسية. الموديل الرياضي المستخدم لمحاكاة انفعال الزحف لفترات طويلة من الزمن بالاعتماد على الداله الاسيه الممتده او الداله المنحلة Kohlrauch- William-Watts(KWW) يرسم خط رئيسي «master line» يظهر بان متراكبات راتنج البولي استر/ woven roving تتفق مع الداله المنحله وسلوك الزمن الطويل . يظهر استقرار انفعال الزحف من الخط الرئيسي (master line) بان في متراكبات-woven roving بكسور حجميه 0.12 و 0.24 إن انفعال الزحف قد ازداد بحوالي 15.5% لكلا الكسرين الحجميين عند الزمن الطويل لمدة 10^5 ساعه. ان اضافة دقائق المنيوم بكسر حجمي 0.06 الى متراكب woven roving يزيد من انفعال الزحف الى 27% بسبب وجود دقائق الالمنيوم.

ABSTRACT

Creep behavior was carried for polyester resin composite prepered of different volume fractions of fiber E-glass(roving), and (aluminum powder)under 4-point flexure test at ambient temperature.Flexure strength of woven roving composites show best values in comparison to particulate of aluminium powder . composites or to mixed WR/Al and composites.The creep strain measured up to 10^3 h for three different stresses namely 15,30 and 45 MPa show that WR composites endures least strain of all other specimens.Creep modulus vs. time show the characteristic behavior of reciprocal creep strain.A mathematical model employed to simulate creep

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strain at extended long period of time according to stretched exponent or Kohlrauch-William- watts(KWW) decay function by plotting a master line , show that woven roving/ polyester resin composites obey the decay function and extended time behavior of creep strain extrapolated from the master line show that in woven roving- composites of 0.12 and 0.24 V_f the creep strains have increased by about 15.5% for both fractions of the intended time of 10^5 h. The addition of 0.06 Al particles to woven roving- composite has increased the creep strain to 27% allowing the composite to creep more due to presence of Al particles.

INTRODUCTION

The long-term behavior of polymer matrix composites (PMC) is a critical issue for many modern engineering application such as aerospace, biomedical and civil engineering infrastructure. The primary concerns in long-term performance of (PMC) are in the screening for final material selection, and in obtaining critical engineering properties that extend over the projected life time of the structure.

Viscoelastic creep among the critical properties needed to assess long term performance of (PMC).

Flexural strength σ using three-point flexural bend procedure is defined by[1-2]:

$$\sigma = \frac{3pL}{bd^2} \text{-----(1)}$$

Where

σ is stress in the outer fibers at midspan, (P_a),

p is Load at a given point of the Load-deflection curve (kg)

L is Support span(m)

b is width of beam tested, of test specimen (m), and,

d is thickness of test specimen(m).

Creep in flexure test is based on the loading configuration shown in Fig(2). The test method is used for determining flexural strength and modulus.

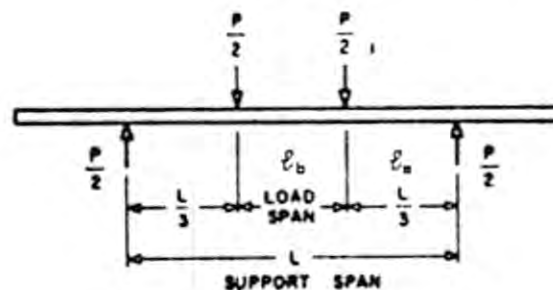


Figure 1: Four Point Flexure Loading [2]

The stress is defined as :

$$\sigma = \frac{3Pl_a}{bd^2} \text{-----}(2)$$

where

P is Load

l_a is right support span

b is width of test specimen

d is thickness test specimen

Strain is the loading parameter in the creep behavior and it is obtained by recording deformation in the test specimen under the loading condition.

For 4-point loading assembly, the strain (ϵ) is defined as [3],

$$\epsilon = \frac{4df}{l_b^2} \times 100 \text{-----}(3)$$

Where d= specimen thickness

f= deformation

l_b = distance between loading noses .

the modulus can be defined by

$$E = \frac{3Pl_al_b^2}{4bh^2f} \text{-----}(4)$$

Where p is the load required, l_a and l_b is the length of the supporting span as shown in Figure (1), b and d are the width and thickness of the sample, f is the values of the deformation [1-3] .

Mathematical Modeling of creep

Few mathematical models have been used for describing the visco-elastic behavior of composite material under constant (static) stress.

One model, the Findley's power law [4-6] expresses the time-dependent creep strain $\epsilon(t)$ by the formula

$$\epsilon(t) = \epsilon(o) + mt^n \text{-----}(5)$$

Where $\epsilon(o)$ is the initial strain n is independent of stress and temperature, but dependent on visco-elastic behavior of resin, volume fraction of fibers and their orientation.

m is dependent on stress and temperature.

The other model, Kohlrausch-Williams-Watts (KWW) decay function [7-8] takes into account the non-thermal and thermal histories in the time-dependent creep strain.

A method for treating the effects of non thermal and thermal histories on non-linearity and non exponentiality of the reduced time-dependent creep strain [$\epsilon(t)/\epsilon(o)$] has been derived by Song et al [7]. according to stretched exponential or Kohlrausch-Williams-Watts (KWW) decay function with a non linear parameter t_0 and non exponential parameter β as

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$$\frac{\epsilon(t)}{\epsilon(0)} = e^{\left(\frac{t}{t_0}\right)^\beta} \quad (0 < \beta < 1) \text{-----(6)}$$

By differentiating Eq.(6) and taking logarithms on both side one obtains:

$$(d\epsilon/dt)(t/\epsilon) = \left(\frac{1}{t_0}\right)^\beta \beta t^{\beta-1} = d \ln \epsilon / d \ln t \text{----- (7)}$$

$$\ln (d \ln \epsilon / d \ln t) = \ln \left[\left(\frac{1}{t_0}\right)^\beta \beta \right] + \beta \ln t \text{----- (8)}$$

β can thus be found from the slope of experimental data of

$\ln (d \ln \epsilon / d \ln t)$ versus $\ln t$.

Next $\epsilon(0)$ and t_0 can be found by rewriting Eq. (6) in the following logarithmic form as

$$\ln \epsilon(t) = \ln \epsilon(0) - \left(\frac{1}{t_0}\right)^\beta t^\beta \text{-----(9)}$$

where $\epsilon(0)$ and t_0 are determined from intercept and slope of line by linear regression.

Finally the master line can be established from

plotting $\ln [\epsilon(t) / \epsilon(0)]$ vs $(t / t_0)^\beta$

This line can be repeatedly established for different loading stresses.

The master line can be established from plotting $\ln [\epsilon(t) / \epsilon(0)]$ vs $(t / t_0)^\beta$.

This line can be repeatedly established for different loading stresses. The master line can be extrapolated to obtain creep behavior at extended long period of time [7-8].

MATERIALS AND METHODS

Polyester as matrix material was used in this study to prepare the polymer matrix composite. The rate of polymerization for this resin is too slow, and for practical purpose the catalyst [Methel Ethel Keton peroxide (MEKP) in a proportion of 0.5 for each 100g of the resin] and accelerator [(cobalt-napthenate catalyst) in a proportion of 0.1gm for each 100g of the resin with in a practical time period].

Accelerator added to the resin was recommended by polyester manufacturer to create a per accelerated resin. This resin was supplied from Sabic Co. Saudi Arabia. Specifications of this resin are listed in Table 1 .

Table 1: Some Specification of polyester resin [9]

Density	1.2 g/cm ³
Service temp.	70– 80 ⁰ C
Stability temp.	220 ⁰ C
Elongation Break at 25 ⁰ C	2%
Compression strength	90 MP _a

Glass Fibers

The E- glass fibers used in this study to reinforce the polyester resin were of two types: woven roving strand mat and chopped strand mat; and their properties are listed in table (2)

Table 2: Specification of E-glass fiber [10]

Color	White
max. Temperature	550 ⁰ C
melting point	1200 ⁰ C
diameter-filaments	6-9 micron
tensile strength – virgin filament	3400 MP _a
Young modulus	74 GPa
thermal conductivity	1.0 W / mK
fire reaction	Incombustible
Loss on ignition	< 1.5 %
dielectric rigidity – glass in bulk	60-100 KV/mm
solvent resistance	Good
acid resistance	good-except fluridic acid

Aluminum powder

Pure and stabilized aluminum fine powder supplied from MERCK Company, was used in this study. Its density was 2.698 g/cm³.

Specimens preparation

Molded sheet were cut into strips of length 39cm and width 2cm for creep test and to strips of 10cm in length and 2cm in with for bending test by using an electric saw blade.

The dimensions of the specimens were chosen according to the ASTM standard for creep and bending tests [2].

Mould preparation

First glass sheets of dimensions 39 X 30 X 0.4cm and glass strips were prepared for casting all specimens. They were coated with paraffin wax for easier separation of composite.

After preparation of the resin with the desired volume fraction it was cast in the glass mould.

Load was put on the top of the glass layer to squeeze out air bubbles during curing.

Polymer composite preparation

Filamentary composites preparation

Some of the specimens were carried out by using woven roving and the others by chopped strand mat, the two types of reinforced fibers were cut as

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sheets in dimensions of (30 X 39)cm², the polyester resin is prepared as mentioned in section (1-1). Volume fraction of the additives and the matrix can be evaluated by eq(10)

$$V_r + V_f + V_p + V_{\text{any additive}} = 1 \quad \text{-----(10)}$$

Where V_r is volume fraction of the resin

V_f is volume fraction of fiber

V_p is volume fraction of particle

$V_{\text{any additive}}$ is volume fraction of any other additive

Specimens with different volume fraction of E-glass type are listed in table (3).

The resin was prepared in a volumetric beaker and is divided equally between the layers of glass fiber.

Hand lay-up method was used to prepare this type of composite applying the amount of the resin into the mold and evenly distributed by using a brush and lying the dry fiber mat on the resin and carefully press on it by a brush to remove the air bubbles. Another amount of the resin was applied on the top of the mat and also evenly distributed by a brush, this sequence is repeated until the desired volume fraction was reached.

Table -3: Summary of composite reinforcement types, and their volume fractions

Specimen type	Volume fraction of fiber filler	Bearing load in creep test MPa
1- neat polyester resin	0.00	15
2- polyester + Woven Roving E-fiber glass	0.06	
	0.12	15 , 30
	0.19	30
	0.25	15 , 30 , 45
3- polyester reinforced by aluminum particles	0.06	30
	0.12	15 , 30
	0.19	30
4- polyester reinforced by aluminum particle and woven roving fiber e-glass	total v.f of reinforcement 0.125 fiber 0.06, Al 0.06	15 , 30
	total v.f of reinforcement 0.24 fiber 0.125 Al 0.125	15 , 30 , 45

Particulate composites

When incorporation by aluminum particles the polyester and filler was prepared according to the desired volume fraction and molded as previously mentioned.

The filler powder was weighted according to the desired volume fraction evaluated from eq.(10) and was gradually added to the resin with through mixing until a homogeneous mixture was obtained. The prepared composite was cast into the mould, and was left out for 24 hours to complete setting, finally it was put in furnace at 60⁰C for four hours post curing.

Filamentary / Particulate composites

- 1- The woven roving E-glass fibers were cut according to the desired molding area.
- 2- The aluminium powder weighted according to the desired volume fraction evaluated from eq.(10), used for preparing, and it was mixed with the prepared resin as mentioned in the previous section.
- 3- This type of specimen was also prepared by hand lay up method as previously mentioned.

The resin was mixed with the filler powder (aluminum) and then evenly distributed on the layers of the glass fibers.

- 4- Prepared specimen were left out at laboratory temperature for 24 hour for setting.

For post curing the specimens were put in an oven for four hours at 60⁰C.

Specimens Cut

Moulded sheet were cut into strips of length 39cm and width 2cm for creep test and to strips of 10cm in length and 2cm in with for bending test.

The dimensions of the specimens were choosen according to the ASTM standard for creep and bending tests[2].

Bending test

Mechanical testing was performed using a computer controlled tensile testing machine, employing 3-point bending test. Dimensions of specimens were prepared according to ASTM [2].

Creep test

For the purpose of this study the device of creep testing was designed and manufactured according to four point loading test in flexure. With the consultation of a diagram in ref. [3]. Figure (2) shows schematic loading assembly. More details cited in Ref [9]. Deformation due to creep was recorded for 45 days under each particular load chosen.

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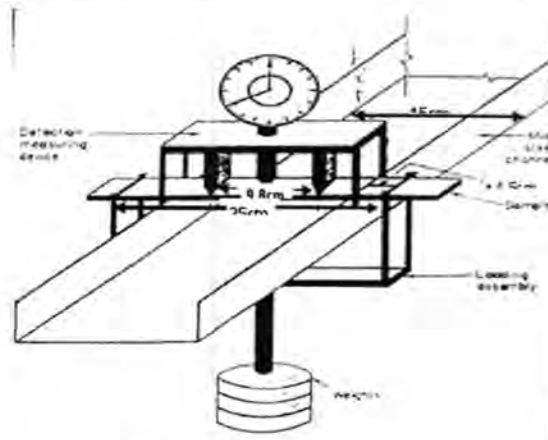


Figure 2: Four point loading assembly showing the deflection measuring device [3]

RESULT AND DISCUSSION

Bending test:

Prior to creep test the specimens were tested by three point bending test to determine the flexural strength in order to assign the range of stresses to be subjected during creep test.

From the load-deflection curve, the flexural strength was calculated using relation (1), and the resulted are illustrated in Table (4)

Table 4: Flexural strength and Strain(%) values(3-point bending test)

Specimen description		V _f	Flextural strength (MPa)	Strain (%)
Resin	Filler			
UP	---	---	133	0.7
	WR	0.06	125	3.3
	WR	0.12	127	3.5
	WR	0.19	138	3.5
	WR	0.25	139	3.4
	Al	0.06	76	1.1
	Al	0.12	60	1.1
	Al	0.19	51	1.0
	WR+Al	0.125	98	3.2
	WR+Al	0.24	103	3.2

Error in $\sigma \pm 5\text{MPa}$

$\epsilon \pm 0.2\%$

We can notice from table (4) that, UP+W.R.fiber E-glass($v_f=0.19,0.25$) has the largest flexural strength because if a long fiber reinforced composite is subject to mechanical loading, the role of fibers is to bear the applied load, whereas the matrix binds the fibers together and ensures the load transfer and distribution to and between the fibers[12], follows by neat UP follows by UP+ W.R fiber E-glass ($v_f = 0.06, 0.12$), because a large bending stiffness is obtained by placing the stiff material in the faces far from the neutral axis. The faces, which can be of different thickness on each side, take up most of the normal stresses in the structure [13], follows by UP+W.R. + Al, in these specimens, flexural strength increased with increasing the volume fractions of the additives, follows by UP+ Al because micro cracks formed by particle cleavage or by particle-matrix interface debonding may cause the crack path deviation[12], in UP+AL specimens, the flexural strength decreased with increasing the volume fraction of the additives.

Creep behavior at ambient temperature

The loading weights requires for applying a particular stress were calculated using relation (2).

The deformation can be obtained from the test, and the strain can be obtained from eq. (3)

The variation of strain with time for specimen tested are shown in figures from (3) to (9) respectively under 15,30,45 MPa stress.

Table (5) illustrate specimen and the strain at the beginning of the test, and Figures (3) to (9) illustrate the result creep behavior at ambient temperature. When a constant load is applied (except for a short initial duration then the strain may increase quite rapidly) to a viscoelastic material, the strain increases steadily. This increase of strain is creep. If creep increases beyond a certain limit, the effective stress owing to a decrease in the cross sectional area increases. The increased stress result in further deformation, which in turn increases the stress even more. Thus, the deformation suddenly accelerates, leading to the failure of the material [14].

The strength of the bonding in a solid does not vary appreciably with temperature. However in a polymer it becomes easier for parts of neighboring chains to slip to a new positions as the temperature rises. This can allow the chain to slide over each other under an applied stress. The longer the sample is left under load the more it will deform. This gives rise to creep in polymers [13]. The effects of strain rate on most polymers may be explained by the Eyring theory of viscosity, which assumes that the deformation of polymer involves the motion of chain molecule over potential energy barriers. Here, the yield stress varies linearly with the logarithm of strain rate. The polymer matrix has less time to localize at higher loading rates [15-17].

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Table 5: Results of creep test for unsaturated polyester composites under different load at room temperature.

Samples	Vf	15 MPa			30MPa			45MPa		
		ϵ_0	ϵ	$\Delta \epsilon$	ϵ_0	ϵ	$\Delta \epsilon$	ϵ_0	ϵ	$\Delta \epsilon$
neat		0.17	0.181	0.011						
UP+W.R.	0.12	0.131	0.142	0.012	0.234	0.246	0.012			
	0.19				0.21	0.219	0.01			
	0.24	0.106	0.111	0.005	0.142	0.151	0.009	0.268	0.277	0.009
UP+Al	0.06				0.411	0.449	0.038			
	0.12	0.145	0.185	0.04	0.247	0.287	0.041			
	0.19				0.408	0.449	0.041			
UP+W.R.+Al	0.12	0.121	0.152	0.031	0.32	0.353	0.033			
	0.24	0.15	0.169	0.02	0.237	0.257	0.02	0.308	0.328	0.02

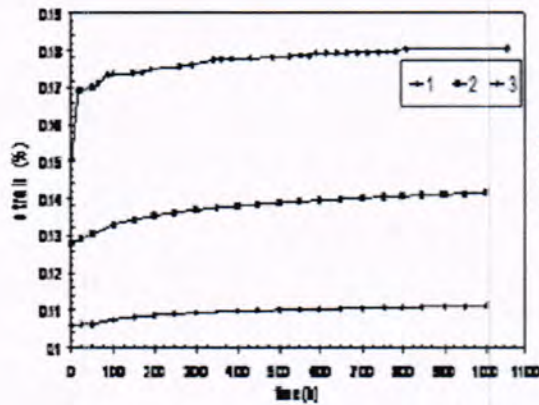


Figure 3: creep behavior for(1) UP+W.R.(vf=0.24),(2)UP+W.R.(vf=0.12),(3) neat UP,loaded under 15 MPa stress

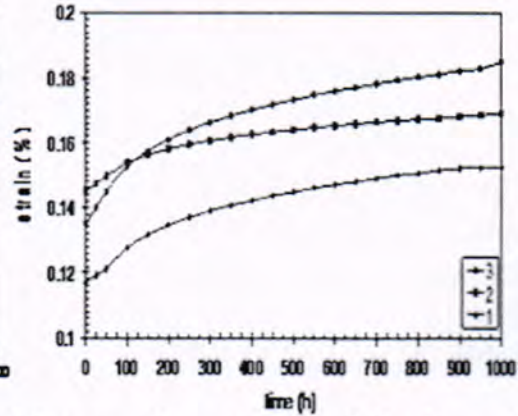


Figure 4: creep behavior for(1) UP+Al(vf=0.06)+W.R.(vf=0.06),(2) UP+Al(vf=0.12)+W.R.(vf=0.12),(3)UP+Al(vf=0.12), loaded under 15 MPa stress

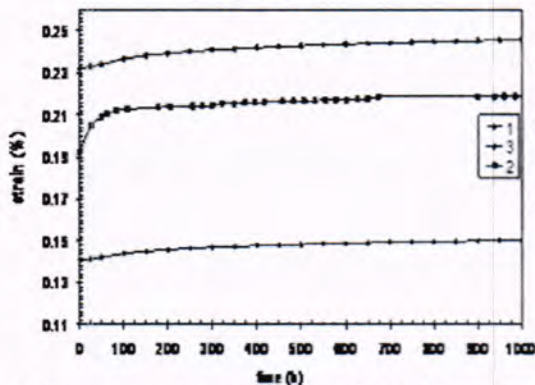


Figure 5: creep behaviour for (1) UP+W.R.(vf=0.24),(2) UP+W.R.(vf=0.19),(3) UP+W.R.(vf=0.12),loaded under 30 MPa

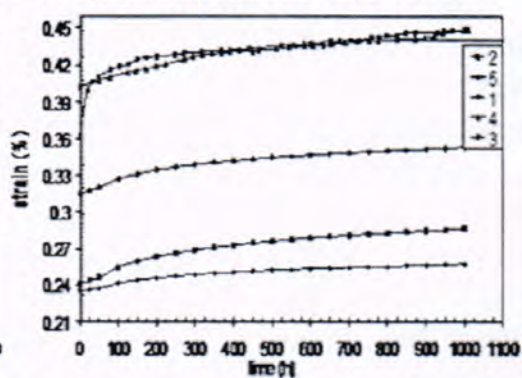


Figure 6: creep behavior for (1)UP+W.R.(vf=0.12)+al(vf=0.12),(2)UP+Al(vf=0.12),(3) UP+Al(vf=0.06)+W.r.(vf=0.06),(4)UP+Al(vf=0.19),(5) Up+Al(vf=0.06),loaded under 30 MPa

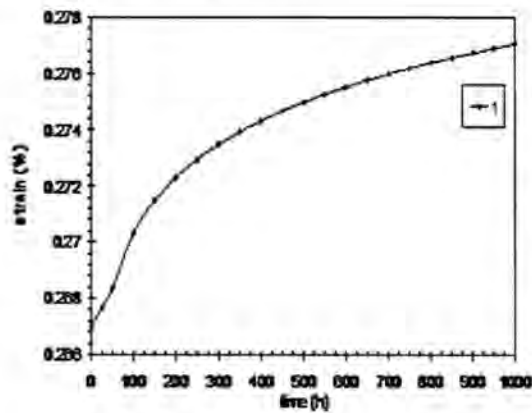


Figure 7: creep behavior for (1) UP+W.R.(vf=0.24) loaded under 45 MPa

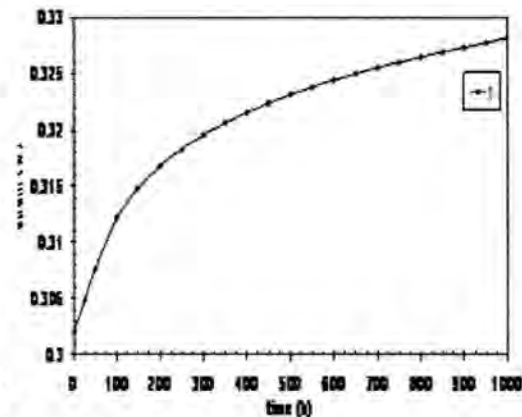


Figure 8: creep behavior for (1)UP+W.R.(vf=0.12)+Al(vf=0.12), loaded under 45 MPa

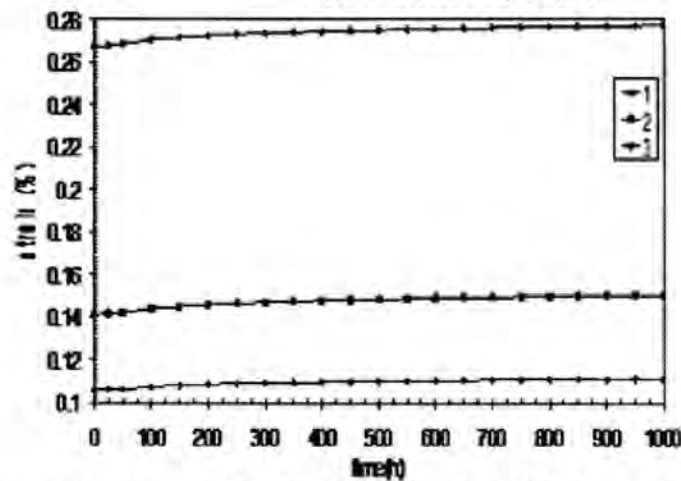


Figure 9: creep behavior for UP+W.R.(vf=0.24), loaded under (1) 15 MPa, (2) 30 MPa, (3) 45 MPa stresses

From figures(3) to(9), and table (5), under 15 MPa stress, in UP+Al (vf=0.12) specimen, the increasing in strain was 0.04, this can be related to the micro cracks formed by particle cleavage or by particle-matrix interface debonding which may cause the crack path deviation [12]., in UP+W.R. (vf=0.06)+Al(vf=0.06) specimen, increasing in strain was 0.31, because if the two components have two different creep resistances the creep of the flow resistance material, owing to adhesion between them. Thus with a higher bond strength between the components, a creep resistance even greater than that of its components should result [18], in UP+W.R.(vf=0.12) specimen, increasing in strain was 0.011, followed by neat polyester specimen, because large bending stiffness is obtained by placing the stiff material in the faces far from the neutral axis. The faces, which can be of different thickness on each side, take up most of the normal stresses in the structure[19], and mechanisms similar to the toughening mechanisms in particle reinforced composites (crack branching, deflection), operate in fiber

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reinforced composites as well[12], in UP+W.R.(vf=0.24) specimen increasing in strain was 0.005 because if a long fiber reinforced composite is subject to mechanical loading, the role of fibers is to bear the applied load ,whereas the matrix binds the fibers together and ensures the load transfer and distribution to and between the fibers[12].Some factors affect creep behavior are:

a. Effect of volume fraction of fibers / particles

From table (5)we can notice that in all specimens contain fiber E-glass in their structure ,creep decreased by increasing volume fraction of the fiber this can be explained by the higher the concentration of fibers (at any orientation), the lower will be the creep rate. This is because there is less of resin available to deform, also glass fiber do not creep a significant amount at room temperature. Creep is a function of the applied stress, fiber orientation, fiber volume fraction, and ductility of the resin [20],where as in specimens contain just particles as aluminum, creep increased by increasing the volume fraction of the particles.

Effect of increasing stress on creep behavior

From table (5) we can notice in all specimens subjected to creep test, as stress increased creep also increased, because increasing mechanical stress has several effects at the molecular level. diffusion of gas and liquids into the polymer matrix is enhanced and some population of chemical bond in the polymer chain will be loaded to higher level, thereby reduction the energy needed to rupture the bond. In turn, at the macroscopic level the time to achieve a characteristic damage state will be reduced [21-23].

Creep Modulus The modulus can be obtained by using Eq.[4]. figures from (10) to (15) illustrate the results of creep modulus for specimens at ambient temperature.

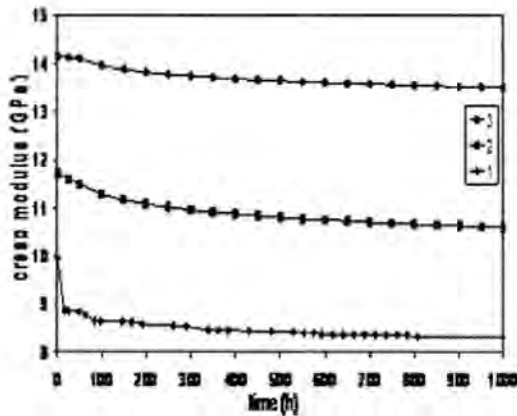


Figure 10: creep modulus, vs. time(h), for (1) neat UP, (2) UP+W.R.(vf=0.12), (3) UP+W.R.(vf=0.24), loaded under 15 MPa

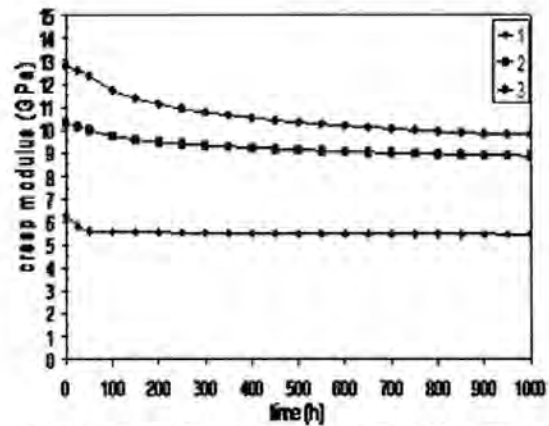


Figure 11: creep modulus, vs. time(h), for (1) UP+Al(vf=0.12), (2) UP+W.R.(vf=0.12)+Al(vf=0.12), (3) UP+W.R.(vf=0.06)+A.L.(vf=0.06), loaded under 15 MPa

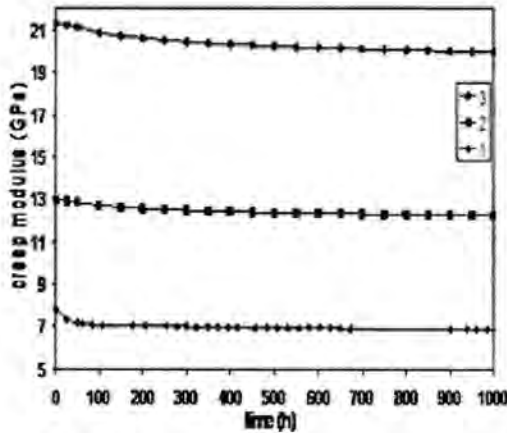


Figure 12: creep modulus, vs. time(h), for (1) UP+W.R.(vf=0.19), (2) UP+W.R.(vf=0.12), (3) UP+W.R.(vf=0.24), loaded under 30 MPa

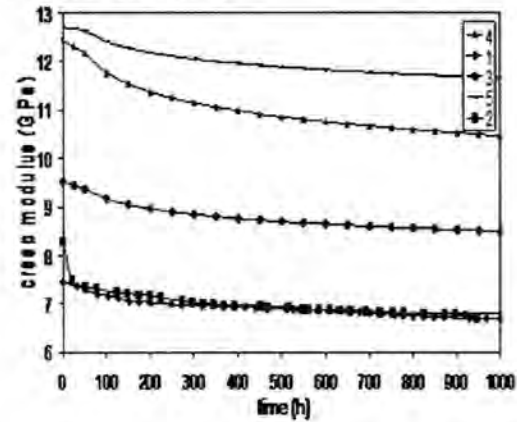


Figure 13: creep modulus, vs. time(h), for (1) UP+Al(vf=0.06), (2) UP+Al(vf=0.19), (3) UP+W.R.(vf=0.06)+Al(vf=0.06), (4) UP+Al(vf=0.12), (5) UP+W.R.(vf=0.12)+Al(vf=0.12) loaded under 30 MPa

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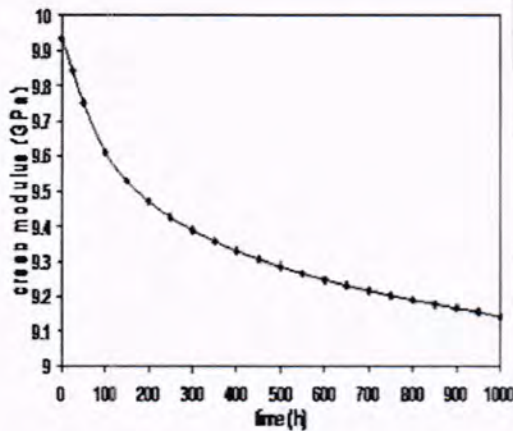


Figure 14: creep modulus,vs.time(h), for UP+W.R.(vf=0.12)+Al (vf=0.12), loaded under 45 MPa

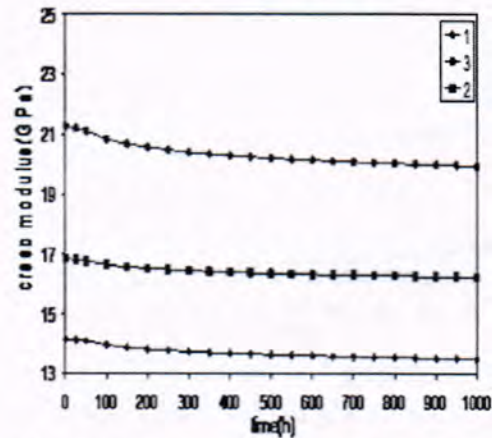


Figure 15: creep modulus,vs.time(h),for UP+W.R.(vf=0.24),loaded under (1) 15 MPa,(2) 45 MPa,(3) 30 MPa stresses

From all the figures we can notice that as strain increased, creep modulus decreased. As creep is defined as time-dependent deformation of a material (or structure) under a constant load, the design process should involve substituting creep modulus for stiffness (a quantitative measure of the elastic deformation produced in a material. A stiff material has a high modulus of elasticity) (or Yong's modulus). The creep modulus is the apparent stiffness as determined by the total deformation to the time defined[22].

If the weight (stress) is left on over a period of time, the amount of bending or elongation continues to increase, and the value for the modulus will decrease with time. This decreasing modulus is a function of time (and even temperature) [22].

The effect of creep is a reduction of the young's modulus. The reduction of young's modulus is denoted as the creep modulus [24].

Creep Mathematical Modeling

Creep curves

Figure(9) shows creep curves of $\epsilon(t)$ versus t for PE+W.R.(0.24) at room temperature and for different stresses. These experimental curves will be treated and unified to a master line which can be extrapolated for means of long term prediction.

Establishment of unified master line Determination of β parameter

Following eq. (8), $\ln(d \ln \epsilon / d \ln t)$ versus experimental data of $\ln t$ are plotted as shown in Fig's (16),(17),(18) for PE/W.R. ($\nu_f=0.24$) at 15,30,45 MPa stresses respectively. β 's was then found from slopes of the lines by linear regression. Finally the values of β at different stresses were averaged.

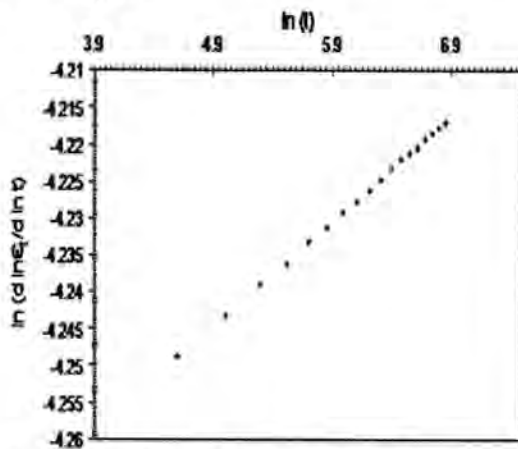


Figure 16: $\ln(d \ln \epsilon / d \ln t)$ vs. $\ln(t)$ for UP+W.R. ($\nu_f=0.24$) loaded at 15 MPa

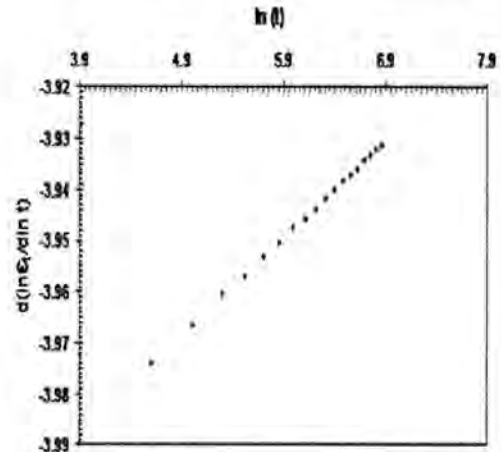


Figure 17: $\ln(d \ln \epsilon / d \ln t)$ vs. $\ln(t)$ for (1) UP+W.R. ($\nu_f=0.24$), loaded under 30 MPa stress

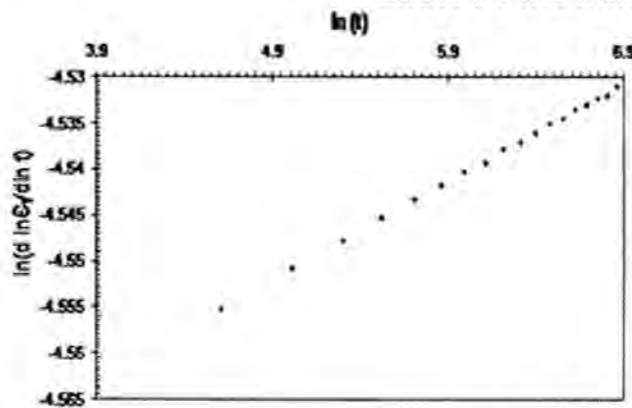


Figure 18: $\ln(d \ln \epsilon / d \ln t)$ vs. $\ln(t)$ for UP+W.R. ($\nu_f=0.24$) loaded under (1) 45 MPa stress

Determination of $\epsilon(0)$ and $t(0)$

Generally, the values of $\epsilon(0)$ and t_0 can be determined directly from experiments. But they can be also obtained from eq.

Fig's (19),(20),(21) shows plotted $\ln \epsilon(t)$ versus t^β for PE/W.R. ($\nu_f=0.24$) at 15,30,45 MPa stresses. Values of $\epsilon(0)$ and $t(0)$ were then found from slopes and intercepts of lines by liner regression. These values are averaged with the experimental values.

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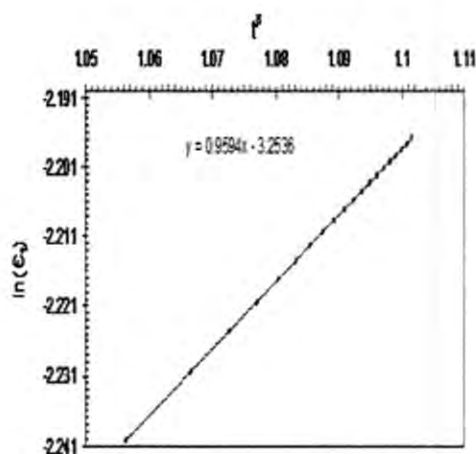


Figure 19: $\ln(\epsilon)$ vs. t^β for UP+W.R.(vf=0.24) loaded under 15 MPa stress

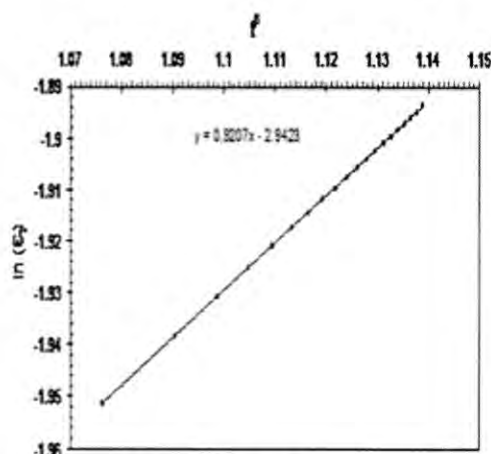


Figure 20: $\ln(\epsilon)$ vs. t^β for UP+W.R.(vf=0.24) loaded under 30 MPa

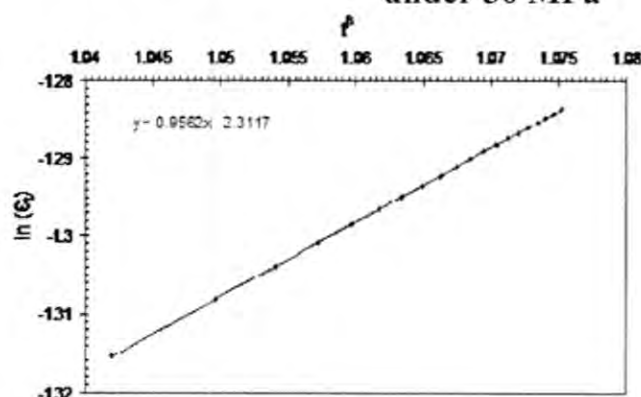


Figure 21: $\ln(\epsilon)$ vs. t^β for UP+W.R.(vf=0.24), loaded under 45 MPa

Plotting of unified master line

Fig(22-26) shows the plotting of $\ln(\epsilon(t)/\epsilon(0))$ versus $(t/t_0)^\beta$ at different stresses. The results show that its very good straight line over wide range of stresses. This is an indication that the unified master line can be used to extrapolate for the prediction of long term behavior of composite under investigation.

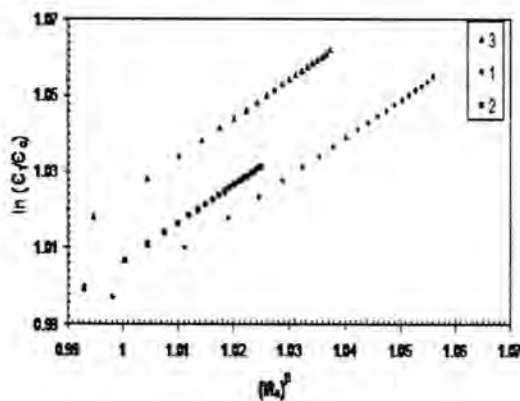


Figure 22: unified master line for UP+W.R.(vf=0.24) loaded under (1) 15 (2) 30 MPa (3) 45 MPa stresses

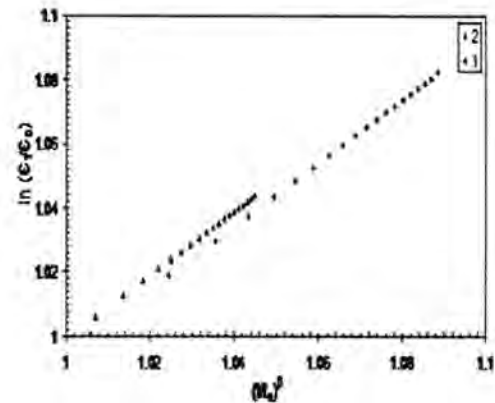


Figure 23: unified master line for UP/W.R.(vf=0.12), loaded under (1) 4 MPa, (2) 8 MPa stresses

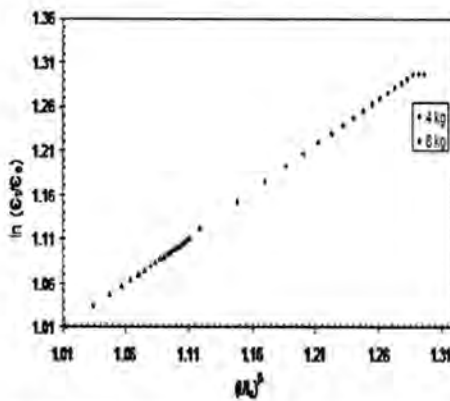


Figure 24: unified master line for UP/W.R.(vf=0.06)/Al(vf=0.06), loaded under (1) 15 MPa, (2) 30 MPa stresses

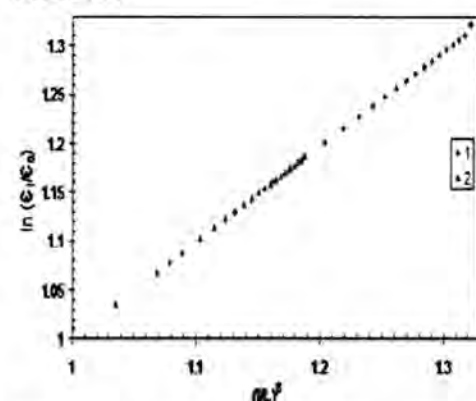


Figure 25: unified master line for UP/Al particles (vf=0.12), loaded under (1) 15 MPa, (2) 30 MPa stresses

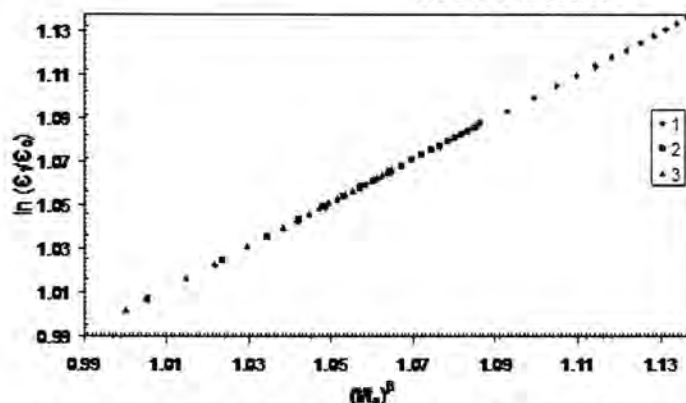


Figure 26: fig.(26) unified master line for UP/W.R.(vf=0.12)/Al(vf=0.12), loaded under (1) 15 MPa, (2) 30 MPa, (3) 45 MPa

Prediction of long term creep behavior

Since the universal creep equation applies to the composite system. It can then be used to predict the long term creep time. If 10^5 hour (ca. 11 years)

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creep time is considered, a PE/W.R.(vf=0.24)composite bearing a loading stress of 20% of its flexural strength would endure creep strain of 0.517%.This value constitute only 15% of the flexural strain of the composite provided the composite is kept on the same condition for the period intended.

Table 6: Illustrate values of strain (€)after1000(h) and strain after 10⁵ (h), and the change in strain according to flexural strain'

Specimens	Applied stress (MPa)	€ (%) at 1000(h)	€(%) at 10 ⁵ (h)	Changing in strain according to flexural strength after 10 ⁵ (h)
UP+W.R. (vf=0.24)	15,30,45	0.179	0.517	15.00%
UP+W.R. (vf=0.12)	15,30	0.194	0.579	16.50%
UP+W.R. (vf=0.12) + Al (vf=0.12)	15,30,45	0.252	0.785	24.53%
UP+W.R. (vf=0.06) +AL (vf=0.06)	15,30	0.253	0.877	27.41%
UP+Al (vf=0.12)	15,30	0.236	0.857	77.91%

From this table we can notice that the best specimen which exhibit the lowest creep after 10⁵(h) with respect to flexural strain was (UP+W.R. (vf=0.24)).

So we can conclude:

- For all specimens with the same volume fraction of the additives, creep was largest in unsaturated polyester incorporated with particles, followed by unsaturated polyester enforced by fiber E glass and particles(with same volume fraction for each one), followed by unsaturated polyester enforced by fiber E- glass.
- For unsaturated polyester incorporated with particles creep increased by increasing volume fraction of the particles.
- lower creep is obtained is obtained by placing the stiff material like woven roving fiber E-glass in the faces far from the neutral axis

- Creep increased by increasing stress.
- In all specimens enforced by fiber E-glass, creep decreased by increasing the volume fraction, where as for specimens incorporated with particles ,creep increased by increasing the volume fraction .
- From studying creep modulus, as strain increased creep modulus decreased.
- For prediction of long-term creep behavior, the largest increase in strain, in specific volume fraction after 10^5 (h) with respect to flexural strain was in unsaturated polyester incorporated with aluminum particles, follows by unsaturated polyester reinforced by aluminum and woven roving fiber E-glass, follows by unsaturated polyester reinforced by woven roving fiber E-glass.

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The Cyclic Decomposition of The Factor Group $\text{cf}(Q_{2m} \times C_2, Z) / \bar{R}(Q_{2m} \times C_2)$ When m is an Odd Number

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الخلاصة

الهدف الرئيسي من هذا البحث هو تحديد التجزئة الدائرية للزمرة الكسرية $\text{Cf}(Q_{2m} \times C_2, Z) / \bar{R}(Q_{2m} \times C_2)$ عندما عدد فردي والتي نرسم لها بالرمز $K(Q_{2m} \times C_2)$. وجدنا ان التجزئة الدائرية للزمرة $K(Q_{2m} \times C_2)$ تعتمد على القواسم الأولية للعدد m ، فإذا كان $m = p_1^{\alpha_1} \cdot p_2^{\alpha_2} \dots p_r^{\alpha_r}$ وان p_1, p_2, \dots, p_r اعداد اولية مختلفة و $\alpha_1, \alpha_2, \dots, \alpha_r$ اعداد صحيحة موجبة فإن:

$$K(Q_{2m} \times C_2) = \bigoplus_{i=1}^2 K(Q_{2m}) \bigoplus_{i=1}^{(\alpha_1+1)(\alpha_2+1)\dots(\alpha_m+1)-1} C_4 \oplus C_8$$

بالاضافة الى ذلك وجدنا جدول الشواخص ذات القيم النسبية للزمرة $Q_{2m} \times C_2$. استعملنا برنامج Matlab لحساب بعض النتائج في هذا البحث.

ABSTRACT

The main purpose of this search is to determine the cyclic decomposition of the finite abelian factor group $\text{Cf}(Q_{2m} \times C_2, Z) / \bar{R}(Q_{2m} \times C_2)$ when m is an odd number, which is denoted by $K(Q_{2m} \times C_2)$.

We have found that the cyclic decomposition of $K(Q_{2m} \times C_2)$ depends on the elementary divisor of m , if $m = p_1^{\alpha_1} \cdot p_2^{\alpha_2} \dots p_r^{\alpha_r}$ where p_1, p_2, \dots, p_r are distinct primes and $\alpha_1, \alpha_2, \dots, \alpha_r$ are positive integers, then:

$$K(Q_{2m} \times C_2) = \bigoplus_{i=1}^2 K(Q_{2m}) \bigoplus_{i=1}^{(\alpha_1+1)(\alpha_2+1)\dots(\alpha_m+1)-1} C_4 \oplus C_8 .$$

Moreover we have found the rational valued characters table of the group $Q_{2m} \times C_2$. We have used the Matlab program to calculate some results of this search.

INTRODUCTION

Let G be a finite group, two elements of G are said to be r -conjugate if the cyclic subgroups they generate are conjugate in G . This defines an equivalence relation on G . its classes are called r -classes.

The Cyclic Decomposition of The Factor Group $\text{cf}(\mathbb{Q}_{2m} \times \mathbb{C}_2, \mathbb{Z}) / \overline{R}(\mathbb{Q}_{2m} \times \mathbb{C}_2)$ When m is an Odd Number

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The \mathbb{Z} -valued class function on the group G , which is constant on the r -classes forms a finitely generated abelian group $\text{cf}(G, \mathbb{Z})$ of a rank equal to the number of r -classes.

The intersection of $\text{cf}(G, \mathbb{Z})$ with the group of all generalized characters of G , $R(G)$ is a normal subgroup of $\text{cf}(G, \mathbb{Z})$ denoted by $\overline{R}(G)$, then, $\text{cf}(G, \mathbb{Z}) / \overline{R}(G)$ is a finite abelian factor group which is denoted by $K(G)$.

Each element in $\overline{R}(G)$ can be written as $v_1\theta_1 + v_2\theta_2 + \dots + v_r\theta_r$, where r is the number of r -classes, $v_1, v_2, \dots, v_r \in \mathbb{Z}$ and $\theta_i = \sum_{\sigma \in \text{Gal}(\mathbb{Q}(\chi_i)/\mathbb{Q})} \sigma(\chi_i)$, where χ_i is an irreducible character of the group G and σ is any element in Galois group $\text{Gal}(\mathbb{Q}(\chi_i)/\mathbb{Q})$.

Let $\equiv^*(G)$ denotes the $r \times r$ matrix which corresponds to the θ_i 's and columns correspond to the r -classes of G .

The matrix expressing $\overline{R}(G)$ basis in terms of the $\text{cf}(G, \mathbb{Z})$ basis is $\equiv^*(G)$.

We can use the theory of invariant factors to obtain the direct sum of the cyclic \mathbb{Z} -module of orders the distinct invariant factors of $\equiv^*(G)$ to find the cyclic decomposition of $K(G)$.

Finally, we have calculated some results and examples by using the Matlab program.

1- Irreducible representations of the Quaternion Group \mathbb{Q}_{2m} when m is an odd number

There are four distinct irreducible representations R_1, R_2, R_3 and R_4 of degree 1, obtained by letting ± 1 and $\pm i$ correspond to x and y in all possible ways. The representation R_1, R_2, R_3 and R_4 are given by the following table:

	x^k	$x^k y$
R_1	1	1
R_2	1	-1
R_3	$(-1)^k$	$i(-1)^k$
R_4	$(-1)^k$	$i(-1)^{k+1}$

Where $0 \leq k \leq 2m-1$ and there are $m-1$ distinct irreducible representations for \mathbb{Q}_{2m} , of degree 2, we denote it by T_h and T_h take the following form:

$$T_h(x) = \begin{bmatrix} \omega^h & 0 \\ 0 & \omega^{-h} \end{bmatrix}, T_h(y) = \begin{bmatrix} 0 & \omega^{-hm} \\ 1 & 0 \end{bmatrix}$$

Now, for all elements of \mathbb{Q}_{2m} the representations T_h is written as follows:

$$T_h(x^k) = \begin{bmatrix} \omega^{hk} & 0 \\ 0 & \omega^{-hk} \end{bmatrix}, \quad T_h(x^k y) = \begin{bmatrix} 0 & \omega^{h(k-m)} \\ \omega^{-hk} & 0 \end{bmatrix}$$

Where $0 \leq k \leq 2m-1$, $1 \leq h \leq m-1$ and $\omega = e^{2\pi i/2m}$.

Definition 1.1

For all positive integer m we define the *generalized quaternion group* Q_{2m} of order $4m$ which is generated by two elements x and y

$$Q_{2m} = \{x, y: x^m = y^2, x^{2m} = 1, yx y^{-1} = x^{-1}\}$$

2- The character table of the quaternion group Q_{2m} when m is an odd number

There are two types of irreducible characters .one of them is the character of the linear representations R_1, R_2, R_3 and R_4 which are denoted by ψ_1, ψ_2, ψ_3 and ψ_4 , respectively as in the following table:

	x^k	$x^k y$
ψ_1	1	1
ψ_2	1	-1
ψ_3	$(-1)^k$	$i(-1)^k$
ψ_4	$(-1)^k$	$i(-1)^{k+1}$

Where $0 \leq k \leq 2m-1$.

The rest characters of irreducible representations T_h of degree 2 are denoted by χ_h such that :

$$\chi_h(x^k) = \omega^{hk} + \omega^{-hk} = e^{\pi i h k / m} + e^{-\pi i h k / m} = 2 \cos(\pi h k / m) \quad \chi_h(x^k y) = 0$$

Where $0 \leq k \leq 2m-1$, $1 \leq h \leq m-1$ and $\omega = e^{2\pi i/2m}$.

So there are $m+3$ irreducible characters of Q_{2m} .

Proposition 2.1: let $\rho^1: G \rightarrow GL(M_1)$ and $\rho^2: G \rightarrow GL(M_2)$ be two linear representations of G , and let χ_1 and χ_2 be their characters. Then The character ψ of the tensor product representation $M_1 \otimes M_2$ is equal to $\chi_1 \cdot \chi_2$.

Theorem 2.2: let $T_1: G_1 \rightarrow GL(n, K)$ and $T_2: G_2 \rightarrow GL(m, K)$ are two matrix representations of the groups G_1 and G_2 , χ_1 and χ_2 be two characters of T_1 and T_2 respectively, then the character of $T_1 \otimes T_2$ is $\chi_1 \cdot \chi_2$.

The Group $Q_{2m} \times C_2$ 2.3: The direct product group $Q_{2m} \times C_2$, where C_2 is a cyclic group of order 2 then

$$|Q_{2m} \times C_2| = 8m.$$

Since, the irreducible representations of the group $Q_{2m} \times C_2$ are the tensor products of those of Q_{2m} and those of C_2 . The group C_2 has two irreducible representations, their characters σ_1 and σ_2 are given in the table:

CL_α	1	r
$ CL_\alpha $	1	1
$ C_G(CL_\alpha) $	2	2
σ_1	1	1
σ_2	1	-1

The Cyclic Decomposition of The Factor Group $\text{cf}(Q_{2m} \times C_2, Z) / \bar{R}(Q_{2m} \times C_2)$ When m is an Odd Number

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$$\equiv (C_2) =$$

According to proposition (1), each irreducible character χ_i of Q_{2m} defines two irreducible characters χ_{i1}, χ_{i2} such that $\chi_{i1} = \chi_i \sigma_1, \chi_{i2} = \chi_i \sigma_2$ of $Q_{2m} \times C_2$. Then $\equiv(Q_{2m} \times C_2) = \equiv(Q_{2m}) \otimes \equiv(C_2)$

3- The group $\bar{R}(G)$

Definition 3.1: Two elements of G are said to be *Γ -conjugate* if the cyclic subgroups they generate are conjugate in G , this defines an equivalence relation on G . its classes are called *Γ -classes*.

Definition 3.2: A class function f on the group G with values in \mathbb{C} is called *a complex-valued class function on G* , the set of all complex-valued class functions will be denoted by $\text{cf}(G)$.

Proposition 3.3: The set of $\text{cf}(G)$ under the operation of addition is an abelian group.

Proposition 3.4: Let $\text{cf}(G, Z)$ be the set of all Z -valued class functions of G which are constant on Γ -classes, then $\text{cf}(G, Z)$ under the operation of addition is an abelian group.

Definition 3.5: The group generated by all generalized characters on \mathbb{C} is called the group of the generalized characters of G and it is denoted by $R(G)$.

Definition 3.6: The intersection of $\text{cf}(G, Z)$ with $R(G)$ forms an abelian group which is called the group of Z -valued generalized characters of G , denoted by $\bar{R}(G)$ and the $\text{cf}(G, Z) / \bar{R}(G)$ is a finite abelian factor group denoted by $K(G)$.

Proposition 3.7: Let ε_n be the complex primitive n -th root of unity, the Galois group $\text{Gal}(Q(\varepsilon_n)/Q) = \Gamma_n$ is a subgroup of the multiplicative group $(Z/nZ)^*$ of invertible elements of Z/nZ , more precisely, if $\sigma \in \text{Gal}(Q(\varepsilon_n)/Q)$, there exists a unique element $t \in (Z/nZ)^*$ such that:

$$\sigma(\varepsilon_n) = \varepsilon_n^t \quad \text{if } \varepsilon_n^n = 1.$$

We denote the image of $\text{Gal}(Q(\varepsilon_n)/Q)$ in $(Z/nZ)^*$ by Γ_Q and if $t \in \Gamma_Q$, we denote σ_t the corresponding element of $\text{Gal}(Q(\varepsilon_n)/Q)$, take as a ground field Q of rational numbers. The Galois group of $Q(\varepsilon_n)$ over Q is the group denoted by Γ .

Theorem [gauss-kronecker] 3.8 $\Gamma = (Z/nZ)^*$.

4- The rational valued characters table

Definition 4.1: A rational valued character θ of G is a character whose values are in Z , which is $\theta(g) \in Z$, for all $g \in G$.

Proposition 4.2: The rational valued characters $\theta_i = \sum_{\sigma \in \text{Gal}(\mathbb{Q}(\chi_i)/\mathbb{Q})} \sigma(\chi_i)$ form basis

for $\overline{R}(G)$, where χ_i are the irreducible characters of G and their numbers are equal to the number of all distinct Γ -classes of G .

Definition 4.3: The information about rational valued characters of finite group G is displayed in a table called *the rational valued characters table of G* .

We denote it by $\equiv^*(G)$ which is $l \times l$ matrix whose columns are Γ -classes and rows are the values of all rational valued characters of G , where l is the number of Γ -classes.

Definition 4.4: A k -th order minor is the determinant of the sub matrix obtained by taking k rows and k columns of A .

divisor over principal ideal domain we can form, a greatest common divisor (g.c.d) of all k -th order minors of A , it is called the k -th determinant divisor of A and denoted $D_k(A)$.

Theorem 4.5: Let $M \in M_{n \times m}(A)$ be a matrix with entries in a principal ideal domain. Then there exist two invertible matrices $P \in GL_n(A)$, $W \in GL_m(A)$ and a quasi-diagonal matrix $D \in M_{n \times m}(A)$ (that is, $d_{ij} = 0$ for $i \neq j$) such that :

- 1- on the one hand, $M = P D W$,
- 2- on the other hand, $d_1/d_2, \dots, d_i/d_{i+1}, \dots$, where the d_j are the diagonal entries of D .

And then, $D_k(PDW) = D_k(M)$ modulo the group of unites of A .

Theorem 4.6: Every matrix $A \in M_{n \times m}(R)$ with entries in a principal ideal domain R is equivalent to a matrix, which has diagonal form

$$B = \text{diag}\{d_{11}, d_{22}, \dots, d_{kk}, 0, \dots, 0\},$$

Where $k \leq \min\{m, n\}$, $d_{ii} \neq 0$ and moreover $d_{11}/d_{22}/\dots/d_{kk}$.

The nonzero diagonal elements of a matrix A are called the invariant factors of A .

Theorem 4.7: Any finitely generated A -module M over a principal ideal domain R is isomorphic to a finite direct sum of cyclic sub modules :

$$M \approx A/d_1A \oplus \dots \oplus A/d_tA \oplus A^{n-t}$$

Where $t \leq n$, and the d_i are non zero non unit elements in A such that $d_1/d_2/\dots/d_t$.

Remark

Suppose $\text{cf}(G, Z)$ is of the rank l , the matrix expressing the $\overline{R}(G)$ basis in terms of the $\text{cf}(G, Z) = Z^l$ basis is $\equiv^*(G)$.

Hence by theorem (3), we can find two matrices P and W with a determinant ± 1 such that $P \cdot \equiv^*(G) \cdot W = D(\equiv^*(G)) = \text{diag}\{d_1, d_2, \dots, d_l\}$,
 $d_i = \pm D_i(\equiv^*(G)) / \pm D_{i-1}(\equiv^*(G))$.

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This yield a new basis for $\overline{R}(G)$ and $cf(G, Z)$, $\{v_1, v_2, \dots, v_l\}$ and $\{u_1, u_2, \dots, u_l\}$ respectively with the property $v_j = d_j u_j$.

Hence by theorem (5) the Z -module $K(G)$ is the direct sum of cyclic sub modules with annihilating ideals $\langle d_1 \rangle, \langle d_2 \rangle, \dots, \langle d_l \rangle$.

Theorem 4.8: $K(G) = \bigoplus \sum C_{d_i}$

Such that $d_i = \pm D_i (\equiv^* (G)) / \pm D_{i-1} (\equiv^* (G))$

Theorem 4.9:

$$|K(G)| = \det(\equiv^* (G))$$

Proposition 4.10: If A and B two matrices of the degree n and m respectively, then

$$\det(A \otimes B) = (\det(A))^m \cdot (\det(B))^n$$

Proposition 4.11: Let A and B be two non-singular matrices of the rank n and m respectively, over a principal ideal domain R and let

$$P_1 A Q_1 = D(A) = \text{diag}\{d_1(A), d_2(A), \dots, d_n(A)\}$$

$$P_2 B Q_2 = D(B) = \text{diag}\{d_1(B), d_2(B), \dots, d_m(B)\}$$

be the invariant factor matrices of A and B .

Then

$$(P_1 \otimes P_2) \cdot (A \otimes B) \cdot (Q_1 \otimes Q_2) = D(A) \otimes D(B)$$

And from this we can write down the invariant factor matrix of $(A \otimes B)$.

Let H and L be P_1 -group and P_2 -group respectively, where P_1 and P_2 are distinct primes. We know that

$$\equiv (H \times L) \equiv (H) \otimes \equiv (L)$$

$(P_1, P_2) = 1$, so we have

$$\equiv^* (H \times L) \equiv^* (H) \otimes \equiv^* (L)$$

Theorem 4.12: Let H and L be P_1 -group and P_2 -group respectively, where

$(P_1, P_2) = 1$, let $\equiv^* (H)$ and $\equiv^* (L)$ be of the ranks n, m respectively.

$$K(H \times L) = \underbrace{K(H) \oplus \dots \oplus K(H)}_{m\text{-times}} \oplus \underbrace{K(L) \oplus \dots \oplus K(L)}_{n\text{-times}}$$

5- The factor group $K(C_n)$ and $K(Q_{2m})$

Proposition 5.1: The rational valued characters table of the cyclic group C_{p^s} of the rank $S+1$ where p is a prime number which is denoted by $(\equiv^* (C_{p^s}))$, is given as follows:

Γ -classes	$[1]$	$[r^{p^{s-1}}]$	$[r^{p^{s-2}}]$	$[r^{p^{s-3}}]$	\dots	$[r^{p^2}]$	$[r^p]$	$[r]$
θ_1	$p^{s-1}(p-1)$	$-p^{s-1}$	0	0	\dots	0	0	0
θ_2	$p^{s-2}(p-1)$	$p^{s-2}(p-1)$	$-p^{s-2}$	0	\dots	0	0	0
θ_3	$p^{s-3}(p-1)$	$p^{s-3}(p-1)$	$p^{s-3}(p-1)$	$-p^{s-3}$	\dots	0	0	0
\vdots	\vdots	\vdots	\vdots	\vdots	\ddots	\vdots	\vdots	\vdots
θ_{s-1}	$p(p-1)$	$p(p-1)$	$p(p-1)$	$p(p-1)$	\dots	$p(p-1)$	$-p$	0
θ_s	$p-1$	$p-1$	$p-1$	$p-1$	\dots	$p-1$	$p-1$	-1
θ_{s+1}	1	1	1	1	\dots	1	1	1

Where its rank $s+1$ represents the number of all distinct Γ -classes.

Proposition 5.2: If p is a prime number, then

$$D(\equiv^*(C_{p^s})) = \text{diag}\{p^s, p^{s-1}, \dots, p, 1\}.$$

Remark for $n = p_1^{\alpha_1} \cdot p_2^{\alpha_2} \cdot \dots \cdot p_m^{\alpha_m}$ where p_i 's are distinct primes and $\alpha_i \in \mathbb{Z}^+$, then:

$$D(\equiv^*(C_n)) = D(\equiv^*(C_{p_1}^{\alpha_1})) \otimes D(\equiv^*(C_{p_2}^{\alpha_2})) \otimes \dots \otimes D(\equiv^*(C_{p_m}^{\alpha_m}))$$

Theorem 5.3: Let p be a prime number, then:

$$K(C_{p^s}) = \bigoplus_{i=1}^s C_{p^i}$$

Lemma 5.4: The rational valued characters table of Q_{2m} when m is an odd number is given as follows:

$$\equiv^*(Q_{2m}) =$$

	Γ -classes of C_{2m}								
	x^{2r}				x^{2r+1}				$[x^k y]$
θ_1	$\equiv^*(C_m)$				$\equiv^*(C_m)$				0
\vdots									\vdots
$\theta_{(I/2)-1}$	1	1	...	1	1	1	...	1	0
$\theta_{(I/2)}$									1
$\theta_{(I/2)+1}$	$\equiv^*(C_m)$				H				0
									\vdots
θ_{I-1}	1	1	...	1	1	1	...	1	0
θ_I									-1
θ_{I+1}	2	2	...	2	-2	-2	...	-2	0

Where $0 \leq r \leq m-1$, I is the number of Γ -classes of C_{2m} , θ_j such that $1 \leq j \leq I+1$ are the rational valued characters of the group Q_{2m} and if we denoted C_{ij} the elements of $\equiv^*(C_m)$ and h_{ij} the elements of H as defined by:

$$h_{ij} = \begin{cases} C_{ij} & \text{if } i = 1 \\ -C_{ij} & \text{if } i \neq 1 \end{cases}$$

And where I is the number of Γ -classes of C_{2m} .

The Cyclic Decomposition of The Factor Group $\text{cf}(Q_{2m} \times C_2, Z) / \overline{R}(Q_{2m} \times C_2)$ When m is an Odd Number

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Theorem 5.5: If m is an odd number, then:

$$K(Q_{2m}) = K(C_{2m}) \oplus C_4$$

Theorem 5.6: The rational valued characters table of the group $Q_{2m} \times C_2$ when m is an odd number is given as follows:

$$\equiv^*(Q_{2m} \times C_2) = \equiv^*(Q_{2m}) \otimes \equiv^*(C_2)$$

Proof:-

Since

$$\equiv(C_2) =$$

And

	h_1'	h_2'
χ_1'	1	1
χ_2'	1	-1

by proposition (7),

$$\equiv^*(C_2) =$$

	h_1'	h_2'
θ_1'	1	1
θ_2'	1	-1

Then,

$$\chi_1'(h_1') = \chi_1'(h_2') = \theta_1'(h_1') = \theta_1'(h_2') = 1$$

$$\chi_2'(h_1') = \theta_2'(h_1') = 1, \chi_2'(h_2') = \theta_2'(h_2') = -1.$$

From the definition of $Q_{2m} \times C_2$, (theorem (1) and proposition(1)),

$$\equiv Q_{2m} \times C_2 = (\equiv Q_{2m}) \otimes (\equiv C_2)$$

each element in $Q_{2m} \times C_2$

$$h_{ns} = h_n \cdot h_s' \quad \forall h_n \in Q_{2m}, h_s' \in C_2 \quad n=1,2,3,\dots,4m, s=1,2$$

And each irreducible character of $Q_{2m} \times C_2$ is

$$\chi_{ij} = \chi_i \chi_j'$$

Where χ_i is an irreducible character of Q_{2m} and χ_j' is an irreducible character of C_2 , then

$$\chi_{ij}(h_{ns}) = \begin{cases} \chi_i(h_n) & \text{if } j=1 \text{ and } s=1,2 \\ \chi_i(h_n) & \text{if } j=2 \text{ and } s=1 \\ -\chi_i(h_n) & \text{if } j=2 \text{ and } s=2 \end{cases}$$

$$\text{From proposition (4.2) } \theta_{ij} = \sum_{\sigma \in \text{Gal}(\mathbb{Q}(\chi_j)/\mathbb{Q})} \sigma(\chi_{ij})$$

Where θ_{ij} is the rational valued of character table of $Q_{2m} \times C_2$

Then ,

$$\theta_{ij}(h_{ns}) = \sum_{\sigma \in \text{Gal}(\mathbb{Q}(\chi_j(h_{ns}))/\mathbb{Q})} \sigma(\chi_{ij}(h_{ns}))$$

(I) if $j=1$ and $s=1,2$

$$\theta_{ij}(h_{ns}) = \sum_{\sigma \in \text{Gal}(Q(\chi_i(h_n))/Q)} \sigma(\chi_i(h_n)) = \theta_i(h_n).1 = \theta_i(h_n).\theta'_j(h'_s)$$

Where θ_i is the rational valued character of Q_{2m} .

(II) (a) if $j=2$ and $s=1$

$$\theta_{ij}(h_{ns}) = \sum_{\sigma \in \text{Gal}(Q(\chi_i(h_n))/Q)} \sigma(\chi_i(h_n)) = \theta_i(h_n).1 = \theta_i(h_n).\theta'_j(h'_s)$$

(b) if $j=2$ and $s=2$

$$\begin{aligned} \theta_{ij}(h_{ns}) &= \sum_{\sigma \in \text{Gal}(Q(\chi_i(h_n))/Q)} \sigma(-\chi_i(h_n)) = - \sum_{\sigma \in \text{Gal}(Q(\chi_i(h_n))/Q)} \sigma(\chi_i(h_n)) \\ &= \sum_{\sigma \in \text{Gal}(Q(\chi_i(h_n))/Q)} \sigma(\chi_i(h_n)).-1 = \theta_i(h_n).-1 = \theta_i(h_n).\theta'_j(h'_s) \end{aligned}$$

From [I] and [II] we have $\theta_{ij} = \theta_i.\theta'_j$

Then $\equiv^*(Q_{2m} \times C_2) = \equiv^*(Q_{2m}) \otimes \equiv^*(C_2)$

5- The cyclic decomposition of the group $K(Q_{2m} \times C_2)$ when m is an odd number

Theorem 5.1: If m is an odd number then :

$$K(Q_{2m} \times C_2) = \bigoplus_{j=1}^2 K(Q_{2m}) \bigoplus_{i=1}^{(\alpha_1+1).(\alpha_2+1).\dots(\alpha_m+1)-1} C_4 \oplus C_8.$$

Proof:

Let H and U are matrices defining of the following :

$$H = \begin{array}{|c|c|c|c|c|c|} \hline & & & 1 & & \\ & & & 0 & & \\ & & & \vdots & & \\ & & & 0 & & \\ \hline & \mathbf{I} & & & & \\ \hline \mathbf{I} & & 1 & 0 & \dots & 0 & 0 \\ & & 0 & 0 & \dots & 0 & 0 \\ & & \vdots & & & \vdots & \vdots \\ & & 0 & \dots & \dots & 0 & 0 \\ \hline 1 & 0 & \dots & 0 & \dots & 0 & 0 \\ & & & 0 & \dots & 0 & 0 \\ \hline \end{array} \quad U = \begin{array}{|c|c|c|c|c|} \hline & & 0 & \dots & 0 & 0 \\ & & \vdots & 0 & \vdots & \vdots \\ & & 0 & \dots & 0 & 0 \\ \hline & \mathbf{I} & & & & \\ \hline \mathbf{-I} & & \mathbf{I} & & & 0 \\ & & & & & \vdots \\ & & & & & 0 \\ \hline 0 & \dots & 0 & -1 & \dots & 1 \\ \hline \end{array}$$

Such that (\mathbf{I}) is an identical matrix of degree the matrix $\equiv^*(C_m)$ and $(-\mathbf{I})$ is an identical matrix and of all their elements multiplied $(-)$ and the matrix of $\equiv^*(Q_{2m} \times C_2)$ defining by theorem (11).

$$\begin{array}{|c|c|} \hline \mathbf{H} & \mathbf{H} \\ \hline \mathbf{0} & \mathbf{-H} \\ \hline \end{array} \equiv^*(Q_{2m} \times C_2). \quad \begin{array}{|c|c|} \hline \mathbf{U} & \mathbf{0} \\ \hline \mathbf{U} & \mathbf{-U} \\ \hline \end{array} = \begin{array}{|c|c|} \hline \mathbf{E} & \mathbf{0} \\ \hline \mathbf{0} & \mathbf{F} \\ \hline \end{array}$$

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Such that E and F of degree H and U

The invariant factors of the matrix $\equiv^* (Q_{2m} \times C_2)$ it's the same invariant factors of the matrices E and F so as will the proof depending on m

The first case: if m is a prime number

$m=p$, then

$$E = \begin{bmatrix} 8 & 8 & 0 & 0 & 0 \\ 4(p-1) & -4 & 0 & 0 & 0 \\ 0 & 0 & 4 & 4 & 0 \\ 0 & 0 & 2(p-1) & -2 & 0 \\ 0 & 0 & 0 & 0 & 2 \end{bmatrix}, F = \begin{bmatrix} -4 & -4 & 0 & 0 & 0 \\ -2(p-1) & 2 & 0 & 0 & 0 \\ 0 & 0 & -2 & -2 & 0 \\ 0 & 0 & -(p-1) & 1 & 0 \\ 0 & 0 & 0 & 0 & -1 \end{bmatrix}$$

Such as $E = -2F$

And we will defined two matrices L_p and R_p , such that:

$$L_p = \begin{bmatrix} 1 & 2 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 2 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}, R_p = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ p-1 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & p-1 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

Such that

$$L_p \cdot E \cdot R_p = \text{diag}\{8p, -4, 4p, -2, 2\}$$

$$L_p \cdot F \cdot R_p = \text{diag}\{-4p, 2, -2p, 1, -1\}$$

$$\begin{aligned} K(Q_{2p} \times C_2) &= \bigoplus_{i=1}^2 K(C_{2p}) \bigoplus_{i=1}^3 C_4 \oplus C_8 \\ &= \bigoplus_{i=1}^2 K(Q_{2p}) \oplus C_4 \oplus C_8 \end{aligned}$$

The second case: if $m=p^h$ (such that p is a prime number and $p \neq 2$ and h is an integer positive number), then

$$E_{p^h} =$$

$ \begin{array}{cccccc} 8 & 8 & 8 & \dots & 8 & 8 & 8 \\ -4 & 4(p-1) & 4(p-1) & & 4(p-1) & 4(p-1) & 4(p-1) \\ 0 & -4p & 4p(p-1) & & 4p(p-1) & 4p(p-1) & 4p(p-1) \\ 0 & 0 & -4p^2 & & 4p^2(p-1) & 4p^2(p-1) & 4p^2(p-1) \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\ 0 & 0 & \dots & 0 & -4p^{k-2} & 4p^{k-2}(p-1) & 4p^{k-2}(p-1) \\ 0 & 0 & \dots & 0 & 0 & -4p^{k-1} & 4p^{k-1}(p-1) \end{array} $	$ \begin{array}{cccccc} 0 & 0 & \dots & & 0 & 0 \\ 0 & 0 & \dots & & 0 & 0 \\ \vdots & \vdots & \ddots & & \vdots & \vdots \\ \vdots & \vdots & & \ddots & \vdots & \vdots \\ 0 & 0 & \dots & \dots & 0 & 0 \end{array} $	$ \begin{array}{c} 0 \\ 0 \\ \vdots \\ \vdots \\ 0 \\ 0 \end{array} $
$ \begin{array}{cccccc} 0 & 0 & \dots & & 0 & 0 \\ 0 & 0 & \dots & & 0 & 0 \\ \vdots & \vdots & \ddots & & \vdots & \vdots \\ \vdots & \vdots & & \ddots & \vdots & \vdots \\ 0 & 0 & \dots & \dots & 0 & 0 \end{array} $	$ \begin{array}{cccccc} 4 & 4 & 4 & \dots & 4 & 4 & 4 \\ -2 & 2(p-1) & 2(p-1) & & 2(p-1) & 2(p-1) & 2(p-1) \\ 0 & -2p & 2p(p-1) & & 2p(p-1) & 2p(p-1) & 2p(p-1) \\ 0 & 0 & -2p^2 & & 2p^2(p-1) & 2p^2(p-1) & 2p^2(p-1) \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\ 0 & 0 & \dots & 0 & -2p^{k-2} & 2p^{k-2}(p-1) & 2p^{k-2}(p-1) \\ 0 & 0 & \dots & 0 & 0 & -2p^{k-1} & 2p^{k-1}(p-1) \end{array} $	$ \begin{array}{c} 0 \\ 0 \\ \vdots \\ \vdots \\ 0 \\ 0 \end{array} $
$ \begin{array}{cccccc} 0 & 0 & \dots & & 0 & 0 \end{array} $	$ \begin{array}{cccccc} 0 & 0 & \dots & & 0 & 0 \end{array} $	$ \begin{array}{c} 2 \\ 2 \end{array} $

$$F_{p^h} =$$

$ \begin{array}{ccccccc} -4 & -4 & -4 & \dots & -4 & -4 & -4 \\ 2 & -2 & (p-1) & -2 & (p-1) & -2 & (p-1) \\ 0 & 2p & -2p & (p-1) & -2p & (p-1) & -2p & (p-1) \\ 0 & 0 & 2p^2 & -2p^2 & (p-1) & -2p^2 & (p-1) & -2p^2 & (p-1) \\ \vdots & \vdots & \ddots & \ddots & \vdots & \ddots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & 0 & 2p^{i-1} & -2p^{i-1} & (p-1) & -2p^{i-1} & (p-1) \\ 0 & 0 & \dots & 0 & 0 & 2p^{i-1} & -2p^{i-1} & (p-1) & -2p^{i-1} & (p-1) \end{array} $	$ \begin{array}{ccccccc} 0 & 0 & \dots & 0 & 0 \\ 0 & 0 & \dots & 0 & 0 \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ \vdots & \vdots & \ddots & \vdots & 0 \\ 0 & 0 & \dots & \dots & 0 & 0 \end{array} $
$ \begin{array}{ccccccc} 0 & 0 & \dots & 0 \\ 0 & 0 & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & \dots & 0 \end{array} $	$ \begin{array}{ccccccc} -2 & -2 & -2 & \dots & -2 & -2 & -2 \\ 1 & -(p-1) & -(p-1) & -(p-1) & -(p-1) & -(p-1) & -(p-1) \\ 0 & p & -p(p-1) & -p(p-1) & -p(p-1) & -p(p-1) & -p(p-1) \\ 0 & 0 & p^2 & -p^2(p-1) & -p^2(p-1) & -p^2(p-1) & -p^2(p-1) \\ \vdots & \vdots & \ddots & \ddots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & 0 & p^{i-1} & -p^{i-1}(p-1) & -p^{i-1}(p-1) \\ 0 & 0 & \dots & 0 & 0 & p^{i-1} & -p^{i-1}(p-1) \end{array} $
$ \begin{array}{ccccccc} 0 & 0 & \dots & 0 \end{array} $	$ \begin{array}{ccccccc} 0 & 0 & \dots & 0 & -1 \end{array} $

Such as $E_{p^h} = -2 F_{p^h}$, For all E_{p^h} and F_{p^h} of degree $(2h+3)$, And we will defined two matrices L_{p^h} and R_{p^h} of degree $(2h+3)$, such that:

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$L_{p^h} =$

$\begin{matrix} 1 & 2 & 2 & \dots & 2 & 2 \\ 0 & 0 & 0 & \dots & 0 & -1 \\ 0 & 0 & \dots & 0 & -1 & -1 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & -1 & \dots & -1 & -1 \\ 0 & -1 & -1 & \dots & -1 & -1 \end{matrix}$	$\begin{matrix} 0 & 0 & \dots & 0 \\ 0 & 0 & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & 0 \end{matrix}$	$\begin{matrix} 0 \\ 0 \\ \vdots \\ 0 \\ 0 \end{matrix}$
$\begin{matrix} 0 & 0 & \dots & 0 \\ 0 & 0 & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & 0 \end{matrix}$	$\begin{matrix} 1 & 2 & 2 & \dots & 2 & 2 \\ 0 & 0 & 0 & \dots & 0 & -1 \\ 0 & 0 & \dots & 0 & -1 & -1 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & -1 & \dots & -1 & -1 \\ 0 & -1 & -1 & \dots & -1 & -1 \end{matrix}$	$\begin{matrix} 0 \\ 0 \\ \vdots \\ 0 \\ 0 \end{matrix}$
$\begin{matrix} 0 & 0 & \dots & 0 & 0 \end{matrix}$	$\begin{matrix} 0 & 0 & \dots & 0 & 0 \end{matrix}$	1

$R_{p^h} =$

$\begin{matrix} p^{h-1}(p-1) & 0 & 0 & \dots & 0 & -1 & 1 \\ p^{h-2}(p-1) & 0 & 0 & \dots & -1 & 1 & 0 \\ p^{h-3}(p-1) & 0 & 0 & \dots & 1 & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\ p^2(p-1) & 0 & -1 & \dots & 0 & 0 & 0 \\ p(p-1) & -1 & 1 & \dots & 0 & 0 & 0 \\ p-1 & 1 & 0 & \dots & 0 & 0 & 0 \\ 1 & 0 & 0 & \dots & 0 & 0 & 0 \end{matrix}$	$\begin{matrix} \mathbf{O} & \mathbf{O} & \dots & \dots & \mathbf{O} \\ \mathbf{O} & \mathbf{O} & \dots & \dots & \mathbf{O} \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ \mathbf{O} & \mathbf{O} & \dots & \dots & \mathbf{O} \end{matrix}$	$\begin{matrix} 0 \\ 0 \\ \vdots \\ 0 \\ 0 \end{matrix}$
$\begin{matrix} \mathbf{O} & \mathbf{O} & \dots & \dots & \mathbf{O} \\ \mathbf{O} & \mathbf{O} & \dots & \dots & \mathbf{O} \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ \mathbf{O} & \mathbf{O} & \dots & \dots & \mathbf{O} \end{matrix}$	$\begin{matrix} p^{h-1}(p-1) & 0 & 0 & \dots & 0 & -1 & 1 \\ p^{h-2}(p-1) & 0 & 0 & \dots & -1 & 1 & 0 \\ p^{h-3}(p-1) & 0 & 0 & \dots & 1 & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\ p^2(p-1) & 0 & -1 & \dots & 0 & 0 & 0 \\ p(p-1) & -1 & 1 & \dots & 0 & 0 & 0 \\ p-1 & 1 & 0 & \dots & 0 & 0 & 0 \\ 1 & 0 & 0 & \dots & 0 & 0 & 0 \end{matrix}$	$\begin{matrix} 0 \\ 0 \\ \vdots \\ 0 \\ 0 \end{matrix}$
$\begin{matrix} 0 & 0 & \dots & \dots & 0 & 0 \end{matrix}$	$\begin{matrix} 0 & 0 & \dots & \dots & 0 & 0 \end{matrix}$	1

Such that

$$\begin{aligned} L_p^h \text{ .E. } R_p^h &= \text{diag}\{8p^h, 4p^{h-1}, 4p^{h-2}, \dots, 4p, 4, 4p^h, 2p^{h-1}, 2p^{h-2}, \dots, 2p, 2, 2\} \\ L_p^h \text{ .F. } R_p^h &= \text{diag}\{-4p^h, -2p^{h-1}, -2p^{h-2}, \dots, -2p, -2, -2p^h, -p^{h-1}, -p^{h-2}, \dots, -p, -1, -1\} \end{aligned}$$

$$\begin{aligned} K(\mathbb{Q}_{2p^h} \times \mathbb{C}_2) &= \bigoplus_{i=1}^2 K(\mathbb{C}_{2p^h}) \bigoplus_{i=1}^{h+2} \mathbb{C}_4 \oplus \mathbb{C}_8 \\ &= \bigoplus_{i=1}^2 K(\mathbb{Q}_{2p^h}) \bigoplus_{i=1}^h \mathbb{C}_4 \oplus \mathbb{C}_8 \end{aligned}$$

The third case: if $m = \prod_{i=1}^r p_i^{\alpha_i}$ (such that p_i is a prime numbers and $p_i \neq 2$ and α_i is an integer positive numbers), then

$$\equiv *(C_m) \equiv *(C_{p_1^{\alpha_1}}) \otimes \equiv *(C_{p_2^{\alpha_2}}) \otimes \dots \otimes \equiv *(C_{p_r^{\alpha_r}})$$

By the proposition (6) the two matrices R_1 and L_1 take the following form:

$$R_1 = R_{p_1^{a_1}} \otimes R_{p_2^{a_2}} \otimes \cdots \otimes R_{p_r^{a_r}}$$

$$L_1 = L_{p_1^{a_1}} \otimes L_{p_2^{a_2}} \otimes \cdots \otimes L_{p_r^{a_r}}$$

Lead to make $\equiv^*(C_m)$ diagonal matrix

Such that these two matrices $R_{p_i^{a_i}}$ and $L_{p_i^{a_i}}$ diagonal the matrix $\equiv^*(C_{p_i^{a_i}})$ for all $i = 1, 2, \dots, r$

Let R, L these two matrices diagonal the two matrices E and F

$L_2 = (\ell_{ij})$ and $L_1 = (L_{ij})$ the elements of matrix L_2 defining as following:

$$(\ell_{ij}) = \begin{cases} L_{ij} & \text{if } (i \neq 1) \quad \vee \quad (i = 1 \wedge j = 1) \\ 2L_{ij} & \text{if } (i = 1) \quad \wedge \quad j \neq 1 \end{cases}$$

Then,

$$L = \begin{array}{|c|c|c|} \hline L_2 & \begin{matrix} 0 & \cdots & 0 \\ \vdots & 0 & \vdots \\ 0 & \cdots & 0 \end{matrix} & \begin{matrix} 0 \\ \vdots \\ 0 \end{matrix} \\ \hline \begin{matrix} 0 & \cdots & 0 \\ \vdots & 0 & \vdots \\ 0 & \cdots & 0 \end{matrix} & L_2 & \begin{matrix} 0 \\ \vdots \\ 0 \end{matrix} \\ \hline \begin{matrix} 0 & \cdots & 0 \\ 0 & \cdots & 0 \end{matrix} & \begin{matrix} 0 & \cdots & 0 \\ 0 & \cdots & 0 \end{matrix} & \begin{matrix} 1 \\ 1 \end{matrix} \\ \hline \end{array}, \quad R = \begin{array}{|c|c|c|} \hline R_1 & \begin{matrix} 0 & \cdots & 0 \\ \vdots & 0 & \vdots \\ 0 & \cdots & 0 \end{matrix} & \begin{matrix} 0 \\ \vdots \\ 0 \end{matrix} \\ \hline \begin{matrix} 0 & \cdots & 0 \\ \vdots & 0 & \vdots \\ 0 & \cdots & 0 \end{matrix} & R_1 & \begin{matrix} 0 \\ \vdots \\ 0 \end{matrix} \\ \hline \begin{matrix} 0 & \cdots & 0 \\ 0 & \cdots & 0 \end{matrix} & \begin{matrix} 0 & \cdots & 0 \\ 0 & \cdots & 0 \end{matrix} & \begin{matrix} 1 \\ 1 \end{matrix} \\ \hline \end{array}$$

$$L \cdot \equiv^*(Q_{2m} \times C_2) \cdot R = \begin{array}{|c|c|} \hline E & \begin{matrix} 0 & \cdots & 0 \\ \vdots & 0 & \vdots \\ 0 & \cdots & 0 \end{matrix} \\ \hline \begin{matrix} 0 & \cdots & 0 \\ \vdots & 0 & \vdots \\ 0 & \cdots & 0 \end{matrix} & F \\ \hline \end{array}$$

From the preceding two cases we observe if the invariant factors of the matrix $\equiv^*(C_m)$ is $\{d_1, d_2, \dots, d_r\}$ then the invariant factors of the matrix E is $\{8d_1, 4d_2, \dots, 4d_r, 4d_1, 2d_2, \dots, 2d_r, 2\}$ and the invariant factors of the matrix F is $\{4d_1, 2d_2, \dots, 2d_r, 2d_1, d_2, \dots, d_r, 1\}$ and since the invariant factors of the matrix $\equiv^*(Q_{2m} \times C_2)$ is the sum the invariant factors of the two matrices E and F .

$$\begin{aligned} \text{Then, } K(Q_{2m} \times C_2) &= \bigoplus_{i=1}^2 K(C_{2m}) \bigoplus_{i=1}^{(\alpha_1+1)(\alpha_2+1)\dots(\alpha_r+1)+1} C_4 \oplus C_8 \\ &= \bigoplus_{i=1}^2 K(Q_{2m}) \bigoplus_{i=1}^{(\alpha_1+1)(\alpha_2+1)\dots(\alpha_r+1)-1} C_4 \oplus C_8 \end{aligned}$$

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Homogeneous Balance Method for Solving Nonlinear Dispersive Dissipative Equation

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الخلاصة

في هذا البحث جرى استخدام طريقة الموازنة المتجانسة بمساعدة حل معادلة ريكانا وذلك لايجاد حل جديد مضبوط للصيغة العامة لمعادلة التبدد غير الخطية , من خلال حل المعادلة الاعتيادية غير الخطية المخفضة لها , وقد تم ايجاد حلول جديدة لبعض المعادلات غير الخطية التي لها علاقة بهذه المعادلة مثل (KdV) و (MKdV) ومقارنة النتائج التي حصلنا عليها.

ABSTRACT

In this paper, we use homogeneous balance method to construct new exact traveling wave solutions of nonlinear dispersive dissipative equation , in which the homogeneous balance method is applied to solve the Riccati equation and the reduced nonlinear ordinary differential equation . Many new exact traveling wave solution for some nonlinear partial differential equation that are related to nonlinear dispersive dissipative equation for example (KdV) and (MKdV) equations and then a comparison of the results are presented.

INTRODUCTION

The investigation of the exact travelling wave solutions of nonlinear partial differential equations plays an important role in the study of nonlinear physical phenomena [11]. Various methods have been utilized to explore different kinds of solutions of physical models described by nonlinear partial differential equations [5]. Nonlinear wave phenomena of dispersion, dissipation, diffusion, reaction and convection are very important in nonlinear wave equations [16]. Some various method for obtaining exact solutions of nonlinear partial differential equations have been presented, such as inverse scattering method, direct algebraic method, tanh function method linearized perturbation technique, the rational expansion method and so on [6]. The homogeneous balance method is one of the important technique for finding exact travelling wave solutions, such as some nonlinear partial differential equations are solved by this method Calogero Degasperis (CD) and Potential Kadomstev-Petviashvili (PKP) equations were solved by Yusufoglu in 2007 [5], the (2+1) dimensional Zakharov Kuznetsov (ZK) equation was solved by Mohammed in 2007[11], one dimensional Burgers, KdV-Burgers, Coupled Burgers and two dimensional Burgers equations were solved by A. A. Soliman in 2008 [1],

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the generalized Hirota-Satsuma coupled KdV system with variable coefficients was solved by Moussa in 2009 [10], equal width wave equation was solved by Taghizadeh in 2010 [17], and Selective nonlinear diffusion-reaction equations was solved by Ranjit Kumer in 2010 [18]. The solutions of the nonlinear dispersive dissipative equation possess their actual physical application, this is the reason why so many methods have been applied to obtain exact solutions of the nonlinear dispersive dissipative equation [19].

In recent years, Wang and Khalafallah used a useful homogeneous balance (HB) method for finding exact solutions of a given nonlinear partial differential equations. Fan used HB method to search for backlund transformation and similarity reduction of nonlinear partial differential equations [17]. Fan showed that there is a close connection among the HB method, Weiss, Tabor, Carnevale (WTC) method and Clarkson, Kruskal (CK) method [8].

In this paper, we used homogeneous balance method to construct more general exact solutions of the nonlinear dispersive dissipative equation and some equations which have relation with this equation such as (KdV) and (MKdV). The rest of this paper is organized as follows : in section (2), the algorithm of finding exact solution for nonlinear partial differential equation by using homogeneous balance method is presented . In section(3), we introduce the application of this method for solving nonlinear dispersive dissipative equation, KdV and MKdV equations. Finally, in the fourth section some conclusions are given.

Algorithm for finding exact solutions by using homogeneous balance method

We will summarize the main steps for using homogeneous balance method as following :

Step (1) : Suppose that $u(x,t) = u(\zeta)$, where $\zeta = x - \beta t$ for a given nonlinear partial differential equation :

$$F(u, u_t, u_x, u_{tt}, u_{tx}, u_{xx}, \dots) = 0 \quad \dots(1)$$

Then equation (1) is reduced to nonlinear ordinary differential equation :

$$G(u, u', u'', u''', \dots) = 0 \quad , \quad / = \frac{d}{d\zeta} \quad \dots(2)$$

Such that u in the form :

$$u(\zeta) = \sum_{i=0}^m q_i \varphi^i(\zeta) \quad \dots(3)$$

where φ satisfies the Riccati equation :

$$\varphi' = a\varphi^2 + b\varphi + c, \quad a \neq 0 \quad \dots(4)$$

and $q_i (i=0,1,2,\dots,m)$, a, b and c are real constants.

Step(2) : Integrate the ordinary differential equation (2) once or twice if the higher order of the derivative is odd or even respectively and put the constants of integration to be zero.

Step(3) : Determine the value of m by balancing the highest order of the derivative for linear term and highest order of nonlinear term in the integrating equation.

Step(4) : Substitute equation (3) and (4) into integrating equation .

Step(5) : Equat the coefficients of the powers of φ^i to zero to give an algebraic system of equations then solve this system such that simple solutions of Riccati equation yield as follows :

Case (1) : When $\Delta = b^2 - 4ac > 0$:

$$\varphi_1 = \frac{-b}{2a} + \left(\frac{\sqrt{\Delta}}{2a} \right) \left(\frac{1+e^{\sqrt{\Delta}\zeta}}{1-e^{\sqrt{\Delta}\zeta}} \right) \quad \dots(5)$$

Case (2) : When $\Delta = b^2 - 4ac = 0$:

$$\varphi_2 = \frac{-b}{2a} - \frac{1}{a\zeta} \quad \dots(6)$$

Case (3) : When $\Delta = b^2 - 4ac < 0$:

$$\varphi_3 = \frac{-b}{2a} + \frac{\sqrt{-\Delta}}{2a} \tan \left(\frac{\sqrt{-\Delta}}{2} \zeta \right), \quad \left| \frac{\sqrt{-\Delta}}{2} \zeta \right| < \frac{\pi}{2} \quad \dots(7)$$

Or

$$\varphi_4 = \frac{-b}{2a} - \frac{\sqrt{-\Delta}}{2a} \cot \left(\frac{\sqrt{-\Delta}}{2} \zeta \right), \quad 0 < \frac{\sqrt{-\Delta}}{2} \zeta < \pi \quad \dots(8)$$

Applications :

In order to illustrate the effectiveness of the proposed method , the nonlinear dispersive dissipative equation ,KdV and MKdV are chosen as follows :

1- Nonlinear dispersive dissipative equation:

Consider the nonlinear dispersive dissipative equation of the form [6]:

$$u_t + uu_x + \alpha u_{xxx} - \gamma (u + \mu uu_x)_x = 0, \quad \alpha \neq 0, \mu \neq 0, -1, \quad x \in \mathbb{R}, \quad t > 0 \quad \dots(9)$$

If $\gamma = 0$, the equation (9) will be KdV equation :

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$$u_t + uu_x + \alpha u_{xxx} = 0 \quad \dots(10)$$

The KdV equation is a models of a variety of nonlinear phenomena , including ion acoustic waves in plasmas , and shallow water waves , the derivatives u_t characterizes the time evolution of the wave propagating in one direction ,the nonlinear term uu_x describes the steepening of the wave and the linear term u_{xxx} accounts for the spreading or dispersion of the wave [20] .To solve this equation by using homogeneous method, use step (1) of algorithm, and suppose that :

$$u(x,t) = u(\zeta) \text{ where } \zeta = x - \beta t \quad \dots(11)$$

Substitute equation (11) into equation (10) ,gives :

$$-\beta u' + uu' + \alpha u''' = 0 \quad \dots(12)$$

Integrating equation (12) once and put the constants of the integrating to be zero , we obtain :

$$-\beta u + \frac{1}{2} u^2 + \alpha u'' = 0 \quad \dots(13)$$

By using step (3) of algorithm , balancing u^2 , u'' , gives $m = 2$. Hence :

$$u(\zeta) = \sum_{i=0}^2 q_i \varphi^i = q_0 + q_1 \varphi + q_2 \varphi^2 \quad \dots(14)$$

From equation (4) and (14) , we obtain :

$$u' = q_1 a \varphi^2 + q_1 b \varphi + q_1 c + 2a q_2 \varphi^3 + 2q_2 b \varphi^2 + 2q_2 c \varphi$$

$$u'' = 2a^2 q_1 \varphi^3 + 3a q_1 b \varphi^2 + 2a q_1 c \varphi + b^2 q_1 \varphi + b c q_1 + 6a^2 q_2 \varphi^4 + 10a q_2 b \varphi^3 + 8a q_2 c \varphi^2 + 4q_2 b^2 \varphi^2 + 6q_2 b c \varphi + 2q_2 c^2 \quad \dots(15)$$

Substituting equation (14) and (15) into equation (13) , we have :

$$\begin{aligned} & -\beta q_0 - \beta q_1 \varphi - \beta q_2 \varphi^2 + \frac{1}{2} [q_0^2 + 2q_0 q_1 \varphi + 2q_0 q_2 \varphi^2 + q_1^2 \varphi^2 + 2q_1 q_2 \varphi^3 + q_2^2 \varphi^4] + \alpha \\ & [2a^2 q_1 \varphi^3 + 3a q_1 b \varphi^2 + 2a q_1 c \varphi + b^2 q_1 \varphi + b c q_1 + 6a^2 q_2 \varphi^4 + 10a q_2 b \varphi^3 + \\ & 8a c q_2 \varphi^2 + 4b^2 q_2 \varphi^2 + 6q_2 b c \varphi + 2q_2 c^2] = 0 \quad \dots(16) \end{aligned}$$

Equating the coefficient of the powers of φ^i to zero , we have :

$$\varphi^0 : -\beta q_0 + \frac{1}{2} q_0^2 + \alpha b c q_1 + 2\alpha q_2 c^2 = 0 \quad \dots(17)$$

$$\varphi^1 : -\beta q_1 + q_0 q_1 + 2a\alpha q_1 c + \alpha b^2 q_1 + 6\alpha q_2 b c = 0 \quad \dots(18)$$

$$\varphi^2: -\beta q_2 + q_0 q_2 + \frac{1}{2} q_1^2 + 3a\alpha q_1 b + 8ac\alpha q_2 + 4b^2\alpha q_2 = 0 \dots(19)$$

$$\varphi^3: q_1 q_2 + 2a^2\alpha q_1 + 10a\alpha q_2 b = 0 \dots(20)$$

$$\varphi^4: \frac{1}{2} q_2^2 + 6a^2\alpha q_2 = 0 \dots(21)$$

From equation (21), we obtain :

$$q_2 = -12 a^2 \alpha, \alpha \neq 0 \dots(22)$$

From equation (20), we have :

$$q_1 = -12 ab \alpha \dots(23)$$

From equation (19), gives :

$$q_0 = \beta - 13 b^2 \alpha - 8ac\alpha \dots(24)$$

From equation (18), we obtain $b = 0$.

$$\text{Hence } q_1 = 0, \quad q_0 = \beta - 8ac\alpha \dots(25)$$

From equation (17), we have :

$$\beta = \mp (4ac) \dots(26)$$

Case (1) : The exponential solutions :

$$u_1 = (\beta - 8ac\alpha) + (-12a^2\alpha) \left[\left(\frac{\sqrt{\beta}}{2a} \right) \left(\frac{1 + e^{\sqrt{\beta}(x-\beta t)}}{1 - e^{\sqrt{\beta}(x-\beta t)}} \right) \right]^2 \dots(27)$$

Case (2) : The rational solutions :

$$u_2 = \frac{-12\alpha}{x^2} \dots(28)$$

Case (3) : The periodic solutions :

$$u_3 = (\beta - 8ac\alpha) + (-12a^2\alpha) \left[\frac{\sqrt{-\beta}}{2a} \tan \left(\frac{\sqrt{-\beta}}{2} (x - \beta t) \right) \right]^2$$

$$\left| \frac{\sqrt{-\beta}}{2} (x - \beta t) \right| < \frac{\pi}{2} \dots(29)$$

Or

$$u_4 = (\beta - 8ac\alpha) + (-12a^2\alpha) \left[-\frac{\sqrt{-\beta}}{2a} \cot \left(\frac{\sqrt{-\beta}}{2} (x - \beta t) \right) \right]^2,$$

$$0 < \frac{\sqrt{-\beta}}{2} (x - \beta t) < \pi \dots(30)$$

If $\beta = -4ac$, then we have the periodic solutions only.

The homogeneous balance method which used in this paper allowed us to find exact solutions and different from those solutions which have obtained by Jie in [7].

Then if $\gamma \neq 0$ in equation (9), suppose $u(x,t) = u(\zeta)$, where $\zeta = x - \beta t$, then equation (9) converts to the ordinary differential equation:

$$-\beta u' + uu' + \alpha u''' - \gamma (-\beta u' + \mu uu') = 0 \quad \dots(31)$$

Integrating equation (31) and put the constants of integration to be zero, we have :

$$-\beta u + \frac{1}{2}u^2 + \alpha u'' - \gamma \beta u' - \gamma \mu uu' = 0 \quad \dots(32)$$

By using step (3) of algorithm, balancing u'' , uu' we obtain :

$m + 2 = m + m + 1 \longrightarrow m = 1$, hence :

$$u(\zeta) = \sum_{i=0}^1 q_i \phi^i = q_0 + q_1 \phi \quad \dots(33)$$

From equation (4) and (33) we obtain :

$$u' = q_1 a \phi^2 + q_1 b \phi + q_1 c$$

$$u'' = 2q_1 a^2 \phi^3 + 3q_1 ab \phi^2 + 2q_1 ac \phi + q_1 b^2 \phi + q_1 bc \quad \dots(34)$$

Substituting equation (33) and (34) into equation (32), gives :

$$\begin{aligned} & -\beta q_0 - \beta q_1 \phi + \frac{1}{2} (q_0^2 + 2q_0 q_1 \phi + q_1^2 \phi^2) + \alpha (2q_1 a^2 \phi^3 + 3q_1 ab \phi^2 \\ & + 2q_1 ac \phi + q_1 b^2 \phi + q_1 bc) - \gamma \beta q_1 a \phi^2 - \gamma \beta q_1 b \phi - \gamma \beta q_1 c \\ & - \gamma \mu [q_0 q_1 a \phi^2 + q_0 q_1 b \phi + q_0 q_1 c + q_1^2 a \phi^3 + q_1^2 b \phi^2 + q_1^2 c \phi] = 0 \quad \dots (35) \end{aligned}$$

Equating the coefficients of the powers of ϕ^i to zero, we have :

$$\phi^0: -\beta q_0 + \frac{1}{2} q_0^2 + \alpha q_1 bc - \gamma \beta q_1 c - \gamma \mu q_0 q_1 c = 0 \quad \dots(36)$$

$$\begin{aligned} \phi^1: & -\beta q_1 + q_0 q_1 + 2\alpha q_1 ac + \alpha q_1 b^2 - \gamma \beta q_1 b - \gamma \mu q_0 q_1 b \\ & - \gamma \mu q_1^2 c = 0 \quad \dots(37) \end{aligned}$$

$$\phi^2: \frac{1}{2} q_1^2 + 3\alpha q_1 ab - \gamma \beta q_1 a - \mu \gamma q_0 q_1 a - \gamma \mu q_1^2 b = 0 \quad \dots(38)$$

$$\phi^3: 2\alpha q_1 a^2 - \mu \gamma q_1^2 a = 0 \quad \dots(39)$$

From equation (39), gives :

$$q_1 = \frac{2\alpha a}{\gamma\mu}, \mu, \gamma \neq 0 \quad \dots(40)$$

From equation (38), we obtain :

$$q_0 = \frac{\alpha + \alpha b \mu \gamma - \beta \gamma^2 \mu}{\mu^2 \gamma^2} \quad \dots(41)$$

From equation (37), we have :

$$\beta = \frac{\alpha}{\mu \gamma^2 (\mu + 1)}, \mu \neq -1 \quad \dots(42)$$

Or

$$\gamma^2 = \frac{\alpha}{\mu \beta (\mu + 1)}, \mu \neq -1 \quad \dots(43)$$

From equation (36), gives :

$$\Delta = (b^2 - 4ac) = \frac{1}{\gamma^2 (\mu + 1)^2}, \mu \neq -1, \gamma \neq 0 \quad \dots(44)$$

$$\Delta = (b^2 - 4ac) = \frac{\mu \beta}{\alpha (\mu + 1)}, \mu \neq -1, \alpha \neq 0 \quad \dots(45)$$

Case (1) : If $\Delta > 0$ gives exponential solutions as follows :

$$u_1 = \frac{\alpha + \alpha b \mu \gamma - \beta \gamma^2 \mu}{\mu^2 \gamma^2} + \frac{2\alpha a}{\mu \gamma} \left[\frac{-b}{2a} + \left(\frac{\sqrt{\frac{\mu \beta}{\alpha (\mu + 1)}}}{2a} \right) \left(\frac{1 + \frac{\sqrt{\frac{\mu \beta}{\alpha (\mu + 1)}} (x - \beta t)}{e}}{1 - \frac{\sqrt{\frac{\mu \beta}{\alpha (\mu + 1)}} (x - \beta t)}{e}} \right) \right] \quad \dots(46)$$

Case (2) : If $\Delta = 0$, gives rational solutions as follows :

$$u_2 = \frac{\alpha + \alpha b \mu \gamma - \beta \gamma^2 \mu}{\mu^2 \gamma^2} + \frac{2\alpha a}{\mu \gamma} \left(\frac{-b}{2a} - \frac{1}{ax} \right) \quad \dots(47)$$

Case (3) : If $\Delta < 0$, gives periodic solutions as follows :

$$u_3 = \frac{\alpha + \alpha b \mu \gamma - \beta \gamma^2 \mu}{\mu^2 \gamma^2} + \frac{2\alpha a}{\mu \gamma} \left(\frac{-b}{2a} + \frac{\sqrt{\frac{-\mu \beta}{\alpha (\mu + 1)}}}{2a} \tan \left(\frac{\sqrt{\frac{-\mu \beta}{\alpha (\mu + 1)}}}{2} (x - \beta t) \right) \right) \quad \dots(48)$$

$$\left| \sqrt{\frac{-\mu \beta}{\alpha (\mu + 1)}} (x - \beta t) \right| < \frac{\pi}{2}$$

Or

$$u_t = \frac{\alpha + ab\mu\gamma - \beta\gamma^2\mu}{\mu^2\gamma^2} + \frac{2\alpha a}{\mu\gamma} \left(\frac{-b}{2a} - \frac{\sqrt{-\mu\beta}}{2a} \cot \left(\frac{\sqrt{-\mu\beta}}{2} (x - \beta t) \right) \right)$$

$$0 < \sqrt{\frac{-\mu\beta}{\alpha(\mu+1)}} (x - \beta t) < \pi \quad \dots (49)$$

These solutions which we obtain above are new , more general and different from those solutions which obtained by Guoliang in [6] .

2- The (1+1) dimensional nonlinear dispersive equation :

Consider the general form of (1+1) dimensional nonlinear dispersive equation [20] in the form :

$$u_t - \alpha u^2 u_x + u_{xxx} = 0 \quad \dots (50)$$

where α is a nonzero positive constant . This equation is called modified KdV equation , which arises in the process of understanding the role of nonlinear dispersion and in the formation of structures like liquid drops , and it exhibits compaction , soliton with compact support [4] . To solve this equation, suppose that :

$$u(x,t) = u(\zeta) \text{ where } \zeta = x - \beta t \quad \dots (51)$$

Substitute equation (51) into equation (50), gives the ordinary differential equation:

$$-\beta u' - \alpha u^2 u' + u''' = 0 \quad \dots (52)$$

integrating equation (52) , once and put the constants of integration to be zero , gives :

$$-\beta u - \frac{\alpha}{3} u^3 + u'' = 0 \quad \dots (53)$$

Now , balance u^3, u'' to give $m = 1$. Hence

$$u(\zeta) = \sum_{i=0}^1 q_i \varphi^i = q_0 + q_1 \varphi, q_i \neq 0 \quad \dots (54)$$

substitute equation (54) and (34) into equation (53) , we obtain :

$$-\beta (q_0 + q_1 \varphi) - \frac{\alpha}{3} [q_0^3 + 3q_0^2 q_1 \varphi + 3q_0 q_1^2 \varphi^2 + q_1^3 \varphi^3] + 2q_1 a^2 \varphi^3 + 3q_1 ab \varphi^2 + 2q_1 ac \varphi + q_1 b^2 \varphi + q_1 bc = 0 \quad \dots (55)$$

equating the coefficients powers of φ^i to zero , gives :

$$\varphi^0: -\beta q_0 - \frac{\alpha}{3} q_0^3 + q_1 bc = 0 \quad \dots(56)$$

$$\varphi^1: -\beta q_1 - \alpha q_0^2 q_1 + 2 q_1 ac + q_1 b^2 = 0 \quad \dots(57)$$

$$\varphi^2: -\alpha q_0 q_1^2 + 3 q_1 ab = 0 \quad \dots(58)$$

$$\varphi^3: \frac{-\alpha}{3} q_1^3 + 2 q_1 a^2 = 0 \quad \dots(59)$$

From equation (59) , we have :

$$q_1 = \mp \sqrt{\frac{6}{\alpha}} a \quad \dots(60)$$

From equation (58) , gives :

$$q_0 = \frac{b}{2} \sqrt{\frac{6}{\alpha}} \quad \dots(61)$$

From equation (57) , we obtain :

$$-2\beta = (b^2 - 4ac) = \Delta \quad \dots(62)$$

Equation (56) is vanished identically.

Case (1) : If $\Delta = b^2 - 4ac > 0$, gives the exponential solutions as follows :

$$u_1 = \frac{b}{2} \sqrt{\frac{6}{\alpha}} + \left(\sqrt{\frac{6}{\alpha}} a \right) \left[\frac{-b}{2a} + \left(\frac{\sqrt{-2\beta}}{2a} \right) \left(\frac{1 + e^{\sqrt{-2\beta}(x-\beta t)}}{1 - e^{\sqrt{-2\beta}(x-\beta t)}} \right) \right] \quad \dots(63)$$

Case (2) : If $\Delta = b^2 - 4ac = 0$, gives the rational solutions as follows :

$$u_2 = -\sqrt{\frac{6}{\alpha}} \left(\frac{1}{x} \right) , \alpha \neq 6 \quad \dots(64)$$

if $\alpha = 6$, then $u = \frac{-1}{x}$ which is the trivial solution .

Case (3) : If $\Delta = b^2 - 4ac < 0$, gives the periodic solutions as follows :

$$u_3 = \frac{b}{2} \sqrt{\frac{6}{\alpha}} + \left(\sqrt{\frac{6}{\alpha}} a \right) \left[\frac{-b}{2a} + \frac{\sqrt{2\beta}}{2a} \tan \left(\frac{\sqrt{2\beta}}{2} (x - \beta t) \right) \right]$$

Where

$$\left| \frac{\sqrt{2\beta}}{2} (x - \beta t) \right| < \frac{\pi}{2} \quad \dots(65)$$

or

$$u_4 = \frac{b}{2} \sqrt{\frac{6}{\alpha}} + \left(\sqrt{\frac{6}{\alpha}} a \right) \left[\frac{-b}{2a} - \frac{\sqrt{2\beta}}{2a} \cot \left(\frac{\sqrt{2\beta}}{2} (x - \beta t) \right) \right]$$

Where

$$0 < \frac{\sqrt{2\beta}}{2} (x - \beta t) < \pi \quad \dots(66)$$

The method used in this paper is straightforward and give exact and general solutions such that the solutions which we obtain above are different from those solutions which obtained by Elsayed in [4].

CONCLUSION

In this paper , we have new exact solutions of the nonlinear dispersive – dissipative , KdV and MKdV equations by using homogeneous balance method then we noted three important points as follows :

First : The value of m will be determine by balancing the highest order derivative of the linear term with the highest order of the nonlinear term, and we remarkable the value of m of nonlinear dispersive dissipative and MKdV are equal (such that it is equal to one) .

Second : This method is more usually used in the case where the odd and even partial differential terms exist simultaneously but the other methods don't used if its exist for example modified F-expansion method , and cosine method etc.

Third : The properties of the shapes in the solution which we obtain by this method new and more general such as of the form exponential solutions , rational solutions and periodic solutions .

This method is straightforward and concise , and it is a powerful method for applying to other nonlinear partial differential equations to find exact solutions.

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Strongly S-Prime Submodules

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الخلاصة

في هذا البحث درسنا المقاسات الجزئية الأولية من النمط S-القوية. كذلك العديد من النتائج أعطيت لتبين العلاقات بين هذا النمط من المقاسات الجزئية مع المقاسات الجزئية المتعلقة به.

ABSTRACT

In this paper we study strongly S-prime submodules. Also several results are given to show the relationships between these classes of submodules and other related concepts.

INTRODUCTION

Let R be a commutative ring with unity and let M be an R -module. A proper submodule N of M is called prime if whenever $r \in R \setminus \{0\}$, $m \in M$, $rm \in N$ implies $m \in N$ or $r \in [N:M]$ where $[N:M] = \{r \in R : rM \subseteq N\}$, [1]. A proper submodule N of M is called S-prime if whenever $f \in \text{END}(M)$, $m \in M$, $f(m) \in N$ implies $m \in N$ or $f(M) \subseteq N$, [2]. Also in [3] studied S-prime submodule. Every S-prime submodule is prime submodule but not conversely, [2], [3]. A proper submodule N of an R -module M is called strongly prime if whenever $r \neq 0$, $r \in R$, $m \in M$, $rm \in N$ implies $m \in N$, [4]. It follows that every strongly prime submodule is prime, but not conversely, [4]. G.Giingoroglu in [2] gave the following definition: a proper submodule N of M is called S-strongly prime if whenever $f \in \text{End}(M)$ $m \in M$ such that $f(m) \in N$ implies $m \in N$. In fact he must say that f is a nonzero mapping. We shall call such submodule strongly S-prime because these class of submodules includes the class of S-prime submodule, moreover we show that this class of submodule is independent with the class of strongly prime submodules.

Our aim is to investigate strongly S-prime submodules. Some interset results are obtained such as a prime multiplication module is quasi-Dedekind (see, Cor.1.5).

1- Basic Properties of Strongly S-Prime Submodules

In this section, we give some basic results about strongly S-prime submodule. Also, we study the behaviour of strongly S-prime submodules in certain class of modules.

Definition 1.1: [4]

A proper submodule N of an R -module M is called strongly S-prime if whenever $f \in \text{End}(M)$, $f \neq 0$, $m \in M$ such that $f(m) \in N$ implies $m \in N$.

Remarks and Examples 1.2:

1- It is clear that every strongly S-prime submodule is S-prime. The converse is not true as the following example shows.

If $N = (\bar{2}) \subseteq Z_4$, N is S-prime, [3].

However, define $f: Z_4 \longrightarrow Z_4$ by $f(\bar{x}) = 2\bar{x}$, $\forall \bar{x} \in Z_4$. It is clear that $f \neq 0$ and $f(\bar{1}) = \bar{2} \in N$, but $1 \notin N$. Thus N is not strongly S-prime.

2- If M is a simple R -module, then (0) is strongly S-prime submodule. For this, let $f \in \text{End}(M)$, $f \neq 0$, $m \in M$ such that $f(m) = 0$. Suppose $m \neq 0$, then $\langle m \rangle = M$ and so $f(M) = 0$ which is a contradiction.

3- The concepts strongly S-prime submodule and strongly prime submodule are different, as these examples show.

a- Let $M = Z \oplus Z$ as Z -module, $N = \{0\} \oplus Z$. Let $r \in Z$, $r \neq 0$. If $(a,b) \in Z \oplus Z$ such that $r(a,b) \in \{0\} \oplus Z$, then $ra = 0$, so $a = 0$. Thus $(a,b) \in \{0\} \oplus Z$. Thus N is strongly prime. But N is not strongly S-prime, for this, let $f: M \longrightarrow M$ defined by $f(a,b) = (0,b)$ for all $(a,b) \in M$. Hence $f(1,2) = (0,2) \in N$ but $(1,2) \notin N$.

b- $(\bar{0})$ in the simple Z -module Z_p (p is prime) is strongly S-prime by part (2). But It is not strongly prime, since $p \cdot \bar{1} = \bar{0}$, but $\bar{1} \notin (\bar{0})$.

4- Let $N < M$. N (as R -submodule of M) is strongly S-prime iff N (as $\bar{R} = R/\text{ann}M$ -submodule of M) is strongly S-prime.

5- Z_{p^∞} as Z -module has no strongly S-prime submodule because it has no prime submodule.

Recall that a nonzero module M is called quasi-Dedekind if $\text{Hom}(\frac{M}{N}, M) = 0$ for all nonzero submodule of M . Equivalently, M is quasi-Dedekind if for any $f \in \text{End}(M)$, $f \neq 0$, then $\ker f = \{0\}$ (i.e. f is 1-1), [5].

Proposition 1.3:

Let M be a nonzero R -module. The following statements are equivalent:

- 1- M is quasi-Dedekind
- 2- $\{0\}$ is strongly S-prime
- 3- $\{0\}$ is S-prime.

Proof: $1 \Rightarrow 2$ Let $f \in \text{End}(M)$, $f \neq 0$, $m \in M$. If $f(m) \in \{0\}$, that is $f(m) = 0$. Hence $m = 0$, since M is quasi-Dedekind.

$2 \Rightarrow 3$ It is clear.

$3 \Rightarrow 1$ Let $f \in \text{End}(M)$, and $f \neq 0$. If $f(m) = 0$. Since (0) is S-prime, then $m = 0$ or $f(M) \subseteq \{0\}$ (i.e. $f = 0$). But $f \neq 0$, so $m = 0$, that is M is quasi-Dedekind.

Notes 1.4:

1- By Prop. 1.3, we have S-prime modules equivalent to quasi-Dedekind, where an R-module is S-prime if $\{0\}$ is S-prime submodule, [3].

2- $\{0\}$ is the only strongly S-prime submodule of Q . Notice that it is well-known that Q as Z -module is quasi-Dedekind. So $\{0\}$ is strongly S-prime by prop. 1.3. But Q has no nontrivial prime submodule, so Q has no nontrivial strongly S-prime.

Recall that an R-module M is called multiplication if for each $N \leq M$, there exists an ideal I of R such that $N = IM$. Equivalently, M is multiplication if for each $N \leq M$, $N = [N:M]M$, [6].

Corollary 1.5:

Let M be a nonzero multiplication R-module. Then the following statements are equivalent:

- 1- M is quasi-Dedekind.
- 2- $\{0\}$ is strongly S-prime.
- 3- $\{0\}$ is S-prime.
- 4- $\{0\}$ is prime (that is; M is a prime module).

Proof: $1 \Leftrightarrow 2 \Leftrightarrow 3$, by prop. 1.3

$3 \Leftrightarrow 4$, by (3, Lemma 2.1.22).

Corollary 1.6:

Let M be a nonzero cyclic R-module. Then the following are equivalent:

- 1- M is quasi-Dedekind.
- 2- $\{0\}$ is strongly S-prime.
- 3- $\{0\}$ is S-prime.
- 4- $\{0\}$ is prime (i.e. M is a prime module).

Proposition 1.7:

If M is a multiplication R-module. Then M has no nontrivial strongly S-prime submodule.

Proof: Let $0 \neq N < M$ such that N is strongly S-prime R-submodule, so N is strongly S-prime (\bar{R} -submodule), where $\bar{R} = R/\text{ann}M$. Since $N < M$, $\exists x \in M$, $x \notin N$.

We claim that $[N :_R M] = (0)$. For this, suppose there exists $\bar{r} = r + \text{ann}M \neq \bar{0}$ such that $\bar{r} \in [N :_R M]$, hence $rM \subseteq N$. But $\bar{r} \neq 0$ implies $r \notin \text{ann}M$, so $rM \neq 0$.

Define $f: M \longrightarrow M$ by $f(m) = rm$ for all $m \in M$. Hence $f \neq 0$ and $f(x) \in N$ and since N is strongly S-prime, $x \in N$ which is a contradiction. Thus $N = [N :_R M]M = 0M = (0)$.

Recall that an R -module is called cohopfian if for every $f \in \text{End}(M)$, f is 1-1, then f is an isomorphism, [7]. It is well known every artinian module is cohopfian.

Proposition 1.8:

Let M be a cohopfian such that (0) is strongly S -prime submodule. Then every nonzero $f \in \text{End}(M)$ is an isomorphism.

Proof: By Prop. 1.3, M is quasi-Dedekind, so for every $f \in \text{End}(M)$, $f \neq 0$, then f is monomorphism and since M is cohopfian, f is an isomorphism.

Recall that an R -module M is called scalar if for every $f \in \text{End}(M)$, $\exists r \in R$, $r \neq 0$ such that $f(m) = rm$ for all $r \in R$, [8].

Proposition 1.9:

Let M be a scalar R -module, $N < M$. Then

- 1- If N is strongly prime, then N is strongly S -prime.
- 2- N is S -prime iff N is prime.

Proof: 1- Let $f \in \text{End}(M)$, $f \neq 0$, $m \in M$ such that $f(m) \in N$. Since M is scalar, $\exists r \in R$, $r \neq 0$ such that $f(x) = rx$. Hence $f(m) = rm \in N$. But N is strongly prime, so $m \in N$.

2- Obviously, N is S -prime implies N is prime. Now, if N is prime. Let $f \in \text{End}(M)$, $m \in M$ such that $f(m) \in N$. Since M is scalar, $\exists r \in R$, $r \neq 0$ such that $f(x) = rx$ for all $x \in M$. Thus $f(m) = rm \in N$. But N is prime, so either $m \in N$ or $rM \subseteq N$. Thus either $m \in N$ or $f(M) \subseteq N$. Therefore N is S -prime.

The converse of Prop.1.9 (1) is not true, even M is scalar (see Rem and Ex. 1.2 (3) b).

Recall that a submodule N of an R -module is said to be relatively divisible (S -relatively divisible) denoted by RD (S - RD) if $rM \cap N = rN$ for each $r \in R$, ($f(M) \cap N = f(N)$ for all $f \in \text{End}(M)$), [3], [9] respectively.

It is clear that (0) , M are RD and S - RD submodules.

Remarks 1.10:

- 1- Every S - RD submodule of a module is RD -submodule.
- 2- Every RD -submodule of a scalar module is S - RD submodule, hence every RD -submodule of finitely generated multiplication (or cyclic) is S - RD submodule, since every finitely generated multiplication module is scalar module.

Proof: Is obvious, so is omitted.

Recall that a submodule N of an R -module M is called fully invariant if $f(N) \subseteq N$ for all $f \in \text{End}(M)$, [9].

Proposition 1.11:

Every fully invariant strongly S-prime submodule of a module M is S-RD submodule.

Proof: Let $N < M$, N is fully invariant strongly S-prime. Let $f \in \text{End}(M)$, if $f = 0$, then it is clear that $f(M) \cap N = f(N)$. If $f \neq 0$. Since N is fully invariant, $f(N) \subseteq N$ and so $f(N) \subseteq f(M) \cap N$. Now let $y \in f(M) \cap N$, then $y = f(m) \in N$ for some $m \in M$. But N is strongly S-prime, so $m \in N$, thus $f(m) \in f(N)$. Therefore $f(M) \cap N \subseteq f(N)$.

Proposition 1.12:

Let M be a quasi-Dedekind R -module. Then every proper S-RD submodule of M is strongly S-prime.

Proof: Let N be a proper S-RD submodule of M . Assume $f \in \text{End}(M)$, $f \neq 0$ and $f(m) \in N$ for some $m \in M$. Hence $f(m) \in f(M) \cap N$. But N is an S-RD submodule, so $f(m) \in f(N)$ and hence $f(m) = f(n)$ for some $n \in N$. This implies $m - n \in \ker f$. On the other hand, M is quasi-Dedekind, so $\ker f = \{0\}$. It follows that $m = n$. Thus $m \in N$ and N is strongly S-prime.

Recall that if M is a module over integral domain R , then $T(M) = \{m \in M : \exists r \in R, r \neq 0, rm = 0\}$, $T(M)$ is called torsion submodule if $M = T(M)$, M is called torsion module and if $0 = T(M)$, M is called torsion free, [10].

It is easy to see that every strongly prime submodule in a torsion module is strongly S-prime.

Proposition 1.13:

Let M be a module over integral domain R . If (0) is strongly S-prime then $T(M)$ is a strongly S-prime, provided $T(M) \neq M$.

Proof: Let $f \in \text{End}(M)$, $f \neq 0$. Assume $f(m) \in T(M)$ for some $m \in M$. Then there exists $r \in R$, $r \neq 0$ such that $r \cdot f(m) = 0$. Hence $f(rm) = 0$. But (0) is strongly S-prime, so $rm = 0$; that $m \in T(M)$. Hence $T(M)$ is strongly S-prime.

Now we look our attention for modules which have no nontrivial strongly S-prime submodule.

Proposition 1.14:

Let M be a faithful module over integral domain R . If M is a torsion module, then M has no nontrivial strongly S-prime.

Proof: Assume $N < M$, $N \neq 0$ and N is strongly S-prime. Since $N < M$, $\exists x \in M$, $x \notin N$. But $M = T(M)$, so there exists $r \in R$, $r \neq 0$ such that $0 = rx$. Define $f: M \rightarrow M$ by $f(m) = rm$ for all $m \in M$, hence $f(x) = rx = 0 \in N$. Since M is faithful, $f \neq 0$ and so $x \in N$. Since N is strongly S-prime, which is a contradiction.

Note 1.15:

If M is a divisible torsion module over integral domain, then (0) is the only strongly S-prime submodule of M .

Proof: By [3, Prop.2.1.7], (0) is the only S-prime submodule of M . This implies (0) is strongly S-prime (see Prop.1.3). Hence (0) is the only strongly S-prime of M by 1.2 (1).

Recall that an ideal I of R is called essential (large) in R (denoted by $I <_e R$) if $I \cap J \neq 0$ for any nonzero ideal J of R , [11].

Recall that if M is an R -module, then $\{m \in M : \text{ann}_e(m) < R\}$ is called a singular submodule of M and is denoted by $Z(M)$. If $M = Z(M)$, then M is singular and if $Z(M) = 0$, then M is called a nonsingular module, [11].

Proposition 1.16:

Let M be an R -module such that (0) is strongly S-prime, then $Z(M)$ is strongly S-prime provided $Z(M) \neq M$.

Proof: If $Z(M) = (0)$ then nothing to prove.

If $Z(M) \neq (0)$. Assume $f \in \text{End}(M)$, $f \neq 0$ such that $f(m) \in Z(M)$ for some $m \in M$. Hence $\text{ann}_R f(m) <_e R$ and so for every $r \in R$, $r \neq 0$, $\exists t \in R$, $t \neq 0$ such that $0 \neq tr \in \text{ann}_R f(m)$. Then $f(trm) = 0$ and so $(tr)m = 0$, since (0) is strongly S-prime. It follows that $0 \neq tr \in \text{ann}(m)$ and so $m \in Z(M)$.

2- More about Strongly S-Prime Submodules:

In this section, several fundamental properties of strongly S-prime submodules are given.

Proposition 2.1:

Let M be an R -module, $N < M$, $I \leq R$. If P is a strongly S-prime submodule such that $IN \subseteq P$, then $N \subseteq P$, provided $I \not\subseteq \text{ann}M$.

Proof: Let $x \in N$. Since $I \not\subseteq \text{ann}M$, $\exists a \in I$ and $a \notin \text{ann}M$. Define $f: M \rightarrow M$ by $f(m) = am$ for all $m \in N$, it is clear that $f \neq 0$ and $f(x) = ax \in IN \subseteq P$. But P is strongly S-prime, so $x \in P$. Thus $N \subseteq P$.

Proposition 2.2:

Let M be an R -module, let $\phi \in \text{End}(M)$, $\phi \neq 0$. If N is a strongly S-prime submodule and N is fully invariant. Then $\phi^{-1}(N)$ is a strongly S-prime.

Proof: Let $f \in \text{End}(M)$ and $f \neq 0$ such that $f(m) \in \phi^{-1}(N)$. Hence $\phi(f(m)) \in N$. Since $\phi \neq 0$ and N is strongly S-prime, $f(m) \in N$ and again $f \neq 0$, N is strongly S-prime, then $m \in N$. But N is fully invariant, so $\phi(N) \subseteq N$; that is $N \subseteq \phi^{-1}(N)$. Hence $m \in \phi^{-1}(N)$ which implies $\phi^{-1}(N)$ is strongly S-prime.

Recall that an R -module M is called A -projective (where A is an R -module) if for every $X < A$ and every homomorphism $\phi: M \longrightarrow \frac{A}{X}$ can be lifted to a homomorphism $\psi: M \longrightarrow M$, [12]. If M is A -projective for each R -module A , M is called projective.

Theorem 2.3:

Let $f: M \longrightarrow M'$ be an epimorphism and let $N < M$ such that $\ker f \leq N$. If N is strongly S -prime, then $f(N)$ is strongly S -prime, provided M' is M -projective.

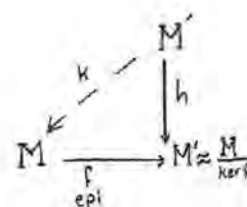
Proof: Let $h: M' \longrightarrow M'$, $h \neq 0$ and let $m' \in M'$ such that $h(m') \in f(N)$. Since f is an epimorphism there exists $m \in M$ and $f(m) = m'$. Since $M' = M$ projective, $\exists k: M' \longrightarrow M$ such that $f \circ k = h$.

But $M \xrightarrow{f} M' \xrightarrow{k} M$, so

$k \circ f \in \text{End}(M)$ and $k \circ f \neq 0$, because if $k \circ f = 0$, then

$0 = (k \circ f)(m) = k(f(m)) = k(m') = 0$;

that is $k = 0$ and so $f \circ k = h = 0$ which is a contradiction.



Now $f[(k \circ f)(m)] = (f \circ k)(f(m)) = h(m') \in f(N)$, hence $f((k \circ f)(m)) = f(n)$ for some $n \in N$. This implies $(k \circ f)(m) - n \in \ker f \subseteq N$ and so $(k \circ f)(m) \in N$. Since $k \circ f \neq 0$ and N is strongly S -prime, $m \in N$ which yields $f(m) = m' \in f(N)$. Thus $f(N)$ is strongly S -prime.

Corollary 2.4:

Let M be an R -module, let $K < N < M$ and N is strongly S -prime. Then $\frac{N}{K}$ is strongly S -prime in $\frac{M}{K}$, provided that $\frac{M}{K}$ is M -projective

Proposition 2.5:

Let M be an R -module and let $K < N < M$ and K is fully invariant. If K and $\frac{N}{K}$ are strongly S -prime in M , $\frac{M}{K}$ respectively, then N is strongly S -prime in M .

Proof: Let $f: M \longrightarrow M$, and $f \neq 0$. If $f(m) \in N$ for some $m \in M$. To prove $m \in N$.

Define $f^*: \frac{M}{K} \longrightarrow \frac{M}{K}$ by $f^*(x + K) = f(x) + K$ for all $x + K$ in $\frac{M}{K}$. It is easy to see that f^* is well-defined. Now if $f^* = 0$, then $f^*(m + K) = f(m) + K$; that is $f(m) \in K$. But K is strongly S -prime in M , so $m \in K \subseteq N$. Thus $m \in N$. If

$f^* \neq 0$, then $f^*(m + K) = f(m) + K \in \frac{N}{K}$. However $\frac{N}{K}$ is strongly S-prime in $\frac{M}{K}$, so $m + K \in \frac{N}{K}$ and this implies $m \in N$. Thus N is strongly S-prime.

Proposition 2.6:

Let M be a projective R -module. If N is a strongly S-prime, then $\frac{M}{N}$ is a quasi-Dedekind R -module.

Proof: To prove $\frac{M}{N}$ is quasi-Dedekind, we shall prove any endomorphism on $\frac{M}{N}$ is either zero mapping or 1-1, let $f: \frac{M}{N} \longrightarrow \frac{M}{N}$ and $f \neq 0$.

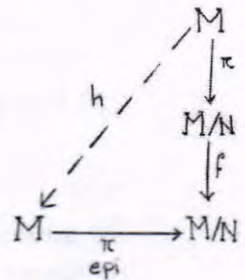
Since M is projective there exists $h: M \longrightarrow M$ such that $\pi \circ h = f \circ \pi$, where π is the natural projection.

Hence for any $m \in M$,

$$\begin{aligned} (\pi \circ h)(m) &= \pi(h(m)) = h(m) + N \\ &= (f \circ \pi)(m) = f(m + N). \end{aligned}$$

If $f(x + N) = 0_{\frac{M}{N}} = N$ for some $x + N$ in $\frac{M}{N}$, then $h(x) + N =$

N and hence $h(x) \in N$.



But we can see easily $h \neq 0$ (if $h = 0$, then $f(\frac{M}{N}) = 0_{\frac{M}{N}}$ which is a contradiction). Hence $x \in N$, since N is strongly S-prime. Thus $x + N = N = 0_{\frac{M}{N}}$, and so that f is 1-1 and $\frac{M}{N}$ is quasi-dedekind.

For a partial answer for the converse of Prop. 2.6 we have the following:

Proposition 2.7:

Let $N < M$ such that N is fully invariant such that $\frac{M}{N}$ is a quasi-Dedekind R -module. Then N is S-prime.

Proof: Let $f \in \text{End}(M)$ and $f(m) \in N$ for some $m \in M$. Define $g: \frac{M}{N} \longrightarrow \frac{M}{N}$ by $g(x + N) = f(x) + N$, $\forall x \in M$. g is well-defined. If $g = 0$, then $f(M) \subseteq N$. If $g \neq 0$, then g is 1-1 and hence $g(m + N) = f(m) + N = N$ implies that $m + N = N$; that is $m \in N$. Thus N is S-prime.

Recall that an R -module M is A -injective (where A is an R -module) if for every $X \leq M$, any homomorphism $\phi: X \longrightarrow A$ can be extended to a

homomorphism $\psi: A \longrightarrow X$, (8), (13). If M is M -injective M is called quasi-injective, [8].

Proposition 2.8:

Let K be a strongly S -prime submodule of an R -module M and let $N < M$ which is M -injective. Then either $N \subseteq K$ or $K \cap N$ is strongly S -prime in N .

Proof: Suppose $N \not\subseteq K$. Hence $K \cap N \subsetneq N$. Let $f \in \text{End}(N)$, $f \neq 0$, $x \in N$ such that $f(x) \in K \cap N$. Since N is M -injective,

$\exists h: M \longrightarrow N$ such that $h \circ i = f$.

It is clear that $h \neq 0$, since $f \neq 0$.

Now, $M \xrightarrow{h} N \xrightarrow{i} M$, so

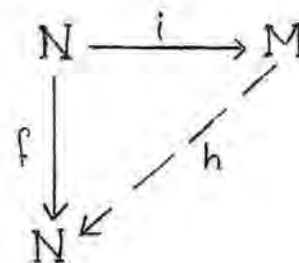
$i \circ h \in \text{End}(M)$ and $i \circ h \neq 0$.

$(i \circ h)(x) = i(h(x))$

$= h(x) \in N$

$= (h \circ i)(x) = f(x) \in K \cap N \subseteq K$.

Thus $(i \circ h)(x) \in K$. But K is strongly S -prime, so $x \in K$ and hence $x \in K \cap N$. Therefore $K \cap N$ is strongly S -prime.



Corollary 2.9:

Let K be a strongly S -prime submodule of a quasi-injective R -module M , and let $N < M$. Then either $N \subseteq K$ or $K \cap N$ is strongly S -prime in N .

Next we turn our attention to direct sum of strongly S -prime submodules.

First we have the following:

Proposition 2.10:

Let $N_1 < M_1$, $N_2 < M_2$. If $N_1 \oplus N_2$ is a strongly S -prime in $M = M_1 \oplus M_2$, then N_1, N_2 are strongly S -prime in M_1 and M_2 respectively.

Proof: Let $f: M_1 \longrightarrow M_2$, $f \neq 0$, $g: M_1 \longrightarrow M_2$, $g \neq 0$ and let $m_1 \in M_1$, $m_2 \in M_2$ such that $f(m_1) \in N_1$, $g(m_2) \in N_2$. Define $h: M_1 \oplus M_2 \longrightarrow M_1 \oplus M_2$ by $h(x_1, x_2) = (f(x_1), g(x_2))$, $\forall (x_1, x_2) \in M_1 \oplus M_2$. It is clear that h is well-defined, $h \neq 0$ and $h(m_1, m_2) \in N_1 \oplus N_2$. Since $N_1 \oplus N_2$ is strongly S -prime, so $(m_1, m_2) \in N_1 \oplus N_2$. Thus $m_1 \in N_1$ and $m_2 \in N_2$.

Remark 2.11:

The converse of Prop. 2.10 is not true in general, for example $(\bar{0})$ in Z_5 and (0) in Z are strongly S -prime in Z_5, Z respectively, but $\{(0,0)\} = (\bar{0}) + (\bar{0})$ is not strongly S -prime in $Z_5 \oplus Z$.

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Comparison of the Bayesian Estimations under Different Loss Function and Maximum Likelihood Estimation for *Rayleigh* Distribution

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الخلاصة

يهتم هذا البحث بمقارنة بعض المقدرات لمعلمة القياس لتوزيع رايلي بتطبيق طريقة بيز تحت دوال خسارة مختلفة (باستخدام معلومات جيفري المسبقة) فضلاً عن طريقة الإمكان الأعظم (ML). استندت المقارنة الى دراسة مونت كارلو. خلال دراسة المحاكاة تمت المقارنة بين أداء هذه المقدرات بالإستناد الى متوسط مربعات الخطأ (MSE) والتوصل الى أنه عندما يكون c صغيراً مقدر بيز مع دالة الخسارة Modified El- Sayyad هي المقدر الأفضل مع احجام العينات الصغيرة والمتوسطة وان ML مع احجام العينات الكبيرة. بينما حين تكون c كبيرة فإنه بالإعتماد على متوسط مربعات الخطأ كانت دالة الخسارة التربيعية هي الأفضل ثم ML.

ABSTRACT

This paper is concerned with the comparison of some estimators for the scale parameter c of the Rayleigh distribution by applying the Bayes' estimators under different loss functions (using Jeffrey prior information) in addition of the Maximum likelihood estimator (ML). The comparison was based on a Monte Carlo study. Through the simulation study comparison was made on the performance of these estimators with respect to the mean square error (MSE) and reach to, if c is small, the Bayes estimator with modified El- Sayyad loss function is the best estimator with small and medium samples size and ML with large samples size. As c become large based upon the squared error loss function was the best estimator then ML.

INTRODUCTION

Siddique (1962) discussed the origin and properties of the Rayleigh distribution. Polovko (1968) and Dyer and Whisenand (1973) noted the importance of this distribution in electro vacuum devices and communication engineering. Dey and Das (2007) obtained Bayesian predictive intervals of the parameter of Rayleigh distribution. [3]

In Bayesian analysis, the unknown parameter θ is regarded as being the value of a random variable from a given probability distribution, with the knowledge of some information about the value of θ prior to observing the data x_1, x_2, \dots, x_n . The object of the present paper is to obtain Bayesian

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estimates of the parameter θ of the Rayleigh distribution, using Jeffrey prior under four loss functions and the Maximum likelihood estimator (ML). In this paper, we mainly consider different estimators and compare their performance through Monte-Carlo simulation. The efficiency of the four Bayes estimators and ML estimator compared according to the mean square error (MSE).

The Bayesian Approach

Suppose that n items have an independent and identically distributed Rayleigh each having unknown parameter (θ), the probability density function of the Rayleigh distribution is given by: [6]

$$f(x, \theta) = \frac{2}{\theta} x e^{-\frac{x^2}{\theta}} \quad , \quad x > 0 \quad , \quad \theta > 0 \quad (1)$$

Let us assume that θ has non-informative prior density defined as using Jeffrey prior information $g(\theta)$ which given by:

$$g(\theta) \propto \frac{1}{\theta^c} \quad , \quad c > 0 \quad (2)$$

The posterior distribution of θ given random sample: $X = (x_1, x_2, \dots, x_n)$ is:

$$h(\theta|x) = \frac{\left(\frac{1}{\theta^c}\right) \frac{2^n}{\theta^n} \prod_{i=1}^n x_i e^{-\frac{\sum_{i=1}^n x_i^2}{\theta}}}{\int_0^\infty \left(\frac{1}{\theta^c}\right) \frac{2^n}{\theta^n} \prod_{i=1}^n x_i e^{-\frac{\sum_{i=1}^n x_i^2}{\theta}} d\theta} \quad (3)$$

Let:

$$y = \frac{\sum_{i=1}^n x_i^2}{\theta}$$

After substitution we find that:

$$h(\theta|x) = \frac{-\left(\sum_{i=1}^n x_i^2\right)^{n+c-1} e^{-\frac{\sum_{i=1}^n x_i^2}{\theta}}}{\theta^{n+c} \Gamma(n+c-1)}$$

Loss Functions

In Bayesian estimation, we consider four types of loss functions [4]:

(i) Squared-Error Loss Function:

$$L_1(\hat{\theta}, \theta) = (\hat{\theta} - \theta)^2$$

(ii) Modified Squared-Error Loss Function:

$$L_2(\hat{\theta}, \theta) = [\theta^r (\hat{\theta} - \theta)^2]$$

(iii) El-Sayyad's Loss Function:

$$L_3(\hat{\theta}, \theta) = [\theta^r (\hat{\theta}^r - \theta^r)^2]$$

(iv) Modified El-Sayyad's Loss Function:

$$L_4(\hat{\theta}, \theta) = \left(\frac{\hat{\theta}}{\theta}\right)^r - r \ln\left(\frac{\hat{\theta}}{\theta}\right) - 1$$

Bayes Estimators

According to the above mentioned loss functions, we drive the corresponding Bayes' estimators for θ using Risk function $R(\hat{\theta} - \theta)$ where: [1]

$$R(\hat{\theta} - \theta) = E[L(\hat{\theta}, \theta)] \quad (4)$$

(i) With squared error loss function, the corresponding Bayes estimator for θ with posterior distribution (3) comes out as:

$$R_1(\hat{\theta} - \theta) = E[L_1(\hat{\theta}, \theta)|X] = \int_0^{\infty} (\hat{\theta} - \theta)^2 h(\theta|X) d\theta$$

Let:

$$\frac{\partial R_1(\hat{\theta} - \theta)}{\partial \hat{\theta}} = 0, \text{ then the Bayes estimator is:}$$

$$\hat{\theta} = E[\theta|x] = \int_0^{\infty} \theta h(\theta|x) d\theta$$

$$\hat{\theta} = \int_0^{\infty} \theta \frac{-(\sum_{i=1}^n x_i^2)^{n+c-1} e^{-\left(\frac{\sum_{i=1}^n x_i^2}{\theta}\right)}}{\theta^{n+c} \Gamma(n+c-1)} d\theta$$

Let:

$$y = \frac{\sum_{i=1}^n x_i^2}{\theta}$$

On simplification, we get,

$$\hat{\theta} = \frac{-(\sum_{i=1}^n x_i^2)^{n+c-1}}{\Gamma(n+c-1)} \int_0^{\infty} e^{-y} \frac{y^{n+c-1}}{(\sum_{i=1}^n x_i^2)^{n+c-1}} \frac{-(\sum_{i=1}^n x_i^2)}{y^2} dy$$

$$\hat{\theta}_1 = \frac{\sum_{i=1}^n x_i^2}{n+c-2} \quad (5)$$

(ii) With modified squared error loss function, the corresponding Bayes estimator for θ with posterior distribution (3) comes out as:

$$R_2(\hat{\theta} - \theta) = E[L_2(\hat{\theta}, \theta)|X] = \int_0^{\infty} \theta^r (\hat{\theta} - \theta)^2 h(\theta|X) d\theta$$

$$\text{By letting, } \frac{\partial R_2(\hat{\theta} - \theta)}{\partial \hat{\theta}} = 0$$

We find that:

$$\hat{\theta} = \frac{E[\theta^{r+1}|x]}{E[\theta^r|x]}$$

$$\text{Where, } E[\theta^r|x] = \int_0^\infty \theta^r h(\theta|x) d\theta$$

By acting in a similar manner as in (i) and after few steps we get:

$$E[\theta^r|x] = \frac{(\sum_{i=1}^n x_i^2)^r \Gamma(n+c-r-1)}{\Gamma(n+c-1)} \quad (6)$$

Similarly,

$$E[\theta^{r+1}|x] = \frac{(\sum_{i=1}^n x_i^2)^{r+1} \Gamma(n+c-r-2)}{\Gamma(n+c-1)} \quad (7)$$

From (6) and (7), we find that:

$$\hat{\theta}_2 = \frac{\sum_{i=1}^n x_i^2}{(n+c-r-2)} \quad (8)$$

(iii) With El- Sayyad loss function, the corresponding Bayes estimators for θ with posterior distribution (3) come out as:

$$R_3(\hat{\theta} - \theta) = E[L_3(\hat{\theta}, \theta)|X] = \int_0^\infty \theta^l (\hat{\theta}^r - \theta^r)^2 h(\theta|X) d\theta$$

For simplicity, let us assume that $l = 1$ and by letting:

$$\frac{\partial L_3(\hat{\theta}, \theta)}{\partial \hat{\theta}} = 0$$

$$\text{We find that: } \hat{\theta} = \left(\frac{E[\theta^{r+1}|x]}{E[\theta^r|x]} \right)^{1/r}$$

From (5) and (7) we find:

$$\hat{\theta}_3 = \left[\frac{(\sum_{i=1}^n x_i^2)^r \Gamma(n+c-r-2)}{\Gamma(n+c-2)} \right]^{1/r} = (\sum_{i=1}^n x_i^2) \left[\frac{\Gamma(n+c-r-2)}{\Gamma(n+c-2)} \right]^{1/r} \quad (9)$$

(iv) With modified El- Sayyad loss function, the corresponding Bayes estimator for θ with posterior distribution (3) comes out as:

$$R_4(\hat{\theta} - \theta) = E[L_4(\hat{\theta}, \theta)|X] = \int_0^\infty \left[\left(\frac{\hat{\theta}}{\theta} \right)^r - r \ln \left(\frac{\hat{\theta}}{\theta} \right) - 1 \right] h(\theta|X) d\theta$$

By letting:

$$\frac{\partial R_4(\hat{\theta} - \theta)}{\partial \hat{\theta}} = 0$$

We reach to:

$$\hat{\theta}^r E \left[\frac{1}{\theta^r} | x \right] = 1$$

Where:

$$E \left[\frac{1}{\theta^r} | x \right] = \int_0^\infty \frac{1}{\theta^r} h(\theta | x) d\theta$$

And by making similar substitution as above we get:

$$E \left[\frac{1}{\theta^r} | x \right] = \frac{\Gamma(n+c+r-1)}{(\sum_{i=1}^n x_i^2)^r \Gamma(n+c-1)}$$

Hence,

$$\hat{\theta}_4 = (\sum_{i=1}^n x_i^2) \left[\frac{\Gamma(n+c-1)}{\Gamma(n+c+r-1)} \right]^{1/r} \quad (10)$$

3. Maximum Likelihood Estimator

Given x_1, x_2, \dots, x_n a random sample of size n from Rayleigh distribution, we consider estimation by the method of maximum likelihood. The log-likelihood for a random sample from (1) is:

$$\ln L(x, \theta) = n \ln 2 - n \ln \theta + \sum_{i=1}^n \ln x_i - \sum_{i=1}^n x_i^2 / \theta \quad (11)$$

$$\frac{\partial \ln L(x, \theta)}{\partial \theta} = \frac{-n}{\theta} + \frac{\sum_{i=1}^n x_i^2}{\theta^2}$$

Setting this expression to zero and solving the equation yields the maximum likelihood

Estimator of θ parameter:

$$\hat{\theta}_{ML} = (\sum_{i=1}^n x_i^2) / n$$

4. Simulation Results

The simulation program is written by using QBASIC and it has been performed to compare the four Bayes estimation and ML estimator depending on Mean Square Errors (MSE)) to compare the efficiency of the four estimators, as follows:

$$MSE(\theta) = \frac{\sum_{i=1}^I (\hat{\theta}_i - \theta)^2}{I}$$

Where I is the number of replications.

We generated $I = 2000$ samples of sizes $n = 25, 50, 100$ from the Rayleigh distribution with $\theta = 0.5, 3$, using $c=1, 3$ and $r = 2, 5$. The mean squared errors (MSE's) were calculated. The results of the simulation study are reported in the following tables:

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Table 1: MSE of estimated parameter of Rayleigh distribution with $c = 1, r = 2$

n	θ	MSE				
		$\hat{\theta}_{ML}$	$\hat{\theta}_1$	$\hat{\theta}_2$	$\hat{\theta}_3$	$\hat{\theta}_4$
25	0.5	0.01048	0.01174	0.01793	0.01585	0.01021
	3	0.37741	0.42256	0.64551	0.57048	0.36741
50	0.5	0.00516	0.00547	0.00686	0.00641	0.00508
	3	0.18561	0.19707	0.24692	0.23083	0.18282
100	0.5	0.00255	0.00262	0.00293	0.00283	0.00253
	3	0.09175	0.09433	0.10550	0.10193	0.09116

Table 2: MSE of estimated parameter of Rayleigh distribution with $c = 3, r = 2$

n	θ	MSE				
		$\hat{\theta}_{ML}$	$\hat{\theta}_1$	$\hat{\theta}_2$	$\hat{\theta}_3$	$\hat{\theta}_4$
25	0.5	0.01048	0.01012	0.01174	0.01099	0.01086
	3	0.37741	0.36440	0.42256	0.39571	0.39104
50	0.5	0.00516	0.00505	0.00547	0.00529	0.00524
	3	0.18561	0.18181	0.19707	0.19035	0.18861
100	0.5	0.00255	0.00253	0.00262	0.00258	0.00259
	3	0.09175	0.09102	0.09433	0.09281	0.09315

Table 3: MSE of estimated parameter of Rayleigh distribution with $c = 1, r = 5$

n	θ	MSE				
		$\hat{\theta}_{ML}$	$\hat{\theta}_1$	$\hat{\theta}_2$	$\hat{\theta}_3$	$\hat{\theta}_4$
25	0.5	0.01048	0.01174	0.04240	0.02388	0.01045
	3	0.37741	0.42256	1.52627	0.85954	0.37616
50	0.5	0.00516	0.00547	0.01132	0.00802	0.00513
	3	0.18561	0.19707	0.40748	0.28863	0.18470
100	0.5	0.00255	0.00262	0.00387	0.00318	0.00256
	3	0.09175	0.09433	0.13918	0.11444	0.09201

Table 4: MSE of estimated parameter of Rayleigh distribution with $c = 3, r = 5$

n	θ	MSE				
		$\hat{\theta}_{ML}$	$\hat{\theta}_1$	$\hat{\theta}_2$	$\hat{\theta}_3$	$\hat{\theta}_4$
25	0.5	0.01048	0.01012	0.02355	0.01425	0.01269
	3	0.37741	0.36440	0.84794	0.51316	0.45683
50	0.5	0.00516	0.00505	0.00799	0.00605	0.00578
	3	0.18561	0.18181	0.28761	0.21766	0.20800
100	0.5	0.00255	0.00253	0.00318	0.00275	0.00275
	3	0.09175	0.09102	0.11433	0.09893	0.09882

It appears from tables 1 and 3 where $c = 1$ and $r = 2, 5$ the best estimator was $\hat{\theta}_4$ which represented Bayes estimator for θ with modified El-Sayyad loss function. It followed by the Maximum Likelihood Estimator ($\hat{\theta}_{ML}$), and then the squared error loss function $\hat{\theta}_2$ in the third order.

The results in tables 2, 4 showed that the best estimator was the squared error loss function $\hat{\theta}_2$, followed by Maximum Likelihood Estimator, and then $\hat{\theta}_4$ (modified El-Sayyad loss function),

In general, we can say that, if c is small, the Bayes estimator with modified El-Sayyad loss function is the best estimator with small and medium samples size and ML with large sample size. As c become large based upon the squared error loss function was the best estimator then ML and El-Sayyad, Modified El-Sayyad

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Results on the Best Approximation for Banach Operator with S-Convex Set in P-Normed Space

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الخلاصة

في هذا البحث قدمنا نتائج حول وجود التقريب الافضل بواسطة تطبيق خاصية النقطة الصامدة المشتركة لتطبيقات غير متبادلة. واستخدمنا الخاصية التحديدية من نوع S في فضاء P-المعياري وشرط مؤثر بناخ لبرهنة مبرهنين حول وجود التقريب الافضل غير المتغير.

ABSTRACT

In this paper, we present some results about the existence of best approximation by applying a property of common fixed point for non commuting mappings. We use the S-convexity in P-normed space and the condition of the Banach operator to prove two theorems about the existence of an invariant best approximation.

INTRODUCTION

The concepts of fixed point and the non convex sets in P-normed space combined in [1]. Recently [2] have obtained some results on commuting mappings and the fixed point theorem in the setting of P-normed spaces. The purpose of this paper is to study the best approximation in the setting of P-normed spaces. We prove common fixed point results with a Banach operator in P-normed spaces and obtain results on best approximation theorem.

The following definition and result will be needed.

Let X be a linear space. A P-norm on X is a real-valued function $\|\cdot\|_p$ on X with $0 < p \leq 1$ [3], satisfying the following conditions:

(a) $\|x\|_p \geq 0$ and $\|x\|_p = 0$ iff $x = 0$.

(b) $\|\lambda x\|_p = |\lambda|^p \|x\|_p$

(c) $\|x + y\|_p \leq \|x\|_p + \|y\|_p$

for all $x, y \in X$ and all scalars λ . The pair $(X, \|\cdot\|_p)$ is called a P-normed space. It is a metric space with $dp(x, y) = \|x - y\|_p$ for all $x, y \in X$, define a translation-invariant metric dp on X . If $p = 1$, we obtain the concept of a normed linear space. It is well-known that the topology of every Hausdorff locally bounded topological linear space is given by some P-norm, $0 < p \leq 1$, [3].

Example 1.1:

The spaces L_p and $L_p[0,1]$, $0 < p < 1$, are P-normed spaces. A p-normed space is not necessarily a locally convex space.

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Let C be a subset of P -normed space X . For any $\hat{x} \in X$, Let $PC(\hat{x}) := \{y \in C: dp(y, \hat{x}) = dp(x, C)\}$, the set of best C -approximants to \hat{x} , where $dp(\hat{x}, C) = \inf_{z \in C} dp(\hat{x}, z)$. $PC(\hat{x})$ is always a bounded subset of X and it is closed or convex if C is so [4].

A map $T: C \longrightarrow C$ is said to be f -contraction if there exists a self-map f on C and a real number $k \in (0, 1)$ such that

$$\|Tx - Ty\|_p \leq k \|fx - fy\|_p \text{ for all } x, y \in C.$$

If in the above inequality $k = 1$, then T is called f -nonexpansive. We denote by $F(T)$ the set of fixed points of T .

Definition 1.2: [4]

A family of maps $\{f_\alpha\}_{\alpha \in X}$ is said to be (S)-convex structure on P -normed space X , if it satisfies the following conditions:

- i. $f_\alpha: [0, 1] \longrightarrow X$, i.e. f_α is map from $[0, 1]$ into X for each $\alpha \in X$,
- ii. $f_\alpha(1) = \alpha$ for each $\alpha \in X$,
- iii. $f_\alpha(t)$ is a jointly continuous in (α, t) , i.e., $f_\alpha(t) \longrightarrow f_{\alpha_0}(t_0)$ for $\alpha \longrightarrow \alpha_0$ in X and $t \longrightarrow t_0$ in $[0, 1]$,
- iv. if f is a map from X into itself, then for any $x \in X$, $f_{Tx}(t) \subseteq Tx$ for all $t \in [0, 1]$,
- v. $\|f_\alpha(t) - f_\beta(t)\|_p \leq [\phi(t)]^p \|\alpha - \beta\|_p$, where ϕ is a function from $[0, 1]$ into itself.

Now, we recall the following property

Property 1.3: [4]

Let $\{f_\alpha\}$ be a (S)-convex structure on a P -normed space X .

A self mapping T of X is said to satisfy the property (C), if for any $t \in [0, 1]$, for all $x \in X$ and for all fx , we have $T(fx(t)) = fTx(t)$.

From [5] we need the following:

Definition 1.4: [5]

The ordered pair (T, g) of two self-maps T and g of a metric space X is called a Banach operator pair, if $T(F(g)) \subset F(g)$.

Remark 1.5:

It is clear that the commute pair (T, f) is a Banach operator but the converse is not true since if $x \in T(F(f)) \Rightarrow \exists y \in F(f)$ s.t. $x = Ty$.

Now, $f(x) = f(Ty) = T(f(y)) = Ty = x \Rightarrow x \in F(f)$.

Remark 1.6: [6]

Let C be a nonempty subset of P -normed space X where $f: C \longrightarrow C$ be continuous in the weak and strong topology on C , affine with $q \in F(f)$ and $f(C) = C$. The weak continuity condition can be dropped, since continuous affine maps are weakly continuous.

Recall that if X is a topological linear space, then its continuous dual space X' is said to separate the points of X if for each $x \neq 0$ in X , there exists an $f \in X'$

such that $fx \neq 0$. In this case the weak topology on X is well-defined, [3]. We mention that if X is not locally convex, then X' need not separate the points of X . For example, if $X = L_p[0,1]$, $0 < p < 1$, then $X' = \{0\}$. However, there are some non-locally convex spaces (such as the P -normed space L_p , $0 < p < 1$) whose dual separates the points [4].

Let X be a complete P -normed space whose dual X' separates the points of X . A map $T: C \subseteq X \longrightarrow X$ is said to be demiclosed if for every sequence $\langle x_n \rangle \subset C$ such that x_n converges weakly to $x \in C$ and Tx_n converges strongly to $y \in X$ then $y = Tx$.

The space X is said to be an Opial space [6] if for every sequence $\langle x_n \rangle$ in X weakly convergent to $x \in X$, the inequality

$$\liminf_{n \rightarrow \infty} \|x_n - x\|_p < \liminf_{n \rightarrow \infty} \|x_n - y\|_p$$

holds for all $y \neq x$.

Theorem 1.7: [5]

Suppose T and g are two self-mapping of a closed subset C of the metric space X with the metric d , such that (T, g) is a Banach operator pair on C and T is g -contraction on C , i.e. $d(Tx, Ty) \leq k d(g(x), g(y))$, for all $x, y \in C$ with fixed $k \in (0, 1)$. If $F(g)$ is nonempty and $\overline{T(C)}$ is complete, then $F(T, g)$ is a singleton.

Lemma 1.8: [6]

Let C be a subset of a p -normed space X . Then, for any $x \in X$, $P_C(x) \subseteq \partial C$ (the boundary of C).

MAIN RESULTS

In this section we have the following common fixed point with S -convex structure for Banach operator in P -normed spaces.

Theorem 2.1:

Let X be a p -normed space with (S) -convex structure. Let $T, h: X \longrightarrow X$ be Banach operators and $C \subseteq X$ such that $T(\partial C) \subseteq C$. Let $x_0 \in F(T) \cap F(h)$. Suppose that T is h -nonexpansive mapping on $P_C(x_0) \cup \{x_0\}$, h is continuous and $T(F(h)) \subseteq F(h)$ on $P_C(x_0)$, $\overline{T(P_C(x_0))}$ is compact. If $P_C(x_0)$ is nonempty, closed and $h(P_C(x_0)) \subseteq P_C(x_0)$ then $P_C(x_0) \cap F(T) \cap F(h) \neq \emptyset$.

Proof:

Let $D = P_C(x_0)$. First, we show that T is a self mapping on D . Let $y \in D$ then $y \in \partial C$ by Lemma (1.8). Also, since $T(\partial C) \subseteq C$ then $Ty \in C$.

Now, since $hy \in D$ by $h(D) \subseteq D$ and Since $Tx_0 = x_0$ and T is a h -nonexpansive mapping, we have

$$\|Ty - x_0\|_p = \|Ty - Tx_0\|_p \leq \|hy - hx_0\|_p$$

As $hx_0 = x_0$, we therefore have

$$\|Ty - x_0\|_p \leq \|hy - x_0\|_p = d_p(x_0, C),$$

Thus Ty is also closest to x_0 , so $Ty \in D$.

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By (S)-convexity property there is a family $\{f_x\}_{x \in D}$ satisfies conditions of definition (1.2), choose $k_n \in (0,1)$ such that $\langle k_n \rangle \longrightarrow 1$, and define T_n as $T_n(x) = f_{Tx}(k_n)$, for all $x \in D$.

It is clear that T_n is well-defined map from D into D for each n .

Now, we have $T_n, T, h : D \longrightarrow D$ and $T(F(h)) \subseteq F(h)$ on D , for all $x, y \in D$, for each n , we have

$$\begin{aligned}\|T_n x - T_n y\|_p &= \|f_{Tx}(k_n) - f_{Ty}(k_n)\|_p \\ &\leq [\phi(k_n)]^p \|Tx - Ty\|_p \\ &\leq [\phi(k_n)]^p \|hx - hy\|_p\end{aligned}$$

i.e.,

$$\|T_n x - T_n y\|_p \leq [\phi(k_n)]^p \|hx - hy\|_p \text{ for all } x, y \in D.$$

Hence T_n is h -contraction on D .

Now, we have to show that $T_n(F(h)) \subseteq F(h)$, if $x \in F(h)$ then $Tx \in F(h)$ by $T(F(h)) \subseteq F(h)$, and $T_n(x) = f_{Tx}(k_n)$ then $f_{Tx}(k_n) \subseteq Tx$ and $Tx \in F(h)$, implies $T_n(x) \in F(h)$. Hence (T_n, h) is Banach operator on D .

Since $\overline{T(D)}$ is compact, each $\overline{T_n(D)}$ is compact, hence $\overline{T_n(D)}$ is complete. By Theorem (1.7), we have, there exists $x_n \in D$ and $T_n x_n = hx_n = x_n$ for all $n \in \mathbb{N}$.

Since $\overline{T_n(D)}$ is compact, there is a subsequence $\langle Tx_{n_i} \rangle$ of a sequence $\langle Tx_n \rangle$ which converges to $y \in C$.

$$x_{n_i} = hx_{n_i} = T_{n_i} x_{n_i} = f_{Tx_{n_i}}(k_{n_i})$$

By the continuity of T , $\{Tx_{n_i}\}$ converges to Ty . But Tx_{n_i} tends to y by the assumption,

$$T_{n_i} x_{n_i} = f_{Tx_{n_i}}(k_{n_i}) \rightarrow f_{Ty}(1) = Ty, \text{ as } i \rightarrow \infty$$

Thus, $Ty = y$.

Also from the continuity of h , we have

$$hy = h(\lim x_{n_i}) = \lim hx_{n_i} = \lim x_{n_i} = y, \text{ as } i \rightarrow \infty, \text{ i.e. } hy = y.$$

hence $D \cap F(T) \cap F(h) \neq \emptyset$.

This complete the proof. ■

As a consequence, we have

Corollary (1): [4]

Let X be a p -normed space with (S)-convex structure. Let $T, h: X \longrightarrow X$ and $C \subseteq X$ such that $T(\partial C) \subseteq C$. Let $x_0 \in F(T) \cap F(h)$. Suppose that T is h -nonexpansive mapping $P_C(x_0) \cup \{x_0\}$, h satisfies property (C), h is continuous, $Th = hT$ on $P_C(x_0)$, $\overline{T(P_C(x_0))}$ is compact on $P_C(x_0)$. Also assume, range of f_α is contained in $h(P_C(x_0))$. If $P_C(x_0)$ is nonempty, closed and if $h(P_C(x_0)) \subseteq P_C(x_0)$ then $P_C(x_0) \cap F(T) \cap F(h) \neq \emptyset$.

Also, we have another result on an invariant best approximation.

Theorem 2.2:

Let X be a p -normed space whose dual separates the points of X with (S)-convex structure. Let $T, h: X \longrightarrow X$ and $C \subseteq X$ such that $T(\partial C) \subseteq C$. Let $x_0 \in F(T) \cap F(h)$. Suppose that T is h -nonexpansive mapping on $P_C(x_0) \cup \{x_0\}$, h is weakly continuous. If $P_C(x_0)$ is nonempty, weakly compact. If $h(P_C(x_0)) \subseteq P_C(x_0)$ and $T(F(h)) \subseteq F(h)$ on $P_C(x_0)$, then $P_C(x_0) \cap F(T) \cap F(h) \neq \emptyset$ provided $(h-T)$ is demiclosed.

Proof:

Let $D = P_C(x_0)$. First, we show that T is a self mapping on D . Let $y \in D$ then $y \in \partial C$ by Lemma (1.8). Also, since $T(\partial C) \subseteq C$ then $Ty \in C$.

Now, since $hy \in D$ by $h(D) \subseteq D$ and $Tx_0 = x_0$ and T is a h -nonexpansive mapping, we have

$$\|Ty - x_0\|_p = \|Ty - Tx_0\|_p \leq \|hy - hx_0\|_p$$

As $hx_0 = x_0$, we therefore have

$$\|Ty - Tx_0\|_p \leq \|hy - x_0\|_p = d_p(x_0, C)$$

Thus Ty is also closest to x_0 , so $Ty \in D$.

By (S)-convexity property there is a family $\{f_x\}_{x \in D}$ satisfies conditions of definition (1.2), choose $k_n \in (0,1)$ such that $\langle k_n \rangle \longrightarrow 1$, and define T_n as $T_n(x) = f_{Tx}(k_n)$, for all $x \in D$.

It is clear that T_n is well-defined map from D into D for each n .

For all $x, y \in D$, for each n , we have

$$\begin{aligned} \|T_n x - T_n y\|_p &= \|f_{Tx}(k_n) - f_{Ty}(k_n)\|_p \\ &\leq [\phi(k_n)]^p \|Tx - Ty\|_p \end{aligned}$$

$$\|T_n x - T_n y\|_p \leq [\phi(k_n)]^p \|hx - hy\|_p$$

i.e.,

$$\|T_n x - T_n y\|_p \leq [\phi(k_n)]^p \|hx - hy\|_p \text{ for all } x, y \in D.$$

Hence T_n is h -contraction on D .

Now, we have to show that $T_n(F(h)) \subseteq F(h)$, if $x \in F(h)$ then $Tx \in T(F(h))$ by $T(F(h)) \subseteq F(h)$, and $T_n(x) = f_{Tx}(k_n)$ then $f_{Tx}(k_n) \subseteq Tx$ and $Tx \in F(h)$, implies $T_n(x) \subseteq F(h)$, therefore $T_n(F(h)) \subseteq F(h)$.

Now, we have $T_n, T, h: D \longrightarrow D$ and hence (T_n, h) is Banach operator on D .

Since $T_n(D) \subseteq D \subseteq X$ then $\overline{T_n(D)} \subseteq X$ and X is a complete then $\overline{T_n(D)}$ is complete. By Theorem (1.7), we have, there exists $x_n \in D$ and $T_n x_n = hx_n = x_n$ for all $n \in \mathbb{N}$.

Since D is weakly compact, there is a subsequence $\langle x_{n_i} \rangle$ of sequence $\langle x_n \rangle$ which converges to $y \in C$.

$$x_{n_i} = hx_{n_i} = T_{n_i} x_{n_i} = f_{Tx_{n_i}}(k_{n_i})$$

From the weakly continuity of h , we have

$$hy = h(\lim x_{n_i}) = \lim hx_{n_i} = \lim x_{n_i} = y, \text{ as } i \rightarrow \infty, \text{ i.e. } hy = y.$$

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Now, we have to show that $\lim_{i \rightarrow \infty} (h - T) x_{n_i} = 0$

$(h - T) x_{n_i} = h x_{n_i} - T x_{n_i} = x_{n_i} - T x_{n_i} = f_{Tx_{n_i}}(k_{n_i}) - T x_{n_i}$, thus

$\lim_{i \rightarrow \infty} (h - T) x_{n_i} = \lim_{i \rightarrow \infty} f_{Tx_{n_i}}(k_{n_i}) - \lim_{i \rightarrow \infty} T x_{n_i}$

$$= f_{Ty}(1) - Ty$$

$\lim_{i \rightarrow \infty} (h - T) x_{n_i} = Ty - Ty = 0$

Now, $(h - T)$ is demiclosed at 0 and the sequence converges weakly to y .

$(h - T)y = 0$ implies that $y = Ty$.

Hence y is fixed point of T in D . Hence $D \cap F(T) \cap F(h) \neq \emptyset$. ■

As a consequence, we have

Corollary (1): [4]

Let X be a complete p -normed space whose dual separates the points of X with (S) -convex structure. Let $T, h: X \longrightarrow X$ and $C \subseteq X$ such that $T(\partial C) \subseteq C$. Let $x_0 \in F(T) \cap F(h)$. Suppose that T is h -nonexpansive on $P_C(x_0) \cup \{x_0\}$, h satisfies property (C), h is weakly continuous $hT = Th$ on $P_C(x_0)$. Also assume, range of f_α is contained in $h(P_C(x_0))$. If $P_C(x_0)$ is nonempty, weakly compact and $h(P_C(x_0)) \subseteq P_C(x_0)$ then $P_C(x_0) \cap F(T) \cap F(h) \neq \emptyset$.

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A Comparison between Generalized Exponential Distribution and Generalized Raleigh Distribution Using Simulation Technique

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الخلاصة

في الآونة الأخيرة ظهرت عائلة جديدة مشتقة من التوزيع الأسّي أطلق عليها اسم التوزيع الأسّي العام (Generalized Exponential Distribution) حيث تمت ملاحظة أن هذا التوزيع ذو المعلمتين (الشكل والقياس) ملائم للتطبيقات التي يحتاج فيها إلى استخدام التوزيع ألتواني ذو المتغيرات العشوائية الموجبة. في هذا البحث تم استخدام تقدير المئينات وبحجوم عينات مختلفة للمقارنة بين هذا التوزيع وتوزيع رالي العام (Generalized Rayleigh Distribution) من خلال تقديم طرق مقترحة وأخرى مدروسة لحساب النتائج وإيجاد أفضل أداء وباستخدام تقنية المحاكاة.

ABSTRACT

Recently a new family of exponential distribution named as generalized exponential (GE) distribution was introduced. It was observed that the two-parameter (scale and shape) GE distribution can be considered for situations where a skewed distribution of a non-negative random variable is needed. In this paper percentile estimator with different samples sizes have been used in comparison between generalized exponential distribution and generalized rayleigh distribution. A studied as well as suggested method was employed to determine the best results throughout simulation technique.

INTRODUCTION

During the last century, vast activities have been observed in generalizing of the distributions. These distributions were formulated by statisticians, mathematicians, and engineers to mathematically model or represent certain behavior. The two parameters generalized exponential (GE) distribution has been introduced and studied quite extensively by the authors Gupta and Kundu (1) and (2). While the two parameters Burr Type X distribution, which can also be described as generalized Rayleigh (GR) distribution have been proposed by Surles and Padgett (3) and (4). It was observed that this particular skewed distribution can be used quite effectively in analyzing lifetime data (3).

The two parameters GE distribution has the distribution function

$$F_G(t; \alpha, \lambda) = (1 - e^{-\lambda t})^\alpha \quad t, \alpha \text{ and } \lambda > 0.$$

The density function

$$f_G(t) = \alpha \lambda (1 - e^{-\lambda t})^{\alpha-1} e^{-\lambda t}$$

Survival function

$$S_G(t) = 1 - F(t; \alpha, \lambda)$$

And hazard function

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$$h_G(t; \alpha, \lambda) = \frac{f(t; \alpha, \lambda)}{1 - F(t; \alpha, \lambda)} = \frac{\alpha \lambda e^{-\lambda t} (1 - e^{-\lambda t})^{\alpha-1}}{1 - (1 - e^{-\lambda t})^\alpha}$$

Here α and λ , are the shape and scale parameters respectively and the two parameters GE distribution will be denoted by GE ($\alpha; \lambda$) (2).

While the two parameters generalized Rayleigh distribution GR ($\alpha; \lambda$) has the distribution function $F_R(t; \alpha, \lambda)$ as following

$$F_R(t; \alpha, \lambda) = \left(1 - e^{-(\lambda t)^2}\right)^\alpha$$

Density function

$$f_R(t) = 2\alpha\lambda^2(1 - e^{-(\lambda t)^2})^{\alpha-1}e^{-(\lambda t)^2}$$

Survival function

$$S_R(t; \alpha, \lambda) = 1 - (1 - e^{-(\lambda t)^2})^\alpha$$

And hazard function

$$h_R(t; \alpha, \lambda) = \frac{f(t; \alpha, \lambda)}{1 - F(t; \alpha, \lambda)} = \frac{2\alpha\lambda^2 e^{-(\lambda t)^2} (1 - e^{-(\lambda t)^2})^{\alpha-1}}{1 - (1 - e^{-(\lambda t)^2})^\alpha}$$

Here α and λ , are the shape and scale parameters respectively, and the two parameters GR distribution will be denoted by GR ($\alpha; \lambda$) (4).

The two distributions belong to one family named as generalized gamma (5). It is clear that the generalized rayleigh distribution is similar to the generalized exponential distribution when the power of $(e^{-(\lambda t)})$ is equal to one (6). The estimating of the two parameters (shape and scale) of these distributions was proposed for different sample sizes and several contrasts (5) and (6). The main aim of this paper is to present a comparison between generalized exponential distribution (GE) and generalized rayleigh distribution (GR) via computer simulation using percentile estimator method. The mean square error was implemented in this approach to indicate the best performance through out data analysis for different samples size.

Estimators Based on Percentiles

The generalized exponential distribution has the explicit distribution function, therefore in this case the unknown parameters α and λ , can be estimated by equating the sample percentile points with the population percentile points and it is known as the percentile method (7).

Among the most easily obtained estimators of the parameters of the weibull distribution are the graphical approximation to the best linear unbiased estimators. It can be obtained by fitting a straight line to the theoretical points obtained from the distribution function and the sample percentile points. In case of a GE distribution also it is possible to use the same concept to obtain the estimators of α and λ based on the percentiles, because of the structure of its distribution function, when both the parameters are unknown(2).

Since

$$F(t; \alpha, \lambda) = (1 - e^{-\lambda t})^\alpha$$

Therefore

$$T = -\frac{1}{\lambda} \ln \left(1 - [F(t; \alpha, \lambda)]^{\frac{1}{\alpha}} \right)$$

If P_i denotes some estimate of $F(t_{(i)}; \alpha, \lambda)$ then the estimate of α and λ can be obtained by minimizing equation (1) as shown below

$$\sum_{i=1}^n [t_{(i)} + \lambda^{-1} \ln(1 - p_i^{(1/\alpha)})]^2 \quad \text{----- (1)}$$

$$\frac{d}{d\lambda} = \sum_{i=1}^n 2[t_{(i)} + \lambda^{-1} \ln(1 - p_i^{(1/\alpha)})][-\lambda^{-2} \ln(1 - p_i^{(1/\alpha)})]$$

Where $P_i = \frac{i}{n+1}$ represent the studied formula

And $E(F(t_i)) = \frac{i}{n+1}$ the expected value

$$\Rightarrow E(t_i) = F^{-1}\left(\frac{i}{n+1}\right)$$

$F(t)$ represents *c.d.f* for distribution, and $E(t_i)$ named (inverse probability of the cumulative sampling distribution) (8).

Then the suggested formula P_i will be (9)

$$P_i = \frac{i - 0.5}{n + 0.5}$$

Algorithms of the Suggested Method (5)

The cumulative distribution function of the generalized exponential distribution can be written in the form:-

$$F(\hat{t}) = (1 - e^{-\lambda \hat{t}})^\alpha \quad \text{----- (2)}$$

Since the model (2) involves α and λ in a nonlinear way as shown in (1) so it can be transformed and taking its logarithms to the base e as follows:-

$$1 - e^{-\lambda \hat{t}} = F(\hat{t})^{1/\alpha}$$

$$e^{-\lambda \hat{t}} = 1 - F(\hat{t})^{1/\alpha}$$

$$-\lambda \hat{t} = \ln(1 - F(\hat{t})^{1/\alpha})$$

Therefore

$$\hat{t} = -\frac{1}{\lambda} \ln(1 - F(\hat{t})^{1/\alpha}) \quad \text{----- (3)}$$

Using uniform distribution and generating U where

$$U = \begin{cases} 1 & t \in [0, 1] \\ 0 & \text{otherwise} \end{cases}$$

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Since $U=1-U$ in-case of generating continuous uniform random variable,

$$F(\hat{t})^{1/\alpha} = 1 - F(\hat{t})^{1/\alpha} \quad \text{----- (4)}$$

Taking the logarithm, for the both side of Eq (3) then the following equation will produce:

$$\ln(\hat{t}) = \ln\left(\frac{1}{\alpha\lambda}\right) + \ln\left[-\ln F(\hat{t})\right] \quad \text{----- (5)}$$

In equation (5), the slope is a constant and equal to 1, which indicate that $\Delta x = \Delta y$, using simple linear regression equation, then

$$Y_i = \beta_0 + \beta_1 x_i + e_i$$

$$\text{Where } \beta_1 = 1, y_i = \ln(\hat{t}_i) \text{ \& } x_i = \ln\left[-\ln F(\hat{t}_i)\right]$$

Employing the initial value of α & λ in the right side of Eq (5) with substitution of the generating uniform values in $F(\hat{t})=u_i$, to obtain the left side $\hat{t} = \exp(\ln \hat{t})$ and if error is added to this model, then

$$t_i = \hat{t}_i + e_i$$

Since that $E(e) = 0$, where $e \sim \exp(1)$, so the errors are independent and uncorrelated. Hence

$$\ln(\hat{t}_i) + e_i = \ln(t_i) = y_i \text{ \& } x_i = \ln[-\ln(u_i)]$$

The estimator $\hat{\beta}_0 = \ln\left(\frac{1}{\alpha\lambda}\right)$ represents the suggested method

Percentile Estimator (Suggested) Method (5)

$$t'_1 = -\ln \alpha - \ln \lambda + \ln\left[-\ln\left(\frac{i}{n+1}\right)\right]$$

$$t'_2 = -\ln \alpha - \ln \lambda + \ln\left[-\ln\left(\frac{i}{n+1}\right)\right]$$

The sum of two equations obtains:

$$\hat{\alpha}(\lambda) = \exp\left\{\ln\left[-\ln\left(\frac{i}{n+1}\right)\right] - \ln \lambda - \frac{1}{2}(t_1 + t_2)\right\}$$

$$\hat{\lambda}(\alpha) = \exp\left\{\ln\left[-\ln\left(\frac{i}{n+1}\right)\right] - \ln \alpha - \frac{1}{2}(t_1 + t_2)\right\}$$

Where:

$$t_1 = \hat{t}_1 + e_1 \text{ and } t_2 = \hat{t}_2 + e_2$$

$\hat{\alpha}(\lambda)$ & $\hat{\lambda}(\alpha)$ in suggested formula of Pi will be as follows

$$\hat{\alpha}(\lambda) = \exp\left\{\ln\left[-\ln\left(\frac{i-0.5}{n+0.5}\right)\right] - \ln \lambda - \frac{1}{2}(t_1 + t_2)\right\}$$

$$\hat{\lambda}(\alpha) = \exp\left\{\ln\left[-\ln\left(\frac{i-0.5}{n+0.5}\right)\right] - \ln \alpha - \frac{1}{2}(t_1 + t_2)\right\}$$

and for generalized rayleigh distribution the same method is employed to estimate $\hat{\alpha}(\lambda)$ & $\hat{\lambda}(\alpha)$ for obtaining: (6)

$$\hat{\alpha}(\lambda) = \left[\exp \left\{ \ln \left[-\ln \left(\frac{i}{n+1} \right) \right] - 2 \ln \lambda - (t_1 + t_2) \right\} \right]^{1/2}$$

$$\hat{\lambda}(\alpha) = \exp \left\{ \frac{1}{2} \ln \left[-\ln \left(\frac{i}{n+1} \right) \right] - \ln \sqrt{\alpha} - \frac{1}{2} (t_1 + t_2) \right\}$$

While $\hat{\alpha}(\lambda)$ & $\hat{\lambda}(\alpha)$ in suggested formula of P_I will be as follows:-

$$\hat{\alpha}(\lambda) = \left[\exp \left\{ \ln \left[-\ln \left(1 - \frac{i}{n+1} \right) \right] - 2 \ln \lambda - (t_1 + t_2) \right\} \right]^{1/2}$$

$$\hat{\lambda}(\alpha) = \exp \left\{ \frac{1}{2} \ln \left[-\ln \left(\frac{i-0.5}{n+0.5} \right) \right] - \ln \sqrt{\alpha} - \frac{1}{2} (t_1 + t_2) \right\}$$

Empirical work

One of the most important applications of computer science is computer simulation. It is an attempt to model a real-life on a computer so that it can be studied to see how the system works. By changing variables, predictions may be made about the behavior of the system computer simulation has become a useful part of modeling many systems in economics, finance, and several applications (10). This analysis may be done, sometimes, through analytical or numerical methods, but the model may be too complex to be dealt with. Essentially, simulation process consists of building a computer model that describes the behavior of a system and experimenting with this computer model to reach conclusions that support decisions (11).

A simulation prototype have been proposed in order to make discriminating between the two distributions which were studied in the previous sections to reach into the best estimated method of the shape parameter and scale parameter. A several assumption of many cases is provided which it can be existed in real world and results of the corresponding simulation model are listed in the tables (1) and (2).

Table 1: Estimation of Scale and Shape Parameters of (GE) for (suggested and studied formula)

The Results of Simulation Methods

Sample	Method	Assumed Parameter		Estimators		Indicator
		α	λ	$\hat{\alpha}$	$\hat{\lambda}$	MSE
20	PCE studied	1	1	0.175853	0.175853	1.00582
		1	2	0.202638	0.346885	1.014435
		2	1	0.352757	0.174889	1.089119
		2	2	0.128318	0.128318	0.98849

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50	PCE suggested	1	1	0.19071	0.19071	1.001856
		1	2	0.186089	0.369685	1.078668
		2	1	0.329006	0.166341	1.139985
		2	2	0.137543	0.137543	1.009131
	PCE studied	1	1	0.211527	0.211527	1.034397
		1	2	0.1339	0.26885	1.043127
		2	1	0.298843	0.146531	1.019789
		2	2	0.167614	0.167614	0.999185
100	PCE suggested	1	1	0.21794	0.21794	0.988838
		1	2	0.138827	0.419052	1.000776
		2	1	0.339917	0.174096	0.971238
		2	2	0.175497	0.175497	0.997316
	PCE studied	1	1	0.249629	0.249629	1.022964
		1	2	0.132157	0.264314	1.01573
		2	1	0.308093	0.147665	1.020181
		2	2	0.173671	0.173671	1.043462
	PCE suggested	1	1	0.259124	0.259124	0.97395
		1	2	0.136998	0.273147	1.001824
		2	1	0.289266	0.144633	0.975676
		2	2	0.180493	0.180493	0.997316

Table 2: Estimation of Scale and Shape Parameters of (GR) for (suggested and studied formula)

The Results of Simulation methods

Sample	Method	Assumed Parameter		Estimators		Indicator
		α	λ	$\hat{\alpha}$	$\hat{\lambda}$	MSE
20	PCE studied	1	1	0.130645	0.130645	3.10325
		1	2	0.205795	0.346934	2.446409
		2	1	0.260983	0.181641	1.614332
		2	2	0.125566	0.177578	2.594462
	PCE suggested	1	1	0.13282	0.13282	1.456683
		1	2	0.184391	0.359877	2.504632
		2	1	0.221384	0.158	2.702558
		2	2	0.127188	0.179871	2.051962

50	PCE studied	1	1	0.168913	0.168913	2.667632
		1	2	0.141036	0.283179	2.082187
		2	1	0.209621	0.146927	1.617342
		2	2	0.149932	0.212036	1.308038
	PCE suggested	1	1	0.1721	0.1721	2.473099
		1	2	0.144298	0.431658	2.478395
		2	1	0.210311	0.149445	1.817146
		2	2	0.153072	0.2164759	3.208128
100	PCE studied	1	1	0.194146	0.194146	1.593123
		1	2	0.118901	0.237803	2.388022
		2	1	0.217849	0.152913	2.73559
		2	2	0.1536	0.2172234	2.011512
	PCE suggested	1	1	0.196815	0.196815	1.753823
		1	2	0.119837	0.240805	2.22064
		2	1	0.217955	0.154118	1.214269
		2	2	0.155098	0.2193424	1.385011

CONCLUSION

Through out the simulation process and estimating the two parameters (shape and scale) of a percentile estimator for the both distributions with taking different sample sizes (20,50,100) and assumed several contrasts $\alpha, \lambda, [(1,1) (1,2) (2,1) (2,2)]$ respectively.

From table (1) & table (2), with using the mean square error as an indicator of performance, it was observed the following:-

1-For the studied method of percentile estimator the following results are obtained:-

(i) Small sample size (n=20)

For the assumed contrast parameters (2, 1), (1, 2), (2, 2) and (1, 1) the (GE) was given the best results.

(ii) Medium sample size (n=50).

For the assumed contrast parameters (2, 2), (2, 1), (1, 2), and (1, 1) the (GE) was given the best result.

(iii) Large sample size (n=100).

For the assumed contrast parameters (1, 1), (2, 2), (1, 2), and (2, 1) the (GE) was given the best result.

2-For the suggested method of percentile estimator the following results are obtained:-

(i) Small sample size (n=20)

For the assumed contrast parameters (1, 1), (2, 2), (1, 2), and (2, 1), the (GE) was given the best result.

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(ii) Medium sample size (n=50)

For the assumed contrast parameters (2, 1), (1, 1), (1, 2) and (2, 2) the (GE) was given the best results.

(iii) Large sample size.(n=100)

For the assumed contrast parameters (2, 1), (2, 2), (1, 1), and (1, 2) the (GE) was given the best results

From the obtaining results it can be concluded that the (GE) distribution has given a better estimator for all employed samples size via implemented the suggested and studied formula in comparison with generalized rayleigh distribution (GR).

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Rational Solutions of First and Second Equations of Burgers' Hierarchy

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الخلاصة

الغاية من البحث هو إيجاد الحلول النسبية لمعادلتين برجرس الأولى والثانية بتبسيط الطريقة المتبعة من قبل العلماء ديكونك , كايميرا وسيكور . طبقت الطريقة على معادله برجرس حيث نوقشت الصعوبات الناتجة عن الطريقة المتبعة من قبل العلماء اعلاه . الان نستطيع تطبيق الطريقة المبسطة على معادلتين برجرس الأولى والثانية حيث تمت دراسة سلوك الاقطاب الخاصة بالحلول النسبية.

ABSTRACT

The aim of this work is to find rational solutions of first and second equations of Burgers' hierarchy by simplifying the method presented by Deconinck ,Kimura and Segure, and have been applied to Burgers' equation. We discuss their technique and it difficulties, then we can easily, apply the simplified technique to the first and second equations of Burgers' hierarchy. In addition, the behavior of the poles of the obtained rational solutions are also examined.

INTRODUCTION

It is well known that the Burgers' hierarchy is a family of nonlinear evolution equation. This hierarchy can be written in the form [2]

$$\frac{\partial u}{\partial t} + \alpha \frac{\partial}{\partial x} \left(\frac{\partial}{\partial x} + u \right)^n u = 0 \quad \dots (1)$$

Where α is nonzero constant. It becomes Burges' equation when $n=1$.

Sharma-Tasso-Oliver equation in short (STO) equation whenever $n=2$.

$$\frac{\partial u}{\partial t} + \alpha \frac{\partial^3 u}{\partial x^3} + 3\alpha \left(\frac{\partial u}{\partial x} \right)^2 + 3\alpha u \frac{\partial^2 u}{\partial x^2} + 3\alpha u^2 \frac{\partial u}{\partial x} = 0 \quad \dots (2)$$

It is well known that the rational function $R(x) = \frac{p(x)}{q(x)}$ is a quotient of two polynomials $p(x)$ and $q(x)$ with no common factors and hence no common zeros. The zeros of $q(x)$ are called poles of $R(x)$ and the order of a pole is by definition equal to the order of corresponding zero of $q(x)$ [5].

Sometimes solutions are expressed as a rational functions. In other cases, they are used to describe the explode-decay waves, the motion of the

vortexes [3]. Deconinck, Kimura and Segure in [1] gives a special form of rational solution of Burgers' equation which is of the form

$$u(x, t) = -2\nu \sum_{k=1}^N \frac{R_k(t)}{x - X_k(t)} \quad \dots (3)$$

where N is the number of poles $X_k(t)$ denotes the positions of the k -th pole. We refer their techniques by DKS technique.

Rational Solutions of Burgers' Equation by DKS technique [1]

The Burgers' equation is given by

$$\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} = \nu \frac{\partial^2 u}{\partial x^2}, \quad \nu \geq 0 \quad \dots (4)$$

A rational solution with N poles is presented by Deconinck, Kimura and Segure of the form

$$u(x, t) = -2\nu \sum_{k=1}^N \frac{R_k(t)}{x - X_k(t)} \quad (3.1)$$

where $X_k(t)$ denotes the time dependent -position of the k -th pole in the complex plane, and $R_k(t)$ be its residue. This representation is valid as long as no poles collide. Substitution in Burgers' equation and assume that $x = X_k + \varepsilon$ give $R_k = 1$ for all $1 \leq k \leq N$ where k is integer. and

$$\frac{dX_k}{dt} = -2\nu \sum_{n \neq k}^N \frac{1}{X_k - X_n}.$$

DKS Algorithm [1]

Let us summarize DKS technique for solving partial differential equations as understood from its applications to Burgers' equation in the following steps:

Step1: Since the procedure will be the same for all poles, hence fix the first pole $X_1(t)$ and let $x = X_1 + \varepsilon$. where ε belong to complex numbers.

Step2: Write the function u as $u = R_1 \varepsilon^{-1} + F(\varepsilon, t)$, where

$$F(\varepsilon, t) = \sum_{k=2}^N \frac{R_k}{(X_1 - X_k + \varepsilon)}, \text{ where } X_1 - X_k + \varepsilon \neq 0$$

Then expand the function F in a Taylor series of ε and then plug u and its derivatives in the given equation.

Step 3: Equate the coefficients of ε^m where m is integer to zero beginning with the most singular term in ε to find the value of $R_k(t)$ and the dynamical system which governs the motion of the k -th pole.

The Simplified DKS Algorithm

When DKS technique is used for seeking rational solution of a PDE, and when expanding in Taylor series the equating to zero will be tedious and it looks as can not be stopped. Hence some simplifications seem to be

necessary. We shall here replace step2 and step3 in DKS algorithm by the following:

Step2* Write u as $u = R_1 \varepsilon^{-n} + F(\varepsilon, t)$, where $F = \sum_{k=2}^N \frac{R_k}{(X_1 - X_k + \varepsilon)^n}$ and then

represent the function F as a polynomial and plug u and its derivatives in the given equation.

Step3* Equate the coefficients to zero beginning with the most positive power of ε or the most singular term alternatively. In [13] the form (3.1) is generalized to the form:

$$u(x, t) = \sum_{k=1}^N \frac{R_k(t)}{[x - X_k(t)]^n} \quad \dots (5)$$

and n is obtained in an algorithmic procedure. Following [13], and using the simplified DKS algorithm, we will obtain some rational solutions to one-dimensional first and second equations of Burgers' hierarchy.

Before we apply the technique, let us rewrite u and its derivatives as:

$$u(x, t) = \frac{R_1}{(x - X_1)^n} + \sum_{k=2}^N \frac{R_k}{(x - X_k)^n} \quad \text{Where } x \text{ belong to complex numbers.}$$

Since $x = X_1 + \varepsilon$, hence $u(x, t)$ will be a function of ε and t , it becomes:

$$u(x, t) = \frac{R_1}{\varepsilon^n} + F(\varepsilon, t), \quad \text{where } F(\varepsilon, t) = \sum_{k=2}^N \frac{R_k(t)}{(X_1 - X_k + \varepsilon)^n}$$

$$\frac{\partial u}{\partial t} = \frac{dR_1}{dt} \varepsilon^{-n} + nR_1 \frac{dX_1}{dt} \varepsilon^{-(n+1)} + G(\varepsilon, t)$$

$$\frac{\partial u}{\partial x} = -nR_1 \varepsilon^{-(n+1)} + H_1(\varepsilon, t)$$

$$\frac{\partial^2 u}{\partial x^2} = n(n+1)R_1 \varepsilon^{-(n+2)} + H_2(\varepsilon, t)$$

$$\frac{\partial^3 u}{\partial x^3} = -n(n+1)(n+2)R_1 \varepsilon^{-(n+3)} + H_3(\varepsilon, t)$$

$$\text{where } G(\varepsilon, t) = \frac{\partial F}{\partial t}, H_1(\varepsilon, t) = \frac{\partial F}{\partial \varepsilon}, H_2(\varepsilon, t) = \frac{\partial^2 F}{\partial \varepsilon^2}, H_3(\varepsilon, t) = \frac{\partial^3 F}{\partial \varepsilon^3}$$

Let

$$F(\varepsilon, t) = F(0, t) + F_\varepsilon(0, t)\varepsilon + \frac{1}{2}F_{\varepsilon\varepsilon}(0, t)\varepsilon^2 + \frac{1}{6}F_{\varepsilon\varepsilon\varepsilon}(0, t)\varepsilon^3 + o(\varepsilon^4) \quad \dots (6)$$

where $\frac{\partial^i F}{\partial \varepsilon^i}$ denotes the i -th derivatives of $F(\varepsilon, t)$ with respect to ε at $\varepsilon = 0$.

$i = 1, 2, 3$.

This yields:

$$H_1(\varepsilon, t) = F_\varepsilon(0, t) + F_{\varepsilon\varepsilon}(0, t)\varepsilon + \frac{1}{2}F_{\varepsilon\varepsilon\varepsilon}(0, t)\varepsilon^2 + o(\varepsilon^3)$$

$$H_2(\varepsilon, t) = F_{\varepsilon\varepsilon}(0, t) + F_{\varepsilon\varepsilon\varepsilon}(0, t)\varepsilon + o(\varepsilon^2)$$

$$H_3(\varepsilon, t) = F_{\varepsilon\varepsilon\varepsilon}(0, t) + o(\varepsilon)$$

$$G(\varepsilon, t) = F_t(0, t) + F_{t\varepsilon}(0, t)\varepsilon + \frac{1}{2}F_{t\varepsilon\varepsilon}(0, t)\varepsilon^2 + \frac{1}{6}F_{t\varepsilon\varepsilon\varepsilon}(0, t)\varepsilon^3 + o(\varepsilon^4)$$

In the following section the form (3.3) with the simplified DKS algorithm is applied to Burgers' equation:

Rational Solution of Burgers' Equation by Simplified DKS Technique

Consider Burgers' equation of the form

$$\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} = \nu \frac{\partial^2 u}{\partial x^2}, \quad \nu \geq 0$$

$$\text{Let } u(x, t) = \sum_{k=1}^N \frac{R_k(t)}{(x - X_k(t))^n}.$$

Be a rational solution of Burgers' equation then we get:

$$\frac{dR_1}{dt}\varepsilon^{-1} + nR_1 \frac{dX_1}{dt}\varepsilon^{-2} + F_t(0, t) + F_{t\varepsilon}(0, t)\varepsilon + \frac{1}{2}F_{t\varepsilon\varepsilon}(0, t)\varepsilon^2 + \frac{1}{6}F_{t\varepsilon\varepsilon\varepsilon}(0, t)\varepsilon^3 -$$

$$R_1^2\varepsilon^{-3} - R_1\varepsilon^{-2} \left\{ F(0, t) + F_\varepsilon(0, t)\varepsilon + \frac{1}{2}F_{\varepsilon\varepsilon}(0, t)\varepsilon^2 + \frac{1}{6}F_{\varepsilon\varepsilon\varepsilon}(0, t)\varepsilon^3 \right\}$$

$$+ R_1\varepsilon^{-1} \left\{ F_\varepsilon(0, t) + F_{\varepsilon\varepsilon}(0, t)\varepsilon + \frac{1}{2}F_{\varepsilon\varepsilon\varepsilon}(0, t)\varepsilon^2 \right\} +$$

$$\left\{ F_\varepsilon(0, t) + F_{\varepsilon\varepsilon}(0, t)\varepsilon + \frac{1}{2}F_{\varepsilon\varepsilon\varepsilon}(0, t)\varepsilon^2 \right\} \times$$

$$\left\{ F(0, t) + F_\varepsilon(0, t)\varepsilon + \frac{1}{2}F_{\varepsilon\varepsilon}(0, t)\varepsilon^2 + \frac{1}{6}F_{\varepsilon\varepsilon\varepsilon}(0, t)\varepsilon^3 \right\}$$

$$= 2\nu R_1\varepsilon^{-3} + \nu F_{\varepsilon\varepsilon}(0, t) + \nu F_{\varepsilon\varepsilon\varepsilon}(0, t)\varepsilon$$

We begin with the most positive term which is ε^5 then

$$F_{\varepsilon\varepsilon\varepsilon}(0, t) = F_{t\varepsilon\varepsilon\varepsilon}(0, t) = 0$$

From the coefficients of the terms of ε^3 get $F_{\varepsilon\varepsilon}(0, t) = F_{t\varepsilon\varepsilon}(0, t) = 0$

The coefficients of ε gives $F_{t\varepsilon}(0, t) + (F_\varepsilon(0, t))^2 = 0$

Solve the above equation we get $F_\varepsilon(0, t) = \frac{1}{t - A_1}$, where A_1 is arbitrary variable, $t \neq A_1$.

From the coefficients of ε^0 we get $F_t(0, t) + F(0, t)F_\varepsilon(0, t) = 0$

Then by solve the above equation we get $F(0, t) = \frac{A_2}{t - A_1}$, where A_2 is

arbitrary constant. Then $F(\varepsilon, t) = \frac{A_2}{t - A_1} + \frac{\varepsilon}{t - A_1}$ where $t \neq A_1$

Now for the singular terms:

The most singular term have the behavior ε^{-3} equating their coefficients to zero get $R_1 = -2\nu$. The coefficients of ε^{-2} gives $\frac{dX_1}{dt} = F(0, t) = \frac{A_2}{t - A_1}$.

Then $X_1 = A_2 \log A_3 (t - A_1)$ where $A_3 (t - A_1)$ is positive.

While the coefficients of ε^{-1} vanish identically.

So the solution will be of the form

$$u(x, t) = R_1 (x - X_1)^{-1} + \frac{A_2}{t - A_1} + \frac{x - X_1}{t - A_1}, \quad t \neq A_1$$

Rational Solution of Sharma -Tasso- Oliver Equation by Simplified DKS Technique

Recall STO equation [12],

$$\frac{\partial u}{\partial t} + \alpha \frac{\partial^3 u}{\partial x^3} + 3\alpha \left(\frac{\partial u}{\partial x} \right)^2 + 3\alpha u \frac{\partial^2 u}{\partial x^2} + 3\alpha u^2 \frac{\partial u}{\partial x} = 0$$

Let $u(x, t) = \sum_{k=1}^N \frac{R_k(t)}{(x - X_k(t))^n}$. By [4] $n=1$, and using (3.3) Then we have

the identity:

$$\begin{aligned} & \frac{dR_1}{dt} \varepsilon^{-1} + R_1 \frac{dX_1}{dt} \varepsilon^{-2} + F_t(0, t) + F_{t\varepsilon}(0, t) \varepsilon + \frac{1}{2} F_{t\varepsilon\varepsilon}(0, t) \varepsilon^2 + \frac{1}{3} F_{t\varepsilon\varepsilon\varepsilon}(0, t) \varepsilon^3 \\ & + \alpha \left[-6R_1 \varepsilon^{-4} + F_{\varepsilon\varepsilon\varepsilon}(0, t) \right] + 3\alpha \left[-R_1 \varepsilon^{-2} + F_{\varepsilon}(0, t) + F_{\varepsilon\varepsilon}(0, t) \varepsilon + \frac{1}{2} F_{\varepsilon\varepsilon\varepsilon}(0, t) \varepsilon^2 \right]^2 \\ & + 3\alpha \left[R_1 \varepsilon^{-1} + F(0, t) + F_{\varepsilon}(0, t) \varepsilon + \frac{1}{2} F_{\varepsilon\varepsilon}(0, t) \varepsilon^2 + \frac{1}{6} F_{\varepsilon\varepsilon\varepsilon}(0, t) \varepsilon^3 \right] \times \\ & \left[2R_1 \varepsilon^{-3} + F_{\varepsilon\varepsilon}(0, t) + F_{\varepsilon\varepsilon\varepsilon}(0, t) \varepsilon \right] \\ & + 3\alpha \left[R_1 \varepsilon^{-1} + F(0, t) + F_{\varepsilon}(0, t) \varepsilon + \frac{1}{2} F_{\varepsilon\varepsilon}(0, t) \varepsilon^2 + \frac{1}{6} F_{\varepsilon\varepsilon\varepsilon}(0, t) \varepsilon^3 \right]^2 \times \\ & \left[-R_1 \varepsilon^{-2} + F_{\varepsilon}(0, t) + F_{\varepsilon\varepsilon}(0, t) \varepsilon + \frac{1}{2} F_{\varepsilon\varepsilon\varepsilon}(0, t) \varepsilon^2 \right] = 0 \end{aligned}$$

The most positive power is ε^8 then equating their coefficients to zero we get $F_{\varepsilon\varepsilon\varepsilon}(0, t) = F_{t\varepsilon\varepsilon\varepsilon}(0, t) = 0$, and from coefficients of ε^5 , ε^2 we get

$$F_{\varepsilon\varepsilon}(0, t) = F_{t\varepsilon\varepsilon}(0, t) = 0, \quad F_{\varepsilon}(0, t) = F_{t\varepsilon}(0, t) = 0$$

respectively. We conclude that $H_1(0, t) = H_2(0, t) = H_3(0, t) = 0$

The most singular term have the behavior ε^{-4} , by equating their coefficients to zero we get that $R_1^3 - 3R_1^2 + 2R_1 = 0$, Since $R_1 \neq 0$

Then $R_1^2 - 3R_1 + 2 = 0$ So that either $R_1 = 1$ or $R_1 = 2$

From the coefficients of ε^{-3} we get $[6\alpha R_1 - 6\alpha R_1^2] F(0, t) = 0$

Now from the coefficients of ε^{-2} we get $\frac{dX_1}{dt} = 3\alpha F^2(0, t)$

and the coefficients of ε^0 gives $F_t(0, t) = 0$, i.e. $F(0, t) = \text{Constant}$

This leads to two rational solutions to the STO equation the first is when $R_1 = R_i = 2$ which implies that $F(0, t) = 0$ and $\frac{dX_1}{dt} = 0$ i.e.

$$X_i(t) = c_i, i = 1, 2, \dots, N$$

and consequently $u = 2 \sum_{i=1}^N \frac{1}{x - c_i}$ which is a function of x only where

$$x \neq c_i, \text{ and the second is when } R_1 = R_i = 1 \text{ and } \frac{dX_i}{dt} = A_i \text{ i.e. } X_i(t) = A_i t + B_i.$$

The solution will be of the form $u(x, t) = \sum_{i=1}^N \frac{1}{x - A_i t - B_i}$. Where $x \neq A_i t + B_i$

So, we conclude:

1. The difference between DKS technique for Burgers' equation and ours is that, in addition to simplicity we can find explicit form for the motion of the poles while for DKS technique they tried the similarity solution.
2. We notice that when the function $F(\varepsilon, t)$ or $F(\varepsilon, y, t)$ are approximated (i.e Taylor series is transited to the third degree or more general to the n -th degree even if $(n \rightarrow \infty)$ many coefficients of ε^n in the series are vanished, that because of the presence of merely the same terms in most of the equations. Thus we can assume that F is linear without loss of generality.
3. Unfortunately, our methodology does not allow us to prove that the technique (simplified DKS) lead to a solution. Nevertheless, we can implement the obtained form in the PDE imposing some conditions to the parameters.

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Bayes Estimator of the Shape Parameter of Generalized Exponential Distribution

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الخلاصة

تم إيجاد مقدر بيز لمعلمة الشكل الى التوزيع الاسي المعمم باستخدام التوزيع الاول لجفري وتوزيع كاما الاول وقد اعتمدت دالة LINEX للخسارة. وتم تصميم تجارب المحاكاة ومن ثم تمت المقارنة بين المقدرات باستخدام متوسط مربعات الخطأ. وقد اظهرت النتائج ان مقدرات بيز ذات توزيع كاما الأولي أفضل من مقدرات بيز ذات التوزيع الاول لجفري ولجميع احجام العينات. أيضا كانت مقدرات البيز أفضل من مقدرات طريقة الإمكان الأعظم ولجميع أحجام العينات.

ABSTRACT

Bayes estimators for the shape parameter of generalized exponential distribution are obtained. Two prior density functions, Jeffery prior information and gamma conjugate prior were used to find the Bayes estimators. LINEX (linear-exponential) error loss function was considered. Simulation study was designed and mean square error criterion was used to compare between the two methods. The results show that the estimators with gamma conjugate prior density function were better than the estimators with Jeffery prior density function at all sample sizes. In addition Bayes estimators with two types of prior density function had lower mean square errors than maximum likelihood estimator for all sample sizes.

INTRODUCTION

The generalized exponential distribution is defined as a particular case of the Gompertz-Verhulst distribution function [1] which is as follows

$$G(x) = (1 - pe^{-\lambda x})^\alpha; x > (1/\lambda \ln p) \dots\dots\dots (1)$$

When $p=1$. Therefore, X is a two-parameter generalized exponential random variable and it has the distribution function

$$F(x; \alpha; \lambda) = (1 - e^{-\lambda x})^\alpha; x > 0, \dots\dots\dots (2)$$

For $\alpha, \lambda > 0$. Here α and λ , play the role of the shape and scale parameters respectively. The two-parameter generalized exponential distribution is a particular member of the family of the three-parameter exponentiated Weibull distribution, introduced by Mudholkar and Srivastava [2]. The two-parameter generalized exponential distribution can be used quite effectively to analyze positive lifetime data, particularly, in place of the two-parameter gamma or two-parameter Weibull distributions [3]. Moreover, when the

shape parameter $\alpha=1$, it coincides with the one-parameter exponential distribution. The generalized exponential distribution also has some nice physical interpretations. Consider a parallel system, consisting of n components, i.e., the system works, only when at least one of the n -components works. If the lifetime distributions of the components are independent identically distributed (i.i.d.) exponential random variables[4], then the lifetime distribution of the system becomes

$$F(x; n; \lambda) = (1 - e^{-\lambda x})^n; \quad x > 0, \dots \quad (3)$$

For $\lambda > 0$. Clearly, (3) represents the generalized exponential distribution function with $\alpha = n$.

The main aim of this study is to estimate shape parameter of the generalized exponential distribution.

If the random variable X has the distribution function in eq.(2), then it has the density function

$$f(x; \alpha; \lambda) = \alpha \lambda (1 - e^{-\lambda x})^{\alpha-1} e^{-\lambda x} \quad x > 0; \dots \quad (4)$$

for $\alpha; \lambda, > 0$. The density functions of the generalized exponential distribution can take different shapes[5]. For $\alpha \leq 1$, it is a decreasing function and for $\alpha > 1$, it is a unimodal, skewed, right tailed similar to the Weibull or gamma density function[6]. Varian[7] and Zellner [8] proposed an asymmetric loss function known as LINEX loss function which is given by

$$L(\Delta) = e^{a\Delta} - a\Delta - 1; \quad a \neq 0, \dots \quad (5)$$

and $\Delta = (\hat{\alpha} - \alpha)$ when $\hat{\alpha}$ is estimation of α . "a" represent the degree of asymmetry. for "a" nears to zero, the LINEX loss function is approximately the squared error loss.

Bayes Estimator using Jeffery prior Information

Assuming that the scale parameter λ is known, with out loss of generality, and we assume that $\lambda=1$. suppose X_1, X_2, \dots, X_n is random sample from the generalized exponential distribution with p.d.f. given in eq.(4)

Jeffery prior^[9] of one parameter is defined by: $g(\alpha) \propto \sqrt{I(\alpha)}$, where

$$\sqrt{I(\alpha)} = \sqrt{\text{Fisher information}}$$

$$I(\alpha) = -n E(\partial^2 \ln f(x, \alpha) / \partial \alpha^2)$$

$f(x, \alpha) = \alpha (1 - e^{-x})^{\alpha-1} e^{-x}$, α is shape parameter of generalized exponential distribution.

$$\ln f(x, \alpha) = \ln \alpha + (\alpha - 1) \ln (1 - e^{-x}) - x$$

$$E\left(\frac{\partial^2 \ln f(x, \alpha)}{\partial \alpha^2}\right) = -1/\alpha^2$$

$$I(\alpha) = n/\alpha^2$$

When $g(\alpha) \propto \sqrt{I(\alpha)}$

$g(\alpha) = M\sqrt{n} / \alpha$, where M is normalizing factor.

The likelihood function of generalized exponential distribution is

$$\alpha^n \prod_{i=1}^n (1 - e^{-x_i})^{\alpha-1} \cdot e^{-\sum x_i} \dots\dots\dots (6)$$

The natural logarithm of eq. (6) is

$$= n \ln \alpha + \sum_{i=1}^n (\alpha - 1) \ln(1 - e^{-x_i}) - \sum_{i=1}^n x_i \dots\dots\dots (7)$$

The maximum likelihood estimate (MLE) of the parameter α had been found by Gupta and Kundu [4] and it was

$$\hat{\alpha}_{m.l.e} = n / - \sum_{i=1}^n \ln(1 - e^{-x_i}) \dots\dots\dots (8)$$

Let $Y = -\ln(1 - e^{-X})$

The c.d.f. of Y is $P(Y \leq y)$

$$= P(-\ln(1 - e^{-X}) \leq y)$$

$$= P(e^{-X} \leq (1 - e^{-y}))$$

$$= 1 - (pr(X \leq (-\ln(1 - e^{-y}))))$$

$$= 1 - (1 - e^{\ln(1 - e^{-y}) \alpha})$$

$$= 1 - e^{-\alpha y} \dots\dots\dots (9)$$

$F(y)$ given in (9) can be seen to be the c.d.f. of the exponential dis. With mean $1/\alpha$. Let $Y_i = -\ln(1 - e^{-X_i})$, where X_1, X_2, \dots, X_n is a $GE(1, 1/\alpha)$ random sample.

Then Y_1, Y_2, \dots, Y_n is an exponential random sample, and it follows that

$Z = \sum_{i=1}^n Y_i$ has a gamma distribution with shape parameter n and scale

parameter $1/\alpha$. thus, the distribution of (αZ) is $\text{gamma}(n, 1)$.

The probability density function of Z is

$$f(Z) = \alpha^n / \Gamma(n) z^{n-1} e^{-\alpha z}, z > 0 \dots\dots\dots (10)$$

the marginal probability density function of Z is given by

$$\int_0^\infty \alpha^n / \Gamma(n) z^{n-1} e^{-\alpha z} \cdot g(\alpha) d\alpha$$

$$= \int_0^\infty M \sqrt{n} \alpha^n / \alpha \Gamma(n) z^{n-1} e^{-\alpha z} d\alpha$$

$$= M z^{n-1} \sqrt{n} / \Gamma(n) \int_0^\infty \alpha^{n-1} e^{-\alpha z} d\alpha$$

$$= M Z^{n-1} \sqrt{n} \Gamma(n) / \Gamma(n) Z^n = M \sqrt{n} / Z$$

the posterior density of α given the data is

$$= \frac{\alpha^{n-1} z^n e^{-\alpha z}}{\Gamma(n)} \dots\dots\dots (11)$$

Using LINEX loss function $L(\hat{\alpha}, \alpha) = (e^{a(\hat{\alpha} - \alpha)} - a(\hat{\alpha} - \alpha) - 1)$, $a \neq 0$

The risk function is $R(\hat{\alpha}, \alpha) = E L(\hat{\alpha}, \alpha)$

$$\begin{aligned} &= \int_0^{\infty} L(\hat{\alpha}, \alpha) \frac{\alpha^{n-1} z^n e^{-\alpha z}}{\Gamma(n)} d\alpha \\ &= \int_0^{\infty} e^{a(\hat{\alpha} - \alpha)} \frac{\alpha^{n-1} z^n e^{-\alpha z}}{\Gamma(n)} d\alpha - \int_0^{\infty} a(\hat{\alpha} - \alpha) \frac{\alpha^{n-1} z^n e^{-\alpha z}}{\Gamma(n)} d\alpha - \int_0^{\infty} \frac{\alpha^{n-1} z^n e^{-\alpha z}}{\Gamma(n)} d\alpha \\ &= \frac{z^n}{\Gamma(n)} e^{a\hat{\alpha}} \int_0^{\infty} e^{-\alpha(a+z)} \alpha^{n-1} d\alpha - \frac{a\hat{\alpha}}{\Gamma(n)} z^n \int_0^{\infty} \alpha^n e^{-\alpha z} d\alpha - \frac{z^n}{\Gamma(n)} \int_0^{\infty} \alpha^{n+1} e^{-\alpha z} d\alpha - \\ &\quad \frac{z^n}{\Gamma(n)} \int_0^{\infty} \alpha^{n-1} e^{-\alpha z} d\alpha = \frac{z^n}{\Gamma(n)} e^{a\hat{\alpha}} \frac{\Gamma(n)}{(a+z)^n} - \frac{a\hat{\alpha}}{\Gamma(n)} \Gamma(n) - \frac{z^n}{\Gamma(n)} \int_0^{\infty} \alpha^{n+1} e^{-\alpha z} d\alpha - \\ &\quad \frac{z^n}{\Gamma(n)} \int_0^{\infty} \alpha^{n-1} e^{-\alpha z} d\alpha \dots\dots\dots (12) \end{aligned}$$

We must drive (12) with respect to $\hat{\alpha}$

$$= \frac{z^n}{(a+z)^n} a e^{a\hat{\alpha}} - a = 0$$

$$e^{a\hat{\alpha}} = ((a+z)/z)^n \rightarrow a\hat{\alpha} = n \ln((a+z)/z)$$

$$\hat{\alpha}_{BI} = n/a \cdot \ln((a+z)/z), \quad a \neq 0 \dots\dots\dots (13)$$

Where $\hat{\alpha}_{BI}$ denoted the LINEX Bayes estimator of shape parameter for generalized exponential distribution using Jeffery prior Information.

Bayes Estimator using gamma conjugate prior density

We assume that α has a gamma conjugate prior $\Gamma(1, \beta)$

$$\pi(\alpha, \beta) = \beta \exp(-\beta\alpha), \quad \alpha > 0, \beta > 0$$

We regard random variable α with prior density as exponential distribution $\exp(\beta)$, which is usually used in Bayesian estimation^[10].

The joint probability density function

$$\begin{aligned} &(\alpha^{n-1} / \Gamma(n) z^{n-1} e^{-\alpha z}) \cdot (\beta \exp(-\beta\alpha)) \\ &= \beta z^{n-1} \frac{\alpha^{n-1}}{\Gamma(n)} e^{-\alpha(\beta+z)} \end{aligned}$$

the marginal probability density function of (z_1, z_2, \dots, z_n) is given by

$$f(Z) = \beta z^{n-1} \int_0^{\infty} \frac{\alpha^{n-1}}{\Gamma(n)} e^{-\alpha(\beta+z)} d\alpha$$

$$\text{Let } m = \alpha(\beta+z)$$

$$f(Z) = \frac{\beta z^{n-1}}{\Gamma(n)} \int_0^{\infty} e^{-m} \cdot m^{n-1} \frac{dm}{(\beta+z)^{n-1} (\beta+z)}$$

$$= \frac{\beta z^{n-1}}{\Gamma(n)(\beta+z)^n} \cdot \Gamma(n)$$

$$= \frac{\beta z^{n-1}}{(\beta+z)^n}$$

the posterior density of α given the data (z_1, z_2, \dots, z_n) is

$$\frac{\alpha^{n-1} e^{-\alpha(\beta+z)} (\beta+z)^n}{\Gamma(n)}, \quad \beta > 0, z > 0, \alpha > 0 \dots\dots\dots(14)$$

The risk function is

$$\int_0^\infty L(\hat{\alpha}, \alpha) \frac{\alpha^{n-1} e^{-\alpha(\beta+z)} (\beta+z)^n}{\Gamma(n)} d\alpha$$

$$= \int_0^\infty e^{a(\hat{\alpha}-\alpha)} \frac{\alpha^{n-1} e^{-\alpha(\beta+z)} (\beta+z)^n}{\Gamma(n)} d\alpha - \int_0^\infty a(\hat{\alpha}-\alpha) \frac{\alpha^{n-1} e^{-\alpha(\beta+z)} (\beta+z)^n}{\Gamma(n)} d\alpha -$$

$$\int_0^\infty \frac{\alpha^{n-1} e^{-\alpha(\beta+z)} (\beta+z)^n}{\Gamma(n)} d\alpha$$

$$= \frac{(\beta+z)^n}{\Gamma(n)} e^{a\hat{\alpha}} \int_0^\infty e^{-\alpha(a+\beta+z)} \alpha^{n-1} d\alpha - \frac{a\hat{\alpha} (\beta+z)^n}{\Gamma(n)} \int_0^\infty \alpha^{n-1} e^{-\alpha(\beta+z)} d\alpha -$$

$$a \frac{(\beta+z)^n}{\Gamma(n)} \int_0^\infty \alpha^{n+1} e^{-\alpha(\beta+z)} d\alpha - \frac{(\beta+z)^n}{\Gamma(n)} \int_0^\infty \alpha^{n-1} e^{-\alpha(\beta+z)} d\alpha$$

$$= \frac{(\beta+z)^n}{(a+\beta+z)^n} e^{a\hat{\alpha}} - \frac{a\hat{\alpha} (\beta+z)^n}{(\beta+z)^n} - \frac{(\beta+z)^n}{\Gamma(n)} \int_0^\infty \alpha^{n+1} e^{-\alpha(\beta+z)} d\alpha -$$

$$\frac{(\beta+z)^n}{\Gamma(n)} \int_0^\infty \alpha^{n-1} e^{-\alpha(\beta+z)} d\alpha \dots\dots\dots(15)$$

We must drive (15) with respect to $\hat{\alpha}$

$$= \frac{(\beta+z)^n}{(a+\beta+z)^n} e^{a\hat{\alpha}} \cdot a - a = 0$$

$$= a \left(e^{a\hat{\alpha}} \frac{(\beta+z)^n}{(a+\beta+z)^n} - 1 \right) = 0$$

$$e^{a\hat{\alpha}} = (a+\beta+z)^n / (\beta+z)^n$$

$$a\hat{\alpha} = n \ln(a+\beta+z) - n \ln(\beta+z)$$

$$\therefore \hat{\alpha}_{B2} = n/a \ln(a+\beta+z) - n/a \ln(\beta+z), \quad a \neq 0, \beta > 0 \dots\dots\dots(16)$$

Where $\hat{\alpha}_{B2}$ denoted the LINEX Bayes estimator of shape parameter for generalized exponential distribution using gamma conjugate prior density function.

NUMERICAL EXPERIMENTS

The simulation program is written by using Matlab program and it has been performed to compare the two Bayes estimation mainly with respect to their mean squared errors (MSE's), for different sample sizes (n)

20,40,60,80,100) , and $(a=2,4,6), (\beta=1,2)$ and for different parametric values $(\alpha=0.5,1,2)$ and $(\lambda=1)$. If U follows uniform distribution in $[0,1]$, then $X = (-\ln(1-U^{1/\alpha})/\lambda)$ follows $GE(\alpha, \lambda)$. Therefore, if one has a good uniform random number generator, then the generation of GE random deviate is immediate. Since λ is the scale parameter and all the estimators are scale invariant, then for each combination of n and α a sample of size n from $GE(\alpha,1)$ is generating and estimate α by two different methods. In experiment it has been compared between two methods (LINEX bayes estimator with Jeffery prior Information and LINEX bayes estimator with gamma conjugate prior) and report mean squared errors (MSE's) over 1000 replications. to observe how the two methods perform in estimating α if λ is known and $(\lambda = 1)$. The results were presented in the four tables for each sample size.

CONCLUSIONS AND DICUSSIONS

The resolute of numerical experiments were presented to compare between the two estimators proposed in equations (13) and (16). Some of the points are quite clear from the numerical results. As expected, it was observed that the performances of all estimators became better when the sample size increases. In the tables (1,2,3,4,5) the MSE's of LINEX Bayes estimator with gamma conjugate prior $\hat{\alpha}_{B2}$ were less than MSE's of LINEX Bayes estimator with Jeffery prior Information $\hat{\alpha}_{B1}$ at all simple sizes of n for $\alpha < 1$. However, for $\alpha \geq 1$ MSE's of $\hat{\alpha}_{B1}$ less than MSE's of $\hat{\alpha}_{B2}$ at all simple sizes. Bayes estimators with two types of prior density function had least mean square errors as compare with maximum likelihood estimator. In Bayes estimators with Jeffery prior Information $\hat{\alpha}_{B1}$ (when $a=6$) MSE's were lower than MSE's of $\hat{\alpha}_{B1}$ (when $a=2,4$) but MSE's of Bayes estimators with gamma conjugate prior $\hat{\alpha}_{B2}$ (when $a=2$) were lower than MSE's of $\hat{\alpha}_{B2}$ (when $a=4,6$) .

Table 1: Estimation values and mean square error within brackets of the estimators of the shape parameter α when $(\lambda=1)$ and sample size $n=20$

n	Estimator	a	β	$\alpha=0.5$	$\alpha=1$	$\alpha=2$
20	$\hat{\alpha}_{B1}$	2	1	0.5153(0.0143)	1.0003(0.0489)	1.9560(0.0902)
		4		0.5021(0.0126)	0.9529(0.0423)	1.8671(0.0911)
		6		0.4898(0.0115)	0.9113(0.0414)	1.7883(0.1068)
	$\hat{\alpha}_{B2}$	2	1	0.5017(0.0126)	0.9505(0.0419)	1.7783(0.1090)
		4		0.4892(0.0114)	0.9077(0.0412)	1.7045(0.1379)
		6		0.4775(0.0107)	0.8698(0.0445)	1.6383(0.1792)
	$\hat{\alpha}_{B2}$	2	2	0.4126(0.0105)	0.9015(0.0464)	1.5785(0.2499)
		4		0.4113(0.0101)	0.8628(0.0496)	1.4684(0.3372)
		6		0.4106(0.0101)	0.8283(0.0556)	1.3766(0.4314)
	$\hat{\alpha}_{m.l.e}$			0.5306(0.0167)	1.0576(0.0609)	2.1158(0.2725)

Table 2: Estimation values and mean square error within brackets of the estimators of the shape parameter α when ($\lambda=1$) and sample size $n=40$

n	Estimator	a	β	$\alpha=0.5$	$\alpha=1$	$\alpha=2$
40	$\hat{\alpha}_{B1}$	2		0.5079(0.0068)	0.9976(0.0247)	1.9560(0.0902)
		4		0.5015(0.0064)	0.9734(0.0231)	1.8671(0.0911)
		6		0.4953(0.0061)	0.9507(0.0228)	1.7883(0.1068)
	$\hat{\alpha}_{B2}$	2	1	0.5014(0.0064)	0.9727(0.0230)	1.8595(0.0928)
		4		0.4951(0.0061)	0.9497(0.0227)	1.7789(0.1101)
		6		0.4890(0.0059)	0.9281(0.0236)	1.7071(0.1379)
	$\hat{\alpha}_{B2}$	2	2	0.4904(0.0058)	0.9727(0.0230)	1.7759(0.1133)
		4		0.4844(0.0056)	0.9497(0.0227)	1.7022(0.1420)
		6		0.4786(0.0056)	0.9281(0.0236)	1.6362(0.1781)
	$\hat{\alpha}_{m.l.e}$	0.5127(0.0064)			1.0122(0.0261)	2.0554(0.1164)

Table 3: Estimation values and mean square error within brackets of the estimators of the shape parameter α when ($\lambda = 1$) and sample size $n=60$

n	Estimator	a	β	$\alpha=0.5$	$\alpha=1$	$\alpha=2$
60	$\hat{\alpha}_1$	2		0.5065(0.0042)	1.0062(0.0169)	1.9755(0.0588)
		4		0.5022(0.0040)	0.9896(0.0159)	1.9137(0.0587)
		6		0.4980(0.0039)	0.9738(0.0155)	1.8567(0.0661)
	$\hat{\alpha}_2$	2	1	0.5027(0.0042)	0.9893(0.0158)	1.9094(0.0604)
		4		0.4985(0.0040)	0.9733(0.0154)	1.8516(0.0682)
		6		0.4944(0.0039)	0.9580(0.0156)	1.7982(0.0819)
	$\hat{\alpha}_2$	2	2	0.4979(0.0039)	0.9703(0.0148)	1.8518(0.0668)
		4		0.4936(0.0038)	0.9549(0.0151)	1.7974(0.0809)
		6		0.4898(0.0037)	0.9401(0.0158)	1.7470(0.0997)
	$\hat{\alpha}_{m.l.e}$			0.5124(0.0046)	1.0188(0.0173)	2.0375(0.0698)

Table 4: Estimation values and mean square error within brackets of the estimators of the shape parameter α when ($\lambda = 1$) and sample size $n=80$

n	Estimator	a	β	$\alpha=0.5$	$\alpha=1$	$\alpha=2$
80	$\hat{\alpha}_{B1}$	2		0.5022(0.0032)	1.0012(0.0120)	1.9737(0.0449)
		4		0.4990(0.0031)	0.9884(0.0115)	1.9268(0.0456)
		6		0.4959(0.0030)	0.9769(0.0114)	1.8827(0.0505)
	$\hat{\alpha}_{B2}$	2	1	0.4990(0.0031)	0.9887(0.0115)	1.9319(0.0471)
		4		0.4959(0.0030)	0.9767(0.0114)	1.8869(0.0515)
		6		0.4928(0.0030)	0.9650(0.0115)	1.8446(0.0545)
	$\hat{\alpha}_{B2}$	2	2	0.4983(0.0029)	0.9794(0.0117)	1.8799(0.0508)
		4		0.4952(0.0028)	0.9666(0.0118)	1.8373(0.0597)
		6		0.4921(0.0028)	0.9552(0.0122)	1.7972(0.0716)
	$\hat{\alpha}_{m.l.e}$	0.5089(0.0032)			1.0124(0.0131)	2.0317(0.0528)

Table 5: Estimation values and mean square error within brackets of the estimators of the shape parameter α when ($\lambda = 1$) and sample size $n=100$

n	Estimator	a	β	$\alpha=0.5$	$\alpha=1$	$\alpha=2$
100	$\hat{\alpha}_{B1}$	2	1	0.5036(0.0026)	0.9987(0.0101)	1.9793(0.0370)
		4		0.5011(0.0026)	0.9888(0.0098)	1.9413(0.0373)
		6		0.4986(0.0025)	0.9792(0.0097)	1.9052(0.0404)
	$\hat{\alpha}_{B2}$	2	1	0.5010(0.0026)	0.9887(0.0098)	1.9406(0.0373)
		4		0.4985(0.0025)	0.9790(0.0097)	1.9040(0.0405)
		6		0.4961(0.0025)	0.9696(0.0099)	1.8692(0.0462)
	$\hat{\alpha}_{B2}$	2	2	0.4991(0.0025)	0.9839(0.0093)	1.8961(0.0405)
		4		0.4966(0.0025)	0.9743(0.0094)	1.8612(0.0468)
		6		0.4941(0.0024)	0.9650(0.0096)	1.8280(0.0553)
	$\hat{\alpha}_{m.l.e}$			0.5072(0.0027)	1.0151(0.0104)	2.0204(0.0400)

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The Equivalence Convergence of Iterative Sequences for Multi-Valued Mappings

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الخلاصة

سوف نبرهن ان تقارب تكرار بيكارد مكافئ لتقارب تكرار مان وايشيكافوا لتطبيقات متعددة القيم الانكماشية و شبه الانكماشية بقوة (ليس من الضروري ان يكون لبشيز) والمعرفة على فضاء بناخ الحقيقي وفضاء بناخ الحقيقي الناعم بانتظام . خلال البحث معنى التكافؤ هو: ان هذه التكرارات تتقارب لنفس النقطة الصامدة.

ABSTRACT

We will show that the convergence of Picard iteration is equivalent to the convergence of Mann and Ishikawa iterations when the mapping is multi-valued contraction and multi-valued strongly pseudo-contraction (not necessary Lipschits) and when the underling space is a real Banach space or a real uniformly smooth Banach space. Here, the meaning of equivalent is: these iterations converge to the same fixed point.

INTRODUCTION AND PRELIMNARIES

Let X be a normed space over a field F and \dot{X} be the dual space of X , for $f \in \dot{X}$ and $x \in X$ we use the convenient notation $\langle f, x \rangle \stackrel{\text{def}}{=} f(x)$. This makes inner product structure available.

For all α, β in F , f, g in \dot{X} and x, y in X , then we have

$$\langle \alpha f + \beta g, x \rangle = \alpha \langle f, x \rangle + \beta \langle g, x \rangle$$

$$\langle f, \alpha x + \beta y \rangle = \alpha \langle f, x \rangle + \beta \langle f, y \rangle$$

$$\text{and } |\langle f, x \rangle| \leq \|f\| \|x\|$$

$$\|f\| = \sup_{\|x\|=1} |\langle f, x \rangle|, \|x\| = \sup_{\|f\|=1} |\langle f, x \rangle| \quad [1, p.79].$$

Definition (1.1) [2, p.99] or [3]

Let X be a normed space, the multi-valued mapping $J: X \longrightarrow \dot{2}^{\dot{X}}$ given by, $J(x) = \{f \in \dot{X} : \langle x, f \rangle = \|f\| \|x\|, \|f\| = \|x\|\}$, $\forall x \in X$ is said to be the *normalized duality mapping*, where \dot{X} is the dual space of X and $\dot{2}^{\dot{X}}$ is the set of all non-empty subsets of \dot{X} .

Definition (1.2) [2,p.107] or [4,p.265]

Let X be a Banach space and $S(X) = \{x \in X: \|x\|=1\}$, then a Banach space X is said to be **smooth** if

$$\lim_{t \rightarrow 0} \frac{\|x + ty\| - \|x\|}{t} \quad \dots(2.1)$$

exists for each $x, y \in S(X)$, and X is said to be **uniformly smooth** if the limit (2.1) is attained uniformly for (x,y) in $S(X) \times S(X)$.

Definition (1.3) [5,p.474]

A normed linear space X is said to be uniformly convex if and only if for every $\varepsilon \in]0,2]$ there is a $\delta(\varepsilon) \in]0,1]$ such that whenever

$\|x\| \leq r, \|y\| \leq r, \|x - y\| \geq \varepsilon, x, y \in X, r > 0$, then it follows that $\|(x + y)/2\| \leq (1 - \delta(\varepsilon))r$.

By depending on the fact " X is uniformly smooth if and only if X is uniformly convex [4,p.265]". We can see that the Hilbert space $\ell_2(\mathbb{R})$ with

$\|x\| = \sqrt{\sum_{i=1}^{\infty} x_i^2}$ is uniformly smooth since the dual space of $\ell_2(\mathbb{R})$ is $\ell_2(\mathbb{R})$

[6,p.122] and $\ell_2(\mathbb{R})$ is uniformly convex [5,p.475]. Also \mathbb{R}^2 with the usual norm is uniformly smooth since the dual space of \mathbb{R}^2 is \mathbb{R}^2 [6,p.121] and \mathbb{R}^2 with the usual norm is uniformly convex, but \mathbb{R}^2 with norm $\|x\| = \max\{|x_1|, |x_2|\}$, $\forall x = (x_1, x_2)$ is not uniformly smooth since the dual space of \mathbb{R}^2 with the same norm is not uniformly convex [5,p.475].

Proposition (1.4): [2,p.99-107] and [7]

Let X be a Banach space and J be the duality mapping of X . Then

- (i) For $x \in X$, $J(x)$ is non-empty bounded closed and convex;
- (ii) $J(0) = \{0\}$;
- (iii) For $x \in X$ and a real α , $J(\alpha x) = \alpha J(x)$;
- (iv) X is a smooth Banach space if and only if J is single-valued;
- (v) X is a uniformly smooth Banach space if and only if J is single-valued and uniformly continuous on any bounded subset of X .

Definition (1.5): [5,p.449]

Let X be a normed space and $A, B \in CB(X)$ which is the set of all closed bounded subset of X . Let $H(A,B)$ denote the **Hausdorff distance of A and B** that is defined as

$H(A,B) = \max\{\sup_{a \in A} d(a,B), \sup_{b \in B} d(b,A)\}$, where $d(a,B) = \inf_{b \in B} d(a,b)$ is the distance from a point a to the set B and d induced by the norm.

Lemma (1.6): [8] or [6, p.61]

Let X be a normed space. If $A, B \in CB(X)$ and $a \in A$, then given $\varepsilon > 0$ there must exist a point $b \in B$ such that $\|a - b\| \leq H(A, B) + \varepsilon$.

Lemma (1.7): [6, p.62]

Let X be a normed space and A_n, B_n be two sequences in $CB(X)$. Then we can choose $a_n \in A_n, b_n \in B_n, \forall n \geq 0$ such that

$$\|a_n - b_n\| \leq H(A_n, B_n) + \varepsilon_n \text{ with } \lim_{n \rightarrow \infty} \varepsilon_n = 0 \quad \dots(1.3)$$

Now. By a *multi-valued mapping*

$$T: M \subseteq X \longrightarrow \overset{Y}{2}. \quad \dots(1.4)$$

We mean a mapping assigns to each point $x \in M$ a subset $T(x) \subseteq M$

Definition (1.8): [10, p.1] and [9, p.447]

Let X be a normed space, M be a non-empty subset of X and $T: M \longrightarrow \overset{M}{2}$ be a multi-valued mapping, the point x in M is said to be a **fixed point** of T if and only if $x \in T(x)$. Let $F(T)$ denote the set of all fixed points of T , that is $F(T) = \{x \in M: x \in T(x)\}$

As a special case the point x in M is said to be a **fixed point** of a single-valued mapping T if and only if $x = T(x)$ and the set of all fixed points of T , that is $F(T) = \{x \in M: x = T(x)\}$. For fixed points of multi-valued mapping T , we introduce the following example:

Example (1.9) [11]

Consider $M = [0, 1] \times [0, 1] \subseteq \mathbb{R}^2$ with the usual norm. Define $T: M \longrightarrow CK(M)$ by $T(x, y) =$ the triangle with vectors $(0, 0), (x, 0)$ and $(0, y)$, for all $x, y \in [0, 1]$.

$F(T) = \{(0, 0)\} \cup \{(x, 0): x \in [0, 1]\} \cup \{(0, y): y \in [0, 1]\}$. Since $(0, 0) \in T(0, 0)$, $(x, 0) \in T(x, 0)$ for all x and $(0, y) \in T(0, y)$ for all y .

Example(1.10):

Consider $X = [a, b]$ with the usual metric. Define $T: X \longrightarrow \overset{x}{2}$ by $T(x) = \{a, x, b\}$. It is clear that every x in X is a fixed point.

Definition (1.11): [10, p.2 – p.35] and [12, p.112]

Let X be a normed space, M be a non-empty subset of X . A mapping $T: M \longrightarrow \overset{x}{2}$ is said to be

(i) **Multi-valued Lipschitz** (or **Lipschitz** when T is single-valued). If there exist a constant $k > 0$ such that

$$H(Tx, Ty) \leq k \|x - y\| \text{ for all } x, y \in M \quad \dots(1.5)$$

$$\text{(or respectively } \|Tx - Ty\| \leq k \|x - y\| \text{ for all } x, y \in M) \quad \dots(1.6)$$

(ii) If $k < 1$ in (1.5) (or in (1.6)), then T is said to be **multi-valued contraction** (or **contraction** respectively).

For the existences of fixed point for the multi-valued contraction mapping we have the following theorem:

Theorem (1.12): (Nadler's Fixed Point Theorem [8, p.62]

Let M be a non-empty closed subset of a Banach space X and $T: M \longrightarrow CB(M)$ be a multi-valued contraction mapping. Then T has a fixed point

Example (1.13): [8]

Consider $M = [0, 1]$ with the usual distance and let $f: M \longrightarrow M$ is given by

$$f(x) = \begin{cases} \frac{x+1}{2}, & \text{if } 0 \leq x < \frac{1}{2} \\ -\frac{x}{2} + 1, & \text{if } \frac{1}{2} \leq x \leq 1 \end{cases}$$

Define $T: M \longrightarrow C(M)$ as the following $T(x) = f(x) \cup \{0\}$ T is multi-valued contraction mapping with respect to Hausdorff distance since for any x, y

$$\text{in } M, H(Tx, Ty) = \max \left\{ \sup_{a \in Ty} d(a, Tx), \sup_{b \in Tx} d(b, Ty) \right\} \leq \frac{1}{2} |x - y|.$$

Since M is complete (every closed subset of complete space is complete), then by Nadler's fixed point theorem, T has a fixed point. Now, to find these fixed point we must discuss the statement $x \in T(x) = f(x) \cup \{0\}$.

It is clear that $0 \in T(0)$ and $\frac{2}{3} \in f(\frac{2}{3})$ and then $\frac{2}{3} \in T(\frac{2}{3})$. Therefore $F(T) = \{0, \frac{2}{3}\}$.

Definition (1.14): [13], [14] and [16]

Let X be a normed space and M be a non-empty subset of X . A mapping $T: M \longrightarrow \overset{x}{2}$ is said to be

(i) **Multi-valued strongly pseudo-contraction** (or **strongly pseudo** when T is single-valued).

If there is a constant $t > 1$ such that for each $x, y \in M$ and for each $\xi \in Tx, \mu \in Ty$ there exists $j(x - y) \in J(x - y)$ with

$$\langle \xi - \mu, j(x - y) \rangle \leq \frac{1}{t} \|x - y\|^2 \quad \dots(1.7)$$

$$(\text{or respectively } \langle Tx - Ty, j(x - y) \rangle \leq \frac{1}{t} \|x - y\|^2) \quad \dots(1.8)$$

The following inequalities are equivalent to (1.7) (or (1.8))

$$\|\xi - \mu\|^2 \leq \|x - y\|^2 + \frac{1}{t} \|(x - \xi) - (y - \mu)\|^2 \text{ for each } x, y \in M, \text{ for each } \xi \in Tx, \mu \in Ty. \quad \dots(1.9)$$

$$\text{(respectively } \|Tx - Ty\|^2 \leq \|x - y\|^2 + \frac{1}{t} \|(I - T)x - (I - T)y\|^2 \text{ for each } x, y \in M) \quad \dots(1.10)$$

(ii) If $t = 1$ in (1.7) and (1.9) (or in (1.8) and (1.10)), then T is said to be **multi-valued pseudo-contraction** (or **pseudo-contraction** respectively).

Example (1.15): [15]

Consider $X = \mathbb{R}$ with the usual norm, the single-valued mapping

$T: X \longrightarrow X$ such that $T(x) = x - \frac{1}{2} \cos x$. Since $(I - T)(x) = \frac{1}{2} \cos x$ and

$$\begin{aligned} \langle Tx - Ty, x - y \rangle &= (Tx - Ty)(x - y) \\ &\leq \frac{1}{2} |\cos x - \cos y| |x - y| \\ &\leq \frac{1}{2} |x - y|^2 \end{aligned}$$

Since $t = 2$, so $(I - T)$ is strongly pseudo contraction mapping, Since the derivative of T is bounded then it is Lipschitzian i.e.

$$|T'(x)| = \left| 1 + \frac{1}{2} \sin x \right| \leq \frac{3}{2}.$$

So $|Tx - Ty| \leq \frac{3}{2} |x - y|$ for all x, y in \mathbb{R} .

Example (1.16): [17]

Consider $X = \mathbb{R}$ with the usual norm, $M = [0, 1]$ and $T: M \longrightarrow M$ be

given as $T(x) = (1 - x^{\frac{2}{3}})^{\frac{3}{2}}$ for all $x \in [0, 1]$, then T is pseudo contraction not Lipschitz, T is pseudo contraction, since T is decreasing. We have $\langle Tx - Ty, x - y \rangle = (Tx - Ty)(x - y) \leq 0 \leq |x - y|^2$.

T is not Lipschitz since $T'x = \frac{-(1 - x^{\frac{2}{3}})^{\frac{1}{2}}}{x^{\frac{1}{3}}}$ is unbounded as $x \longrightarrow 0$.

So, there is no constant k which bounds $\frac{|Tx - Ty|}{|x - y|}$.

Now, we recall three well-known types of iterations for multi-valued mappings and single-valued mappings which are Picard, Mann and Ishikawa. Then, we present two examples for convergence of Mann sequence which the Picard fails to converge and convergence of Ishikawa sequence which Mann fails to converge.

Definition(1.17):[8]or[6,p.48]

Let X be a normed space, M be a non-empty subset of X , $T:M \longrightarrow \overset{x}{2}$ be a multi-valued mapping and for $x_0 \in M$. If the sequence $\{x_n\} \subset M$ is defined by

$$x_{n+1} \in T(x_n), \forall n \geq 0 \quad \dots(1.11)$$

or

$$x_{n+1} = \xi_n, \text{ where } \xi_n \in T(x_n), \forall n \geq 0 \quad \dots(1.12)$$

Then the sequence $\{x_n\}$ is said to be **Picard iteration** process for T .

As a special case, when T is a single-valued mapping, Picard iteration is defined by

$$x_{n+1} = T(x_n), \forall n \geq 0 \quad \dots(1.13)$$

Definition (1.18): [18] and [19]

Let X be a normed space, M be a non-empty subset of X , $T:M \longrightarrow \overset{x}{2}$ be a multi-valued mapping and for $x_0 \in M$. If the sequence $\{u_n\} \subset M$ is defined by

$$u_{n+1} \in (1 - \alpha_n)u_n + \alpha_n Tu_n, \forall n \geq 0 \quad \dots(1.14)$$

or

$$u_{n+1} = (1 - \alpha_n)u_n + \alpha_n v_n \text{ where } v_n \in Tu_n, \forall n \geq 0 \quad \dots(1.15)$$

Then the sequence $\{u_n\}$ is said to be **Mann iteration process** for T , where α_n be a non-negative real sequence in $(0,1)$ satisfying some additional conditions.

Also, when T is a single-valued mapping, Mann iteration is defined by

$$u_{n+1} = (1 - \alpha_n)u_n + \alpha_n Tu_n, \forall n \geq 0 \quad \dots(1.16)$$

Definition (1.19): [13] and [20]

Let X be a normed space, M be a non-empty subset of X , $T:M \longrightarrow \overset{x}{2}$ be a multi-valued mapping and for $x_0 \in M$. If the sequence $\{x_n\} \subset M$ is defined by

$$\begin{aligned} x_{n+1} &\in (1 - \alpha_n)x_n + \alpha_n Ty_n \\ y_n &\in (1 - \beta_n)x_n + \beta_n Tx_n, \forall n \geq 0 \end{aligned} \quad \dots(1.17)$$

or

$$\begin{aligned} x_{n+1} &= (1 - \alpha_n)x_n + \alpha_n \mu_n, \text{ where } \mu_n \in Ty_n, \forall n \geq 0 \\ y_n &= (1 - \beta_n)x_n + \beta_n \xi_n, \text{ where } \xi_n \in Tx_n, \forall n \geq 0 \end{aligned} \quad \dots(1.18)$$

Then the sequence $\{x_n\}$ is said to be **Ishikawa iteration** process for T , where α_n and β_n be two non-negative real sequences in $(0,1)$ satisfying some additional conditions.

Also, when T is a single-valued mapping, Ishikawa iteration is defined by

$$y_n = (1 - \beta_n)x_n + \beta_n Tx_n, \forall n \geq 0 \quad \dots(1.19)$$

It is clear that Ishikawa iteration in definition (1.19) implies Mann iteration in definition (1.18) when $\beta_n=0, \forall n \geq 0$. And Mann iteration in definition (1.18) implies Picard iteration in definition (1.17) when $\alpha_n = 1, \forall n \geq 0$.

Example (1.20): [21]

Let $X = \mathbb{R}$ with the usual norm, $M = [\frac{1}{2}, 2]$. Define $T: M \longrightarrow M$ by $T(x) = \frac{1}{x}$, for all x in M . Then it is clear that $F(T) = \{1\}$ (i.e. $T(1) = 1, 1 \in [\frac{1}{2}, 2]$) and the Picard iterative sequence for any $x_0 \neq 1$ is

$$T^n x = \begin{cases} x, & \text{if } n \text{ is even} \\ \frac{1}{x}, & \text{if } n \text{ is odd} \end{cases}$$

So the Picard iteration process of T does not converge to the fixed point of T . Moreover $\{T^n x\}$ fails to converge to any point in X , for all x_0 in $M \setminus \{1\}$.

The Mann iteration process of T with $\alpha_n = \frac{n}{2n+1}, n \geq 0$ and $x_0 = 2$ converge to 1, the unique fixed point of T , see table (1)

Table 1: The Mann iteration for example (1.20)

N	0	1	2	3	4	∞
Mann Iteration	2	1.5	1.166	1.034	1.0042	1

Mutangadure and Chidume [22] gave an example of a mapping T with some contractive conditions defined on a compact convex subset M of a Hilbert space and they proved that the Ishikawa iterative sequence of any point x_0 in M converges to a fixed point of T , but every non-trivial Mann sequence fails to converge. Here, we mention to this example without details, since such details consist of something other concepts.

Example (1.21): [22]

Let X be the real Hilbert space \mathbb{R}^2 with the usual inner product. If $x = (a, b) \in X$ we define $x^\perp \in X$ to be $(b, -a)$. Then we have $\langle x, x^\perp \rangle = 0$, $\|x^\perp\| = \|x\|$, $\langle x^\perp, y^\perp \rangle = \langle x, y \rangle$, $\|x^\perp - y^\perp\| = \|x - y\|$ and $\langle x^\perp, y \rangle + \langle x, y^\perp \rangle = 0$ for all x, y in X . We take the closed and bounded convex set M to be the

closed unit ball in X and set $M_1 = \{x \in X: \|x\| \leq \frac{1}{2}\}$, $M_2 = \{x \in X: \frac{1}{2} \leq \|x\| \leq 1\}$,

we define $T: M \longrightarrow M$ by
$$Tx = \begin{cases} x + x^\perp, & \text{if } x \in M_1 \\ \frac{x}{\|x\|} - x + x^\perp, & \text{if } x \in M_2 \end{cases}$$

It is easy to show that the origin is the only fixed point of T (i.e. $T(0,0) = (0,0) + (0,0)^\perp = (0,0)$, $(0,0) \in M_1$). Chidume [22] show that no Mann iteration sequence for T converge to any non-zero starting point.

The main aim of this paper is to study some cases for coincidence the limits of the convergent which are Picard, Mann and Ishikawa iterations for multi-valued non-Lipschits mappings .we give a simple example to illustrate the convergence Ishikawa, Mann and Picard iteration for Lipschitz mapping. And then we prove a result about the equivalence convergence of these three iterations for multi-valued contraction mapping.

Also,we show that the Ishikawa and Mann iterations for strongly pseudo contraction are equivalent in two cases when X is a real uniformly smooth Banach space and when X is a real Banach space.

MAIN RESULTS

Firstly, we begin with the following example to explain the equivalent of the convergence of the three above iterations when apply to a Lipschitz mapping:-

Example (3.1):

Consider $X = \mathbb{R}$, $M = [0,2]$ and $T: M \longrightarrow M$ defined by $Tx = \frac{2}{x+1}$.

Obviously, T is a Lipschitzian mapping with Lipschitz constant $k = 2$ and T has a fixed point $p = 1 \in M$. Let's choice the sequences $\{\alpha_n\}$ and $\{\beta_n\}$ such that $\alpha_n = \frac{1}{n+1}$ and $\beta_n = \frac{1}{n+2}$, and $z_0 = u_0 = x_0 = 0.1 \in M$. Then the sequences in conditions (2.13), (2.16) and (2.19) are converge to 1, see table (2). The results in this example has been obtained by basic visual programming language.

Table 2: The Equivalence of Picard, Mann and Ishikawa Iteration

	Picard Iteration	Mann Iteration	Ishikawa Iteration
$n = 0$	0.1	0.1	0.1
$n = 1$	1.81818181818182	0.959090909090909	0.448550724637681
$n = 2$	0.709677419354839	0.97968782957182	0.892617654617736
$n = 3$	1.16981132075472	0.987330944576236	0.936195790783592
$n = 4$	0.921739130434783	0.991139737611865	0.957326451856968

$n = 5$	1.04072398190045	0.993358088774786	0.969305718175472
$n = 6$	0.980044345898004	0.994782936250789	0.976787900564533
$n = 7$	1.01007838745801	0.995761988483085	0.981788194941084
$n = 8$	0.994986072423398	0.996468823704831	0.985302185451399
$n = 9$	1.00251326445127	0.996998812430618	0.987869851551889
$n = 10$	0.998744944917027	0.99740827029606	0.989805444391452
$n = 11$	1.00062792157957	0.997732376629439	0.991302267728289
$n = 12$	0.999686137750654	0.997994124478976	0.992484683106121
$n = 13$	1.00015695575592	0.998209111634372	0.993435724930864
$n = 14$	0.999921528280336	0.998388253973529	0.994212595664891
$n = 15$	1.00003923739935	0.998539395785704	0.994855769729909
$n = 16$	0.999980381685213	0.99866830402408	0.995394555224867
$n = 17$	1.00000980925361	0.998779303335904	0.99580607667597
$n = 18$	0.999995095397248	0.998875693743733	0.996240215671364
$n = 19$	1.00000245230739	0.998960032522647	0.996575826410003
\vdots	\vdots	\vdots	\vdots
$n = 120$	1	0.999908410570588	0.999809389229063
\vdots	\vdots	\vdots	\vdots
\downarrow	\downarrow	\downarrow	\downarrow
∞	1	1	1

Theorem (3.5):

Let X be a real Banach space, M be a non-empty convex subset of X and $T : M \rightarrow CB(M)$ be a multi-valued contraction mapping. Suppose that $\lim_{n \rightarrow \infty} \|z_n - z_{n+1}\| = 0$. Let $z_0 = u_0 = x_0 \in M$ and define $\{z_n\}$, $\{u_n\}$ and $\{x_n\}$ by conditions (1.12), (1.15) and (1.18) with $\{\alpha_n\}$, $\{\beta_n\}$ satisfying

(i) $0 < \alpha_n, \beta_n < 1$

(ii) $\lim_{n \rightarrow \infty} \beta_n = 0$

(iii) $\sum_{n=1}^{\infty} \alpha_n = \infty$,

then the following are equivalent

- (a) Picard iteration converges to P ,
- (b) Mann iteration converges to P ,
- (c) Ishikawa iteration converges to P .

Proof:

By Nadler's Theorem, T has a fixed point, say p . Firstly, we prove (a) implies (b) From $z_{n+1} = \zeta_n$, where $\zeta_n \in T(z_n)$

$u_{n+1} = (1 - \alpha_n) u_n + \alpha_n v_n$, where $v_n \in Tu_n$,

From conditions (1.3) and (1.5), we get

$$\begin{aligned} z_{n+1} - u_{n+1} &= (1 - \alpha_n)(\zeta_n - u_n) + \alpha_n(\zeta_n - v_n) \\ \|z_{n+1} - u_{n+1}\| &= \|(1 - \alpha_n)(\zeta_n - u_n) + \alpha_n(\zeta_n - v_n)\| \\ &\leq (1 - \alpha_n)\|\zeta_n - u_n\| + \alpha_n\|\zeta_n - v_n\| \\ &= (1 - \alpha_n)\|\zeta_n - z_n + z_n - u_n\| + \alpha_n\|\zeta_n - v_n\| \\ &\leq (1 - \alpha_n)\|\zeta_n - z_n\| + (1 - \alpha_n)\|z_n - u_n\| + \alpha_n H(Tz_n, Tu_n) + \alpha_n \varepsilon_n \\ \|z_{n+1} - u_{n+1}\| &\leq (1 - \alpha_n)\|\zeta_n - z_n\| + (1 - \alpha_n)\|z_n - u_n\| + \alpha_n k\|z_n - u_n\| + \alpha_n \varepsilon_n \\ &\leq (1 - \alpha_n(1 - k))\|z_n - u_n\| + (1 - \alpha_n)\|z_{n+1} - z_n\| + \alpha_n \varepsilon_n \end{aligned}$$

Let us denote be

$$a_n := \|z_n - u_n\|$$

$$\lambda_n := \alpha_n(1 - k) \in (0, 1), \forall n \geq 0$$

$$\sigma_n := (1 - \alpha_n)\|z_{n+1} - z_n\| + \alpha_n \varepsilon_n$$

for each $n \in \mathbb{N}$, the inequality of Lemma (2.2) is satisfied. Therefore

$$\lim_{n \rightarrow \infty} \|z_n - u_n\| = 0 \quad \dots (2.1)$$

Since Picard iteration $\{z_n\}$ converges to p and using condition (2.1), we get

$$\|u_n - p\| \leq \|z_n - p\| + \|z_n - u_n\|$$

which implies that $\lim_{n \rightarrow \infty} \|u_n - p\| = 0$. Thus $\lim_{n \rightarrow \infty} u_n = p$

Secondly, we prove (b) implies (c).

From $u_{n+1} = (1 - \alpha_n) u_n + \alpha_n v_n$, where $v_n \in Tu_n$,

$$x_{n+1} = (1 - \alpha_n) x_n + \alpha_n \mu_n, \text{ where } \mu_n \in Ty_n,$$

$$y_n = (1 - \beta_n) x_n + \beta_n \xi_n, \text{ where } \xi_n \in Tx_n,$$

From conditions (1.3) and (1.5), we get

$$u_{n+1} - x_{n+1} = (1 - \alpha_n)(u_n - x_n) + \alpha_n(v_n - \mu_n)$$

$$\begin{aligned} \|u_{n+1} - x_{n+1}\| &= \|(1 - \alpha_n)(u_n - x_n) + \alpha_n(v_n - \mu_n)\| \\ &\leq (1 - \alpha_n)\|u_n - x_n\| + \alpha_n\|v_n - \mu_n\| \\ &\leq (1 - \alpha_n)\|u_n - x_n\| + \alpha_n H(Tu_n, Ty_n) + \alpha_n \varepsilon_n \\ &\leq (1 - \alpha_n)\|u_n - x_n\| + \alpha_n k\|u_n - y_n\| + \alpha_n \varepsilon_n \end{aligned}$$

$$\begin{aligned}
\|u_{n+1} - x_{n+1}\| &= (1 - \alpha_n) \|u_n - x_n\| + \alpha_n k \|u_n - (1 - \beta_n)x_n - \beta_n \xi_n\| + \alpha_n \varepsilon_n \\
&= (1 - \alpha_n) \|u_n - x_n\| + \alpha_n k \|(u_n - x_n) + \beta_n (x_n - \xi_n)\| + \alpha_n \varepsilon_n \\
&\leq (1 - \alpha_n) \|u_n - x_n\| + \alpha_n k \|u_n - x_n\| + \alpha_n \beta_n k \|x_n - \xi_n\| + \alpha_n \varepsilon_n \\
&= (1 - \alpha_n) \|u_n - x_n\| + \alpha_n k \|u_n - x_n\| + \alpha_n \beta_n k \|x_n - p + p - \xi_n\| + \alpha_n \varepsilon_n \\
&\leq (1 - \alpha_n) \|u_n - x_n\| + \alpha_n k \|u_n - x_n\| + \alpha_n \beta_n k \|x_n - p\| + \\
&\quad \alpha_n \beta_n k \|p - \xi_n\| + \alpha_n \varepsilon_n \\
&\leq (1 - \alpha_n) \|u_n - x_n\| + \alpha_n k \|u_n - x_n\| + \alpha_n \beta_n k \|x_n - p\| + \\
&\quad \alpha_n \beta_n k H(Tp, Tx_n) + \alpha_n \beta_n k \bar{\varepsilon}_n + \alpha_n \varepsilon_n \\
&\leq (1 - \alpha_n) \|u_n - x_n\| + \alpha_n k \|u_n - x_n\| + \alpha_n \beta_n k \|x_n - p\| + \\
&\quad \alpha_n \beta_n k^2 \|p - x_n\| + \alpha_n \beta_n k \bar{\varepsilon}_n + \alpha_n \varepsilon_n \\
&\leq (1 - \alpha_n (1 - k)) \|u_n - x_n\| + \alpha_n \beta_n k A + \alpha_n \beta_n k^2 A + \alpha_n \beta_n k \bar{\varepsilon}_n + \alpha_n \varepsilon_n
\end{aligned}$$

for some positive A since $\{\|x_n - p\|\}$ is bounded sequence.

Let us denote

$$a_n := \|u_n - x_n\|$$

$$\lambda_n := \alpha_n (1 - k) \in (0, 1), \forall n \geq 0$$

$$\sigma_n := \alpha_n \beta_n k A + \alpha_n \beta_n k^2 A + \alpha_n \beta_n k \bar{\varepsilon}_n + \alpha_n \varepsilon_n$$

for each $n \in \mathbb{N}$, the inequality of Lemma (2.2) is satisfied. Therefore

$$\lim_{n \rightarrow \infty} \|u_n - x_n\| = 0 \quad \dots (2.2)$$

Since Mann iteration $\{u_n\}$ converges to p and using condition (2.2), we get

$$\|x_n - p\| \leq \|u_n - x_n\| + \|u_n - p\|$$

which implies that $\lim_{n \rightarrow \infty} \|x_n - p\| = 0$. Thus, $\lim_{n \rightarrow \infty} x_n = p$

Thirdly, we prove (c) implies (a)

From conditions (1.18), (1.15), (1.3) and (1.5), we get

$$z_{n+1} - x_{n+1} = (1 - \alpha_n) (\zeta_n - x_n) + \alpha_n (\zeta_n - \mu_n)$$

$$\begin{aligned}
 \|z_{n+1} - x_{n+1}\| &= \|(1 - \alpha_n)(\zeta_n - x_n) + \alpha_n(\zeta_n - \mu_n)\| \\
 &\leq (1 - \alpha_n)\|\zeta_n - x_n\| + \alpha_n\|\mu_n - \zeta_n\| \\
 &\leq (1 - \alpha_n)\|\zeta_n - x_n\| + \alpha_n H(Ty_n, Tz_n) + \alpha_n \varepsilon_n \\
 &\leq (1 - \alpha_n)\|\zeta_n - x_n\| + \alpha_n k\|y_n - z_n\| + \alpha_n \varepsilon_n \\
 &= (1 - \alpha_n)\|\zeta_n - z_n + z_n - x_n\| + \alpha_n k\|(1 - \beta_n)x_n + \beta_n \xi_n - z_n\| + \alpha_n \varepsilon_n \\
 &\leq (1 - \alpha_n)\|\zeta_n - z_n\| + (1 - \alpha_n)\|z_n - x_n\| + \\
 &\quad \alpha_n k\|(1 - \beta_n)(x_n - z_n) + \beta_n(\xi_n - z_n)\| + \alpha_n \varepsilon_n \\
 &\leq (1 - \alpha_n)\|z_{n+1} - z_n\| + (1 - \alpha_n)\|z_n - x_n\| + \\
 &\quad \alpha_n k(1 - \beta_n)\|x_n - z_n\| + \alpha_n k\beta_n\|\xi_n - z_n\| + \alpha_n \varepsilon_n \\
 &= (1 - \alpha_n)\|z_{n+1} - z_n\| + (1 - \alpha_n)\|z_n - x_n\| + \alpha_n k(1 - \beta_n)\|x_n - z_n\| + \\
 &\quad \alpha_n \beta_n k\|\xi_n - z_{n+1} + z_{n+1} - z_n\| + \alpha_n \varepsilon_n, \quad \text{where } z_{n+1} \in Tz_n \\
 &\leq (1 - \alpha_n)\|z_{n+1} - z_n\| + (1 - \alpha_n)\|z_n - x_n\| + \alpha_n k(1 - \beta_n)\|x_n - z_n\| + \\
 &\quad \alpha_n \beta_n k\|\xi_n - z_{n+1}\| + \alpha_n \beta_n k\|z_{n+1} - z_n\| + \alpha_n \varepsilon_n \\
 &\leq (1 - \alpha_n)\|z_{n+1} - z_n\| + (1 - \alpha_n)\|z_n - x_n\| + \alpha_n k(1 - \beta_n)\|x_n - z_n\| + \\
 &\quad \alpha_n \beta_n kH(Tx_n, Tz_n) + \alpha_n \beta_n k\|z_{n+1} - z_n\| + \alpha_n \beta_n k\bar{\varepsilon}_n + \alpha_n \varepsilon_n \\
 &\leq (1 - \alpha_n)\|z_{n+1} - z_n\| + (1 - \alpha_n)\|z_n - x_n\| + \alpha_n k(1 - \beta_n)\|x_n - z_n\| + \\
 &\quad \alpha_n \beta_n k^2\|x_n - z_n\| + \alpha_n \beta_n k\|z_{n+1} - z_n\| + \alpha_n \beta_n k\bar{\varepsilon}_n + \alpha_n \varepsilon_n \\
 &= (1 - \alpha_n + \alpha_n k(1 - \beta_n) + \alpha_n \beta_n k^2)\|x_n - z_n\| + (1 - \alpha_n)\|z_{n+1} - z_n\| + \\
 &\quad \alpha_n \beta_n k\|z_{n+1} - z_n\| + \alpha_n \beta_n k\bar{\varepsilon}_n + \alpha_n \varepsilon_n \\
 &\leq (1 - \alpha_n + \alpha_n k(1 - \beta_n) + \alpha_n \beta_n k)\|x_n - z_n\| + (1 - \alpha_n)\|z_{n+1} - z_n\| + \\
 &\quad \alpha_n \beta_n k\|z_{n+1} - z_n\| + \alpha_n \beta_n k\bar{\varepsilon}_n + \alpha_n \varepsilon_n \\
 &\leq (1 - \alpha_n(1 - k))\|x_n - z_n\| + (1 - \alpha_n)\|z_{n+1} - z_n\| + \alpha_n \beta_n k\|z_{n+1} - z_n\| + \\
 &\quad \alpha_n \beta_n k\bar{\varepsilon}_n + \alpha_n \varepsilon_n
 \end{aligned}$$

Let us denote

$$a_n := \|x_n - z_n\| \quad \lambda_n := \alpha_n(1 - k) \in (0, 1), \quad \forall n \geq 0$$

$$\sigma_n := (1 - \alpha_n)\|z_{n+1} - z_n\| + \alpha_n \beta_n k\|z_{n+1} - z_n\| + \alpha_n \beta_n k\bar{\varepsilon}_n + \alpha_n \varepsilon_n$$

for each $n \in \mathbb{N}$, the inequality of Lemma (2.2) is satisfied. Therefore

$$\lim_{n \rightarrow \infty} \|x_n - z_n\| = 0 \quad \dots (2.3)$$

Since Ishikawa iteration $\{x_n\}$ converges to p and using condition (2.3), we get

$$\|z_n - p\| \leq \|z_n - x_n\| + \|x_n - p\|$$

which implies that $\lim_{n \rightarrow \infty} \|z_n - p\| = 0$. Thus, $\lim_{n \rightarrow \infty} z_n = p$. ■

Now, we show that two cases for the equivalent between the convergence of Ishikawa iteration and the convergence of Mann iteration when applied to multi-valued strongly pseudo contraction. For this purpose we recall the following Lemmas :

Lemma(2.4) : [24] Let X be a real normed space and $J: X \longrightarrow \overset{\cdot}{2}$ be the normalized duality mapping, then

$$\|x + y\|^2 \leq \|x\|^2 + 2 \langle y, j(x + y) \rangle, \forall x, y \in X, \forall j(x + y) \in J(x + y).$$

Lemma (2.5) : [2]

Let X be a real normed space and $J: X \longrightarrow \overset{\cdot}{2}$ be the normalized duality mapping, then

$$\langle j(x), y \rangle \leq \|x\| \|y\|, \forall x, y \in X, \forall j(x) \in J(x).$$

Theorem (3.6):

Let X be a real uniformly smooth Banach space, M be a non-empty convex and bounded subset of X and $T : M \longrightarrow \overset{M}{2}$ be a multi-valued strongly pseudo-contraction mapping. Suppose that $P \in F(T)$. Let $u_0 = x_0 \in M$ and define $\{u_n\}$, and $\{x_n\}$ by condition (1.15) and (1.18) with α_n, β_n satisfying the following conditions:

- (i) $0 < \alpha_n, \beta_n < 1$
- (ii) $\lim_{n \rightarrow \infty} \alpha_n = \lim_{n \rightarrow \infty} \beta_n = 0$
- (iii) $\sum_{n=1}^{\infty} \alpha_n = \infty$,

then the following are equivalent

- (a) Mann iteration $\{u_n\}$ converges to P ,
- (b) Ishikawa iteration $\{x_n\}$ converges to P .

Proof:

We prove (a) implies (b)

From $x_{n+1} = (1 - \alpha_n) x_n + \alpha_n \mu_n$, where $\mu_n \in Ty_n$,

$$y_n = (1 - \beta_n) x_n + \beta_n \xi_n, \text{ where } \xi_n \in Tx_n,$$

$$u_{n+1} = (1 - \alpha_n) u_n + \alpha_n v_n, \text{ where } v_n \in Tu_n.$$

From Lemma (2.4), Lemma (2.5) and condition (2.7), we get

$$x_{n+1} - u_{n+1} = (1 - \alpha_n) (x_n - u_n) + \alpha_n (\mu_n - v_n)$$

$$\begin{aligned}
 \|x_{n+1} - u_{n+1}\|^2 &= \|(1 - \alpha_n)(x_n - u_n) + \alpha_n(\mu_n - v_n)\|^2 \\
 &\leq (1 - \alpha_n)^2 \|x_n - u_n\|^2 + 2\alpha_n \langle \mu_n - v_n, j(x_{n+1} - u_{n+1}) \rangle + \\
 &\quad = (1 - \alpha_n)^2 \|x_n - u_n\|^2 + \\
 &\quad \quad 2\alpha_n \langle \mu_n - v_n, j(x_{n+1} - u_{n+1}) - j(y_n - u_n) + j(y_n - u_n) \rangle \\
 \|u_{n+1} - x_{n+1}\|^2 &\leq (1 - \alpha_n)^2 \|x_n - u_n\|^2 + 2\alpha_n \langle \mu_n - v_n, j(y_n - u_n) \rangle + \\
 &\quad 2\alpha_n \langle \mu_n - v_n, j(x_{n+1} - u_{n+1}) - j(y_n - u_n) \rangle \\
 &\leq (1 - \alpha_n)^2 \|x_n - u_n\|^2 + 2\alpha_n k \|y_n - u_n\|^2 + \\
 &\quad 2\alpha_n \|\mu_n - v_n\| \|j(x_{n+1} - u_{n+1}) - j(y_n - u_n)\| \\
 &\leq (1 - \alpha_n)^2 \|x_n - u_n\|^2 + 2\alpha_n k \|y_n - u_n\|^2 + \\
 &\quad 2\alpha_n A_1 \|j(x_{n+1} - u_{n+1}) - j(y_n - u_n)\|, \quad \dots(2.4)
 \end{aligned}$$

for some positive constant A_1 since $\{\|\mu_n - v_n\|\}$ is bounded sequence.

Now, we prove that, when $n \rightarrow \infty$

$$j(x_{n+1} - u_{n+1}) - j(y_n - u_n) \rightarrow 0. \quad \dots(2.5)$$

When X uniformly smooth Banach space, j is uniformly continuous on every bounded set of X . To prove (2.5), it is sufficient to see that

$$\begin{aligned}
 \|(x_{n+1} - u_{n+1}) - (y_n - u_n)\| &= \|(x_{n+1} - y_n) - (u_{n+1} - u_n)\| \\
 &= \|-\alpha_n x_n + \alpha_n \mu_n + \beta_n x_n - \beta_n \xi_n + \alpha_n u_n - \alpha_n v_n\| \\
 &\leq \alpha_n (\|x_n\| + \|\mu_n\| + \|u_n\| + \|v_n\|) + \beta_n (\|x_n\| + \|\xi_n\|) \\
 &\leq (\alpha_n + \beta_n) A \rightarrow 0 \quad (n \rightarrow \infty),
 \end{aligned}$$

where $A = \sup(\|x_n\| + \|\mu_n\| + \|u_n\| + \|v_n\|, \|x_n\| + \|\xi_n\|)$ and it is clear that A is finite. Since the boundeness of M makes all the sequences $\{x_n\}$, $\{u_n\}$, $\{\mu_n\}$, $\{\xi_n\}$, and $\{v_n\}$ are bounded.

So, (2.5) holds. We define

$$\sigma_n = 2\alpha_n A_1 \|j(x_{n+1} - u_{n+1}) - j(y_n - u_n)\| \quad \dots(2.6)$$

From condition (1.18) and Lemma (2.4), we get

$$\begin{aligned}
 \|y_n - u_n\|^2 &= \|(1 - \beta_n)(x_n - u_n) + \beta_n(\xi_n - u_n)\|^2 \\
 &\leq (1 - \beta_n)^2 \|x_n - u_n\|^2 + 2\beta_n \langle \xi_n - u_n, j(y_n - u_n) \rangle + \beta_n^2 \|\xi_n - u_n\|^2 \\
 &\leq \|x_n - u_n\|^2 + 2\beta_n A_2,
 \end{aligned} \quad \dots(2.7)$$

for some positive constant A_2 since $\{\langle \xi_n - u_n, j(y_n - u_n) \rangle\}$ is bounded.

Replacing (2.6) and (2.7) in (2.4), we obtain

$$\begin{aligned}\|x_{n+1} - u_{n+1}\|^2 &\leq (1 - \alpha_n)^2 \|x_n - u_n\|^2 + 2\alpha_n k \|x_n - u_n\|^2 + \sigma_n + 4k\alpha_n \beta_n A_2 \\ &= (1 - 2(1 - k)\alpha_n + \alpha_n^2) \|x_n - u_n\|^2 + o(\alpha_n).\end{aligned}\quad \dots\dots(2.8)$$

The condition $\lim_{n \rightarrow \infty} \alpha_n = 0$ implies the existence of a positive integer number

n_0 such that for all $n \geq n_0$, we get

$$\alpha_n \leq (1 - k) \quad \dots(2.9)$$

Substituting (2.9) into (2.8), we get

$$(1 - 2(1 - k)\alpha_n + \alpha_n^2) \leq 1 - 2(1 - k)\alpha_n + (1 - k)\alpha_n = 1 - (1 - k)\alpha_n$$

Finally,

$$\|x_{n+1} - u_{n+1}\|^2 \leq (1 - (1 - k)\alpha_n) \|x_n - u_n\|^2 + o(\alpha_n)$$

Let us denote

$$a_n := \|x_n - u_n\|^2$$

$$\lambda_n := (1 - k)\alpha_n \in (0, 1)$$

and using Lemma (2.2), we obtain $\lim_{n \rightarrow \infty} a_n = 0$.

Thus

$$\lim_{n \rightarrow \infty} \|x_n - u_n\|^2 = 0 \quad \dots(2.10)$$

Since Mann iteration $\{u_n\}$ converges to p and using condition (2.10), we get

$$\|x_n - p\| \leq \|x_n - u_n\| + \|u_n - p\|$$

which implies that $\lim_{n \rightarrow \infty} \|x_n - p\| = 0$. That is $\lim_{n \rightarrow \infty} x_n = p$.

Analogously, $\lim_{n \rightarrow \infty} x_n = p$ implies that $\lim_{n \rightarrow \infty} u_n = p$. ■

The next result hold when X is a real Banach space:

Theorem (3.7):

Let X be a real Banach space, M be a non-empty convex subset of X and $T : M \longrightarrow 2^M$ be a multi-valued strongly pseudo contraction mapping. Suppose that $P \in F(T)$ and the sequences $\{\xi_n\}$, $\{\mu_n\}$ and $\{v_n\}$ are bounded sequences, when $\xi_n \in Tx_n$, $\mu_n \in Ty_n$ and $v_n \in Tu_n$ and the following conditions are satisfied

$$\lim_{n \rightarrow \infty} \|\xi_{n+1} - \mu_n\| = 0, \lim_{n \rightarrow \infty} \|v_{n+1} - v_n\| = 0, \text{ where } \xi_{n+1} \in Tx_{n+1}, v_{n+1} \in Tu_{n+1},$$

let $x_0 = u_0 \in M$ and defined $\{u_n\}$, $\{x_n\}$ by conditions (1.15) and (1.18) with α_n, β_n satisfying

$$(i) \quad 0 < \alpha_n, \beta_n < 1$$

$$(ii) \quad \lim_{n \rightarrow \infty} \alpha_n = 0$$

$$(iii) \quad \sum_{n=1}^{\infty} \alpha_n = \infty,$$

Then the following are equivalent

- Mann iteration $\{u_n\}$ converges to P ,
- Ishikawa iteration $\{x_n\}$ converges to P .

Proof:

We prove (a) implies (b) Set $A := \max \{ \sup \{ \|\xi_n\| \}, \sup \{ \|\mu_n\| \}, \sup \{ \|\nu_n\| \}, \|x_0\| \}$

It is clear that $\|x_0\| \leq A$. Supposing that $\|x_n\| \leq A$, we prove that $\|x_{n+1}\| \leq A$.

Indeed, from $x_{n+1} = (1 - \alpha_n)x_n + \alpha_n \mu_n$, where $\mu_n \in Ty_n$

We have

$$\begin{aligned} \|x_{n+1}\| &\leq (1 - \alpha_n)\|x_n\| + \alpha_n\|\mu_n\| \\ &\leq (1 - \alpha_n)A + \alpha_n A \end{aligned}$$

That is $\|x_{n+1}\| \leq A, \forall n \in \mathbb{N}$

Similarly, we get $\|u_{n+1}\| \leq A, \forall n \in \mathbb{N}$

We get, by use of $\|x_{n+1} - u_{n+1}\| \leq \|x_{n+1}\| + \|u_{n+1}\| \leq 2A$,

$$u_{n+1} = (1 - \alpha_n)u_n + \alpha_n v_n, \text{ where } v_n \in Tu_n,$$

$$x_{n+1} = (1 - \alpha_n)x_n + \alpha_n \mu_n, \text{ where } \mu_n \in Ty_n,$$

$$y_n = (1 - \beta_n)x_n + \beta_n \xi_n, \text{ where } \xi_n \in Tx_n.$$

From Lemma (2.4), Lemma (2.5) and condition (1.8), we get

$$x_{n+1} - u_{n+1} = (1 - \alpha_n)(x_n - u_n) + \alpha_n(\mu_n - v_n)$$

$$\begin{aligned} \|x_{n+1} - u_{n+1}\|^2 &= \|(1 - \alpha_n)(x_n - u_n) + \alpha_n(\mu_n - v_n)\|^2 \\ &\leq (1 - \alpha_n)^2 \|x_n - u_n\|^2 + 2\alpha_n \langle \mu_n - v_n, j(x_{n+1} - u_{n+1}) \rangle \\ &= (1 - \alpha_n)^2 \|x_n - u_n\|^2 + \\ &\quad 2\alpha_n \langle \mu_n - \xi_{n+1} + \xi_{n+1} - v_{n+1} + v_{n+1} - v_n, j(x_{n+1} - u_{n+1}) \rangle \end{aligned}$$

where $\xi_{n+1} \in Tx_{n+1}$, $v_{n+1} \in Tu_{n+1}$

$$\begin{aligned} \|x_{n+1} - u_{n+1}\|^2 &= (1 - \alpha_n)^2 \|x_n - u_n\|^2 + 2\alpha_n \langle \xi_{n+1} - v_{n+1}, j(x_{n+1} - u_{n+1}) \rangle + \\ &\quad 2\alpha_n \langle \mu_n - \xi_{n+1}, j(x_{n+1} - u_{n+1}) \rangle + 2\alpha_n \langle v_{n+1} - v_n, j(x_{n+1} - u_{n+1}) \rangle \\ &\leq (1 - \alpha_n)^2 \|x_n - u_n\|^2 + 2\alpha_n k \|x_{n+1} - u_{n+1}\|^2 + \\ &\quad 2\alpha_n \langle \mu_n - \xi_{n+1}, j(x_{n+1} - u_{n+1}) \rangle + 2\alpha_n \langle v_{n+1} - v_n, j(x_{n+1} - u_{n+1}) \rangle \\ &\leq (1 - \alpha_n)^2 \|x_n - u_n\|^2 + 2\alpha_n k \|x_{n+1} - u_{n+1}\|^2 + \\ &\quad 2\alpha_n \|\mu_n - \xi_{n+1}\| \|x_{n+1} - u_{n+1}\| + 2\alpha_n \|v_{n+1} - v_n\| \|x_{n+1} - u_{n+1}\| \\ &\leq (1 - \alpha_n)^2 \|x_n - u_n\|^2 + 2\alpha_n k \|x_{n+1} - u_{n+1}\|^2 + \\ &\quad 4\alpha_n \|\mu_n - \xi_{n+1}\| A + 4\alpha_n \|v_{n+1} - v_n\| A \end{aligned}$$

Thus,

$$\|x_{n+1} - u_{n+1}\|^2 \leq \frac{(1 - \alpha_n)^2}{(1 - 2\alpha_n k)} \|x_n - u_n\|^2 + \frac{4\alpha_n A}{(1 - 2\alpha_n k)} (\|\mu_n - \xi_{n+1}\| + \|v_{n+1} - v_n\|).$$

Since $\alpha_n \rightarrow 0$ as $n \rightarrow \infty$, there exists a positive integer n_0 such that $2\alpha_n < 1$. Hence $1 - 2\alpha_n k > 1 - k$, $\forall n \geq n_0$, and so

$$\|x_{n+1} - u_{n+1}\|^2 \leq \frac{(1 - \alpha_n)^2}{(1 - 2\alpha_n k)} \|x_n - u_n\|^2 + \frac{2\alpha_n A}{(1 - k)} (\|\mu_n - \xi_{n+1}\| + \|v_{n+1} - v_n\|) \dots (2.11)$$

We have

$$\frac{(1 - \alpha_n)^2}{(1 - 2\alpha_n k)} = \frac{(1 - 2\alpha_n + \alpha_n^2)}{(1 - 2\alpha_n k)} = \frac{(1 - 2\alpha_n k) + 2\alpha_n k - 2\alpha_n + \alpha_n^2}{1 - 2\alpha_n k} = 1 - \left(\frac{2(1 - k) - \alpha_n}{1 - 2\alpha_n k} \right) \alpha_n$$

$$\text{and } \left(\frac{2(1 - k) - \alpha_n}{1 - 2\alpha_n k} \right) \rightarrow 2(1 - k) \text{ as } n \rightarrow \infty.$$

Therefore there exists $n_1 \geq n_0$ such that for any $n \geq n_1$ the following holds:

$$\left(\frac{2(1 - k) - \alpha_n}{1 - 2\alpha_n k} \right) > 1 - k \Rightarrow - \left(\frac{2(1 - k) - \alpha_n}{1 - 2\alpha_n k} \right) < -(1 - k).$$

Hence for any $n \geq n_1$ from (2.11), we get

$$\|x_{n+1} - u_{n+1}\|^2 \leq (1 - (1 - k)\alpha_n) \|x_n - u_n\|^2 + \frac{4\alpha_n A}{(1 - k)} (\|\mu_n - \xi_{n+1}\| + \|v_{n+1} - v_n\|).$$

Let us denote

$$a_n := \|x_n - u_n\|^2$$

$$\lambda_n := (1 - k)\alpha_n \in (0, 1), \forall n \geq 0$$

$$\sigma_n = \frac{4\alpha_n A}{(1 - k)} (\|\mu_n - \xi_{n+1}\| + \|v_{n+1} - v_n\|),$$

and using Lemma (2.2), we obtain $\lim_{n \rightarrow \infty} a_n = 0$. Thus

$$\lim_{n \rightarrow \infty} \|x_n - u_n\|^2 = 0 \quad \dots (1.12)$$

Since Mann iteration $\{u_n\}$ converges to p and using condition (2.12), we get

$$\|x_n - p\| \leq \|x_n - u_n\| + \|u_n - p\| \text{ which implies that } \lim_{n \rightarrow \infty} \|x_n - p\| = 0.$$

That is, $\lim_{n \rightarrow \infty} x_n = p$. Analogously, $\lim_{n \rightarrow \infty} x_n = p$ implies that $\lim_{n \rightarrow \infty} u_n = p$. ■

Finally, all above results hold when T is singleton mapping.

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Development and Implementation of Software Based on (Judd-Ofelt) Model for Spectral Characteristics Measurement of (Nd³⁺:Glass) Laser Media

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الخلاصة

تم في هذا البحث إجراء التحليلات الطيفية لثلاث نماذج من الأوساط الليزرية الزجاجية نوع (النيديميوم - زجاج) بالاعتماد على النموذج الرياضي (الموديل) (Judd-ofelt). يتركز تطوير أداء الموديل عن طريق تعشيق منظومة الفحوصات الطيفية مباشرة مع الحاسوب عن طريق المخرج (RS323) لضمان انتقال وتسجيل البيانات المتعلقة بالقياسات الطيفية لطيف الامتصاص للنماذج مباشرة وبدقة عالية. تم بناء البرامجيات المتعلقة بالتعشيق وفق معطيات النموذج الرياضي والتي تمكنا من استنتاج وتوقع قياسات طيف الفلورة بالاعتماد على معلمات قياس طيف الامتصاص المدخلة كبيانات أولية. حيث تم اختيار البرنامج لثلاث نماذج من الأوساط الليزرية نوع البورايت والبوروفوسفات لنفس الوسط المضيف ونسب تطعيم مختلفة وكذلك لأوساط مضيئة مختلفة ونسب تطعيم ثانية. تم الحصول على نتائج جيدة وبدقة عالية من خلال مقارنتها بالنشریات العلمية المماثلة.

ABSTRACT

The spectroscopic analysis for three samples of (Nd³⁺: Glass) laser media has preformed utilizing the standard (Judd-ofelt) model. Our development concerned on performing the process for computer interfacing to spectrophotometer system utilizing serial port (RS323) to secure the best (on-line) data coupling and transferring approach to guarantee accuracy in measurement spectroscopic absorption parameter values. Software was build concerning the interface process for the implementation of (Judd-ofelt) model stages, which lead to get an estimated value of fluorescence parameters depending mainly on absolute absorption spectrum input data. Absorption data from three (Nd³⁺: Glass) samples with different doping concentration of (Nd³⁺) active ion doping in same Borate Glass host, and different (Borophosphate & borate) Glass hosts doped with same (Nd³⁺) ion concentration were used input data to our above developed program and result obtained with accuracy is being acquired as a consequence of applying software instead of the statistical methods used in the previous researchers.

INTRODUCTION

The solid state laser material consists ordinarily of a transparent host material doped by active ions that replaces some atoms or ions of the original materials. The host must have good optical, mechanical and thermal properties to withstand the severe operating conditions of practical laser and these properties include hardness, chemical inertness, and absence of internal strain, refractive index variation, existence to radiation-induced color centers, low cost and ease of fabrication. the basic host for the neodymium is YAG and glass, here glass as non crystalline host material has been tackled from the point of view of studying a (Nd³⁺ Glass) laser, which is the present work topic. The laser action has been achieved from trivalent rare earth ions (Nd³⁺, Er³⁺, Ho³⁺, Tm³⁺, Pr³⁺, Gd³⁺, Eu³⁺, Yb³⁺), divalent rare earth ions (Sm²⁺, Dy²⁺, Tm²⁺), transition metals (Cr³⁺, Ni³⁺, Co³⁺) and materials. [3]

The produced laser action covering a spectral wavelength range from (0.55-3.36)µm, the trivalent Nd³⁺ ion represent the first rare earth element used in laser field as it is the most important one of this group.

Laser media is an effective element with the laser system, manufacturing process of this media is very costly; therefore it has been based upon taking small laboratory sample of different media to be studied. [4] [3]

The laser medium must posse's sharp fluorescent lines and strong absorption bands and high quantum efficiency for the fluorescence transition of interest.

(JUDD-OFELT) MODEL

This is a mathematical model to calculate irradiative transition probabilities between electronic energy levels of trivalent rare earth ions in solids which has been developed by Judd [1] and Ofelt [2], and became perfect theoretical model called (J-O) model.

This model is used successfully to compute spectroscopic parameters for rare-earth ions in solids to determine transition probabilities. The properties of active laser medium could be determined by spectral measurement as the absolute absorption spectrum and fluorescence spectrum using small samples.

Absorption Spectrum Measurements

The following figure(1) show the flowchart of the procedure used to compute the spectral parameters for the absorption transitions initiated at the ground state ⁴I_{9/2} for the studied data samples, When data is received from the (spectrophotometer) which determines the value of absorption spectrum

as (Y-axis in cm) and values of wavelength as (X-axis) where several steps are implemented to the model for calculating the functions in the following steps. [6]

First step : is plotting the absolute absorption spectra where its data was taken at room temperature using the (spectrophotometer) for each sample and typically there are nine absorption bands lying between (430-900)nm and originating from the $^4I_{9/2}$ ground state.

Second step: is taking the numerical integration for five main absorption bands of wavelength for the measured absolute absorption spectrum.

These five bands centered approximately at (530,580,750,810,880)nm using (least square fitting)program, The area under the absorption curve of every absorption band $\left(\int_{band} k_{\lambda} d_{\lambda}\right)$ can be calculated within the integrated absorption spectrum (Simpson rule).

Third step: is calculation of Nd^{3+} ion density (ρ). The calculation of peak absorption cross-section and radiative transition probabilities from absorbance measurements requires knowledge of Nd-ion density $[(\rho)$ (ion/cm³)] in the studied samples. The ion density was determined from the following equation. [5]

$$\rho = \frac{2PNd}{M} \quad \dots \dots \dots (1)$$

Where:

P: rate doping

N: Avogadro number (6.023×10^{23} /mole).

M: the molecular weight of Nd_2O_3 (336.48)

D: the active medium density.

Forth step: is to calculate the absorption coefficient, the absorption coefficient is defined by Bear-Lambert law:

$$I\nu(x) = I\nu_{(0)} \exp(-K(\nu) * x) \quad \dots \dots \dots (2)$$

Where:

$I\nu_{(0)}$: is the incident radiation intensity.

$I\nu_{(x)}$: The radiation intensity of the penetrating ray of frequency (ν) at depth x.

K (ν): is the absorption coefficient.

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Fifth step: is the line strength measuring values (S_m).

The absorption spectrum is determined using spectrophotometers in accordance with (J-O) model.

The measured values of line strength could be determined by performing numerical integration on basic absorption bands to evaluate $(\int_{band} K_\lambda D_\lambda)$ the following equation gives (S_m) values.

$$(\int_{band} K_\lambda D_\lambda) = \frac{8\pi^3 e^2 \lambda}{3ch(2J+1)n} \left[\frac{(n^2+2)^2}{9} \right] S_{ED} \quad \dots \dots \dots (3)$$

Where

K_λ : is the absorption coefficient at wavelength λ .

ρ : The Nd³⁺ ion concentration.

λ : The peak wavelength of the absorption band.

J : is the total angular momentum of the initial level ($J=9/2$ in Nd³⁺)

$n=n(\lambda)$: is the index of the fraction at wavelength λ .

$(n^2+2)^{2/9}$: factor represents the local field correction for the ion in a dielectric medium.

h : is blanks constant (6.626×10^{-34} Js).

Sixth step: calculation of intensity parameters (Ω).

According to the (J-O) model, the line strength between initial (J) manifold (S,L)J and terminal J manifold (S,J)J may be written in the form:

$$S = \sum_{t=2,4,6} \Omega_t |(S,L)J| U^{(t)} |(S,L)J|^2 \quad \dots \dots \dots (4)$$

The parameters ($\Omega_2, \Omega_4, \Omega_6$) represent intensity parameters for the theoretical (J-O) model which reflects symmetry of the crystal field applied on the active ions locations.

These parameters determined the transition strength between any two energy levels in these active ions. By using the (S_m) values that obtained from equation (2-8) into equation (2-9) in addition to the element of $|U^{(t)}|$, the intensity parameters (Ω_t) of the (J-O) model is obtained.

Seventh step : measuring the oscillator strength (F).

The strength of transition between levels (a,b) can be described by the dimensionless quantity, oscillator strength that is denoted by (F) and calculated by [14].

$$F_{(ba)} = \frac{8\pi^2 m \nu}{3he^2 g_a} S_{(ba)} = \frac{8\pi^2 m \nu}{3he^2 g_a} \sum_{(ba)} |\langle \Psi_a | U | \psi_b \rangle|^2 \quad \dots \dots \dots (5)$$

Where

ν : is the transition frequency, thus $E_b - E_a = h\nu$.

g_a : is the statistical weight for the level (a) $= 2J_a + 1$

h : is Planck constant (6.626×10^{-34} Js)

eighth step: absorption cross section calculation (σ).

If absorption between level (a,b) were under ED conditions, then the line strength S_{ED} and oscillator strength F_{ED} are related to ($\sigma(\nu)$) by the following equation. [5]

$$\int \sigma(\nu) d\nu = \frac{\int k(\nu) d\nu}{\rho} = \frac{\pi e^2}{mc} \left[\frac{(n^2 + 2)^2}{9} \cdot \frac{1}{n} \right] f_{ED} = \frac{8\pi^3 \nu}{3hc g_a} \left[\frac{(n^2 + 2)^2}{9} \cdot \frac{1}{n} \right] S_{ED} \dots \dots \dots (6)$$

The quantity $\int k(\nu) d\nu$ is known as the integrated absorption cross-section where n represents the refractive index of the material.

ninth step: calculation of absorption line-strength (S_C).

The absorption line strength can be calculated by multiplying the value of intensity parameter with the value of unit tensor $|U^{(0)}|^2$ that return to Nd^{+3} ions as follows:

$$S_c = \Omega \cdot U \dots \dots \dots (7)$$

It worth's to mention that the value of (S_c & S_m) are in agreement with the literature, this reflect the efficiency of both the (J-O) model and the software utilized.

Tenth step: oscillator strength calculation (F_C)

This function is calculated by substituting the (calculated absorption line strength S_c) in the following equation: [5]

$$F_c = \frac{8\pi^2 m \nu_i}{3h(2J + 1)} (S_c)^T \dots \dots \dots (8)$$

Fluorescence Spectrum Measurement

Figure (1) shows the flowchart of the procedure used to calculate the spectral parameters for fluorescence transition from the excited levels ($^4I_{9/2}$, $^4I_{1/2}$, $^4I_{3/2}$, $^4I_{5/2}$), it shows the fluorescence line at (0.88, 1.06, 1.35, 1.88) μm respectively and the following steps illustrate the method used to calculate the parameters of radiative fluorescence transition. [5] [7]

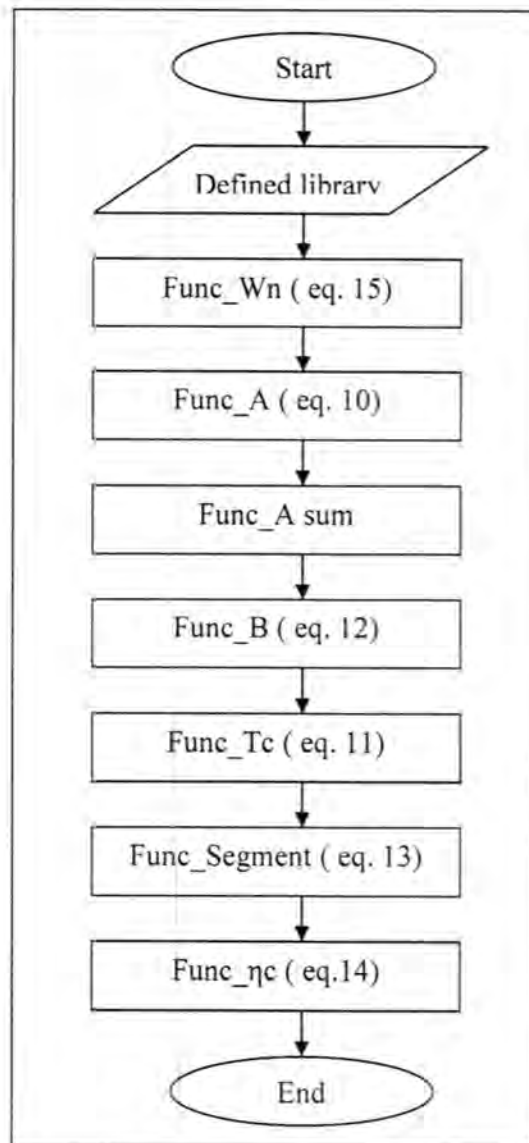


Figure 1: Shows the flowchart of the procedure used to calculate the spectral parameters for fluorescence transition from the excited levels ($^4I_{9/2}$, $^4I_{1/2}$, $^4I_{3/2}$, $^4I_{5/2}$).

First step:- is fluorescence line strength.

These values are calculated for different wavelengths by substituting the values of intensity parameter (Ω_t) and the numerical values of the matrix $|U^{(t)}|^2$ using the following equation.

$$S_f = \Omega * U \quad \dots \dots \dots (9)$$

Second step:- is calculation of spontaneous emission probability(A).

By substituting the above value (S_f) in addition to the refractive indices for the studied sample within the range of fluorescence line in the following equation:

$$A[(S, L)J; (\bar{S}, \bar{L})\bar{J}] = \frac{64\pi^2 e^2}{3h(2J+1)\lambda^3} n \left[\frac{(n^2 + 2)^2}{9} \right] \sum_{l=2,4,6} \Omega_l \left| \langle (S, L)J \| U^l \| (\bar{S}, \bar{L})\bar{J} \rangle \right|^2 \dots \dots \dots (10)$$

The values of the spontaneous emission probabilities are calculated for fluorescence transition $A(^4F_{3/2} \rightarrow ^4I_J)$, where ($J=9/2, 11/2, 13/2, 15/2$).

Third step:- lifetime calculation (τ_{rad}^c).

The lifetime of radiation (τ_{rad}^c) is calculated for the level $^4F_{3/2}$ after the total values for the spontaneous emission probabilities are found by summing conjugate probabilities for every fluorescence transition in $^4F_{3/2}$ level, from the following equation.

$$\tau_{rad}^c = \left\{ \sum_{\bar{S}, \bar{L}, \bar{J}} A[(S, L)J; (\bar{S}, \bar{L})\bar{J}] \right\}^{-1} = A_{total}^{-1} \dots \dots \dots (11)$$

Fourth step:- branching ratio calculation (β).

The branching ratio for every fluorescence transition originating from $^4F_{3/2}$ level is calculated by substituting the spontaneous emission probabilities value for fluorescence transition and A_{sum} values in the following equation.

$$\beta[(S, L)J; (\bar{S}, \bar{L})\bar{J}] = \frac{A[(S, L)J; (\bar{S}, \bar{L})\bar{J}]}{\sum_{\bar{S}, \bar{L}, \bar{J}} A[(S, L)J; (\bar{S}, \bar{L})\bar{J}]} \dots \dots \dots (12)$$

Fifth step:- emission cross-section calculation (σ_{em}).

The peak induced emission cross-section can be calculated by using the following equation.

$$\sigma_{em} = \frac{\lambda_p^4}{8\pi c n^2 \Delta \lambda_{eff}} A[(^4F_{3/2}) \rightarrow (^4I_{11/2})] \dots \dots \dots (13)$$

Sixth step:- radiative quantum efficiency calculation (η_c).

The radiative quantum efficiency can be calculated from the following equation.

$$\eta = \frac{\tau_f^m}{\tau_{rad}^c} \dots \dots \dots (14)$$

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Also we can calculate the average of nonradiative decay from the following equation:

$$W_{nr} = \frac{1}{\tau_f^m} - \sum_b A_{(ab)} \quad \dots \dots \dots (15)$$

3- Hardware Interface:-

The connection operation between the spectrophotometer device and the (PC) was carried out through the serial port RS232 ,data transfer from this port to (PC) was done using an interfacing program and saving this data as a file in the (PC) and then processing it .

Experimentally, two computers were connected using COM1 serial port so that the first computer became data transmitter and the second one as a data receiver; the (PC) connect to the device.

So now the device became a data transmitter and the (PC) as a data receiver, the following figure (2) present the flowchart of the procedure used to receive data from serial port RS232. [8] [9]

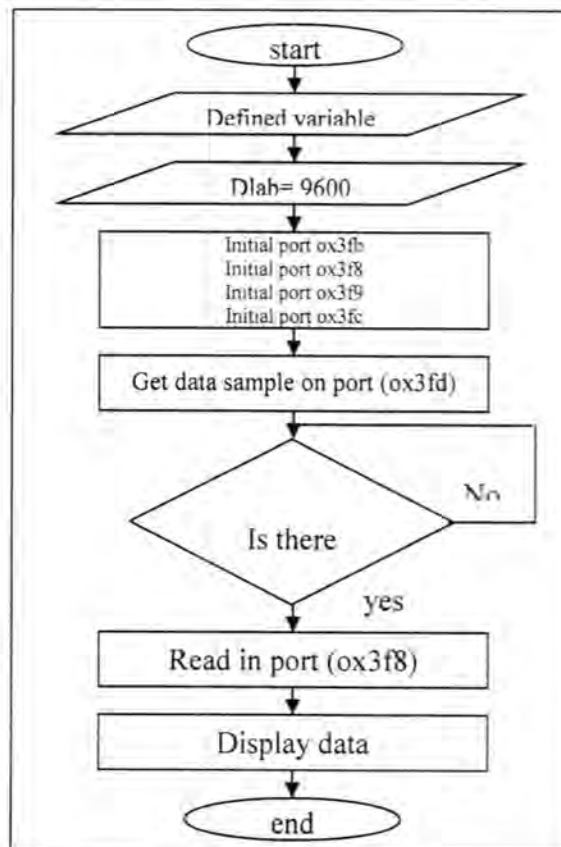


Figure 2: Present the flowchart of the procedure used to receive data from serial port RS232.

EXPERIMENTATION RESULT

The following table present the spectroscopic parameter of the absorption spectrum measurement initial from the ground state, after taking absolute absorption spectrum to five bands at different wavelength from different host (Borate and Borophosphate) we can calculate the line strength (measured and calculated) also we can calculate oscillator strength (measured and calculated), by using the previous value of line strength and the element of $|U^{(i)}|$ matrix we can calculate the intensity parameter. [4]

Sample designation		Sh2		Sh3		B3	
Band no.	$\left(\frac{1}{\lambda}\right) \mu m$	S_m	S_c	S_m	S_c	S_m	S_c
1	0.88	8.809	8.97	3.35	-1.24	1.857	3.14
2	0.81	9.85	2.06	2.24	8.34	1.15	9.20
3	0.75	9.78	1.72	3.23	2.78	1.75	8.77
4	0.58	3.19	5.15	1.27	1.78	1.35	2.27
5	0.35	3.84	1.23	9.23	-4.69	5.31	5.00
Band no.	$\left(\frac{1}{\lambda}\right) \mu m$	S_m	S_c	S_m	S_c	S_m	S_c
1	0.88	1.08	1.107	4.14	-1.53	2.29	3.88
2	0.81	1.32	2.77	3.002	1.11	1.55	1.23
3	0.75	1.41	2.49	4.67	4.03	2.54	1.27
4	0.58	5.97	9.64	2.38	3.33	2.54	4.26
5	0.35	7.87	2.53	1.89	-9.61	1.08	1.02
Host Glass		Borate			Borophosphate		
(J-O) Intensity parameters		Ω_2	3.08	5.51	1.59		
		Ω_4	3.34	-6.56	1.07		
		Ω_6	2.37	4.66	1.25		

The following table presents the spectroscopic parameter of the fluorescence spectrum measurement initial from the terminal state, by using the previous value of the intensity parameter we can calculate the spontaneous emission probability and branching ratio and fluorescence line strength and calculated life time.

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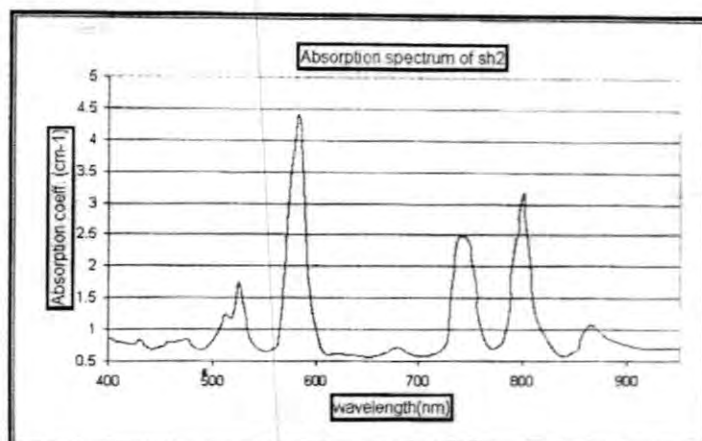


Figure3 : Present the integrated absorption spectrum of sample (sh2)
from Borate host at rate doping (2%)

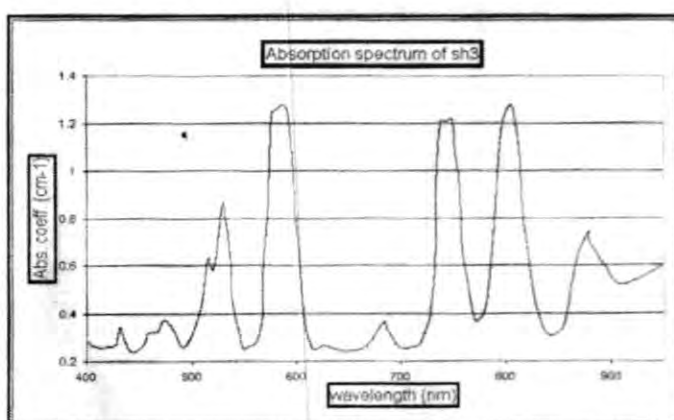


Figure 4 : Present the integrated absorption spectrum of sample (sh3)
from Borate host at rate doping (3%)

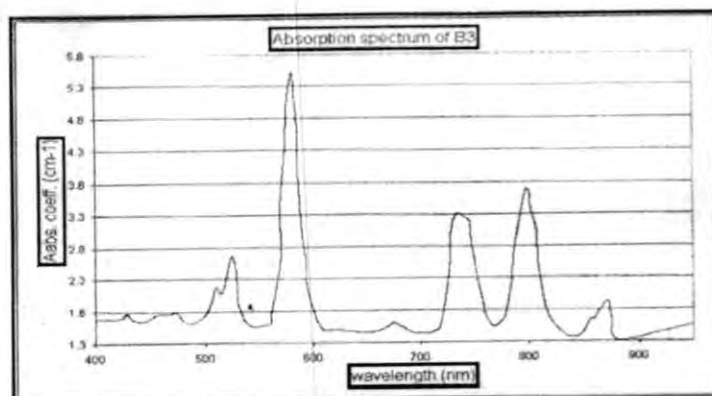


Figure 5: Present the integrated absorption spectrum of sample (B3)
from Borophosphate host at rate doping (3%)

Sample designation				Sh2		
$\left(\bar{S}, \bar{L}\right) \bar{J}$	$\left(\bar{\lambda}_{\mu}\right)$	$\left\langle U^4\right\rangle$	$\left\langle U^6\right\rangle$	$S_{\left(\bar{\lambda}\right)}$	$A_{\left(S^{-1}\right)}$	B _c
$^4 I_{9 / 2}$	0.88	0.23	0.056	9.03	0.08	0.48
$^4 I_{11 / 2}$	1.06	0.142	0.407	1.44	0.08	0.44
$^4 I_{13 / 2}$	1.35	0.0	0.212	5.04	0.01	0.07
$^4 I_{15 / 2}$	1.88	0.0	0.028	6.65	6.73	0.03
(J-O) Intensity parameters			Ω_2	3.08		
			Ω_4	3.34		
			Ω_6	2.37		
$A_{(total)}\left(\text{Sec}^{-1}\right)$						
$\tau_{rad}^c(\mu s)$			54.09			

Sample designation				Sh3		
$\left(\bar{S}, \bar{L}\right) \bar{J}$	$\left(\bar{\lambda}_{\mu}\right)$	$\left\langle U^4\right\rangle$	$\left\langle U^6\right\rangle$	$S_{\left(\bar{\lambda}\right)}$	$A_{\left(S^{-1}\right)}$	B _c
$^4 I_{9 / 2}$	0.88	0.23	0.056	-1.24	-0.012	3.05
$^4 I_{11 / 2}$	1.06	0.142	0.407	9.65	0.054	-1.35
$^4 I_{13 / 2}$	1.35	0.0	0.212	0.88	0.026	-0.67
$^4 I_{15 / 2}$	1.88	0.0	0.028	1.30	0.013	-0.03
(J-O) Intensity parameters			Ω_2	5.51		
			Ω_4	-6.56		
			Ω_6	4.66		
$A_{(total)}\left(\text{Sec}^{-1}\right)$						
$\tau_{rad}^c(\mu s)$			-248.4			

Sample designation				B3		
$\left(\bar{S}, \bar{L}\right) \bar{J}$	$\left(\bar{\lambda}_{\mu}\right)$	$\left\langle U^4\right\rangle$	$\left\langle U^6\right\rangle$	$S_{\left(\bar{\lambda}\right)}$	$A_{\left(S^{-1}\right)}$	B_c
$^4 I_{9 / 2}$	0.88	0.23	0.056	3.16	0.031	0.40
$^4 I_{11 / 2}$	1.06	0.142	0.407	6.62	0.037	0.49
$^4 I_{13 / 2}$	1.35	0.0	0.212	2.65	0.072	0.09
$^4 I_{15 / 2}$	1.88	0.0	0.028	3.51	3.55	0.04
(J-O) Intensity parameters			Ω_2	1.59		
			Ω_4	1.07		
			Ω_6	1.25		
$A_{\text {total }}\left(\text {Sec}^{-1}\right)$						
$\tau_{\text {rad }}^c(\mu s)$			131.18			

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CONCLUSION

- 1- Result accuracy is being acquired as a consequence of applying software instead of the statistical methods used in the previous researches. [4]
- 2- Using (object oriented programming) of the programs increased the software efficiency.
- 3- The calculated values of the spectroscopic parameters of fluorescence transition are dependent on the intensity parameters (Ω_t) of the (J-O) model which were calculated from absorption spectra.
- 4- The width of the absorption bands was increased due to the increase in the neodymium ion density.

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Aerial Photointerpretation in Extracting Soil Hydromorphic Condition and Canals Density Calculation in the Semi-Arid Tigris Floodplain Region

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الخلاصة

المنطقة تحت الدراسة هي جزء من السهل الفيزيائي لنهر دجلة. سوف نراجع ونوضح الطريقة والقواعد والنتائج في تحليل اشكال الارض. لاحقاً سوف نحسب كثافة القنوات المائية وعلاقتها مع سطح الارض وفي النهاية علاقتها مع حالات وتنوع التربة. كنتيجة للاستخدام الشديد (المفرط) لنظام الري والبزل فان النظام الزراعي الطبيعي للبزل في المنطقة قد تعرض للتدهور التدريجي. من اجل إعطاء الحل العلمي لمشكلة الري و البزل، فان تحليل الأرض بواسطة بيانات التحسس النائي الجوية قد استعملت. أسباب التدهور التدريجي للبزل والري ربطت وقورنت بالعمليات الجيومورفولوجية المسؤولة عن تكوين سطح الأرض. أهم حقيقة توصل اليها البحث ، الا وهي بان مساحات الأراضي زراعية شاسعة تركت وأهدرت من خلال استخدام طرق الري والبزل القديمة ، وذلك من حلال تعرضها لمشكلتي التملح والتصحر ، هذه الطرق القديمة يجب ان تستبدل بالطرق الحديثة.

ABSTRACT

The area under study is part of the Tigris flood plain region. We will review and clarify the method, principles and results in of the landscape analysis Density of hydromorphic channel has been calculated and its relation to the landscape and finally its relation to soil conditions. As a result of intensive irrigation land drainage practices, the region's arable land has been subjected to progressive deterioration. In order to give a scientific solution for the drainage and irrigation problem, the landscape analysis of aerial remote sensing data was employed. Causes of drainage and irrigation. deterioration were correlated with Geomorphic processes. The most important factreached, that huge arable land were wasted and abandoned Through employing old irrigation and drainage practices, by exposing these lands to desertification and salinization problems, These old practices should be replaced by modern ones.

INTRODUCTION

This study represents a practical application of landscape aerial photo interpretation technique to determine the density of irrigation canals as a clues for soil conditions and soil drainage deterioration in the region , the objective is to highlight the density of irrigation canals and the physical factors affecting soils and soil drainage conditions , the study predicts the behaviour of another expanded agricultural areas based on the performance of similar site and material conditions existing in the areas already under use. Further more it is aimed at providing proposals for recovery and optimal utilization of affected areas, the contribution of physical factors towards deterioration in soil drainage conditions needs quantitative verification based on spatial distribution of the problem areas. The description of the region enumerates its physical characteristics employed during the process of landscape photo interpretation . Excellent work has been carried out by (Townshend , 1981) [1] , and (Avery , 1992) , [2] , in the field soil information and remot sensing .

Spatial Setting

The area is about 21 km² square kilometers occurring 30 km south of Baghdad along the Tigris river in the lower Mesopotamian plain (fig 1. Location map).

Geomorphologically the area called Flood plain, It is used for intensive cultivation except for the parts which are Salt-affected . The Salt-free areas have a very high agricultural value , the saline flats and channel remnants are unused and serve as recipient sites for runoff and uncontrolled effluent from the adjoining area , the land price of these landscapes is low because of their location being away from the city infrastructure . The Tigris river attains a meandering character in the region and its course has been properly trained by construction of earthen embankments on either side. As a result of continuous sedimentation by the Tigris river on areas falling between the embankment, the river course lies at a somewhat higher elevation than the adjacent basins, consequently it appears that the river course is located on a sort of extensive ridge.[3]

Climate

The climate of the region is subtropical semi-desert type, winter is characterized by high pressure while low pressure in summer. It has

a very dry season for larger part of the year and larger diurnal and seasonal fluctuation of temperatures .The mean annunal rainfall is about 122 mm , Evaporation generally far exceeds the rainfall. Relative humidity varies considerably, it is highest in December (70 %) and lowest in june (28 %). Wind occurs throughout the year. Mean monthly maximum temperature fluctuates between (31.0 C) and (14.7 C°). [1]

Geology

The geology of the area is part of the southern extensive geosyncline, which at the bottom (approximately 3 Km under the present surface) is filled up with older shelf sediments , on top of which erosional products have been deposited . The upper part consist of very young fine river sediments[4] .

The geologic history of the area is classified as recent Holocene age which belongs to the Quaternary period . The geomorphological processes acting upon the area are erosion and deposition by fluvial and Aeolian activities.

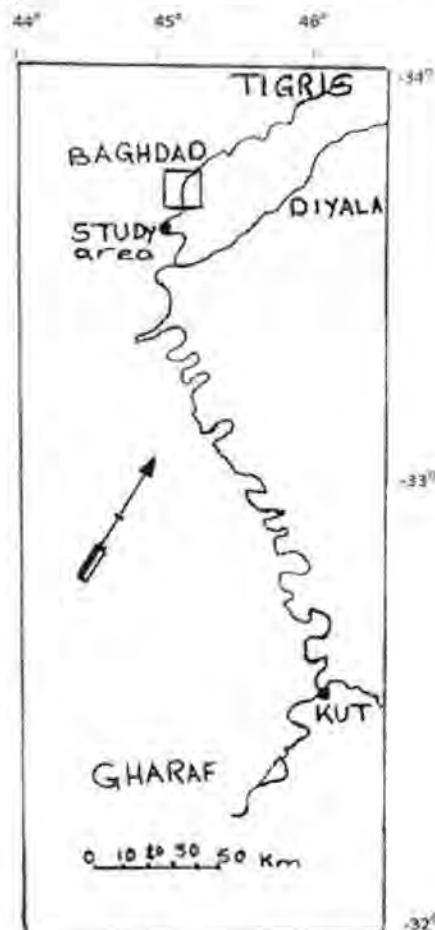


Figure 1: Location Map of Studied Area

Review of Soil Survey Inventories

In 1975, adequate technology was available in Iraq in respect of modern landscape soil surveys based on aerial photo interpretation .

Through this technique soil survey of some areas in Iraq had already been conducted and results of studies published. Reference Knowledge gathered from these survey had revealed certain geomorphological aspects which have an important bearing on the study of drainage conditions of the region .

Soils were identified and mapped as natural bodies having well defined landscapes and unique sets of profile characteristics. soil drainage as a land quality was inferred both from the landscape characteristics (landform, landuse, relief and surface salinity), and profile characteristics (texture, structure and porosity) [5].

According to these studies ,the region is an old flood plain marked by fluvial features. The sediments are fluvatile in nature and are deposited by river floods of abruptly decreasing velocity .[4] They are sorted from sand to silt to clay.

The Relation Between Soil Moisture and Soil Drainage

Soil drainage represent's the rapidity and extent to which a soil is capable of disposing off its surplus water externally (run off) and internally (leaching). The concept holds good regardless of the regional land use. How easily and effectively soil is drained depends on depth of watertable, soil permeability, depth of bedrock, flooding and slope .[6]. Drainage conditions are best studied under stereoscopes by landforms, relief graytone and site conditions , relation of these photo elements with soil is high.[7].

Landscape Photographic Interpretation

Three adjacent Aerial photographs (1:20,000 scale) were examined stereoscopically to identify the main land types of the studied area. Each land type was analysed in detail under Ziess-Aerotopo stereoscope using panchromatic, black and white aerial photos taken 1975 ,parallax bar was used for length measurements . The resulting land type units were described in detail . The landscape analysis was excuted by air-photo interpretation leading to understanding of the type of sediments, their mode of occurrence in the terrain and of the factors affecting the drainage conditions in the area. The aim of this analysis is to find and describe features in the photo

which are characteristics of certain geomorphic processes ,in turn will provide traces for delineating the soil pattern condition [8].

Land Type Units

The region represents several land type units varying in land form.

- A. P Flood plain the flood plain is subdivided into two sub land types
P1; Natural levees (high elevation) with coarse sediments
P2; Basins (low elevation) with finer sediments
- B. I; man made irrigation canals
I1; present irrigation canals
I2; former irrigation canals
- C. R; ruins and tells

They are shown on air photo (fig. 2)



Figure 2 : Air photograph of the area(1:20.000) [9]

Aerial Photointerpretation in Extracting Soil Hydromorphic Condition and Canals Density Calculation in the Semi-Arid Tigris Floodplain Region

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The flood plain makes up the matrix of the Tigris left and right banks of the area. The area is generally flat but small-scale unevenness associated with meander river feature formations. Based on photo image characteristics and geomorphic processes involved in evolution of the landscape two sublandtypes were identified.

P1: Natural levees. This unit is characterized by high relief lighter gray tone, profuse meander river activity in the form of numerous channels (nearly parallel to each other) perpendicular to the Tigris river meander and by seasonal vegetation. This unit is formed by bank-topping floods of the Tigris.

P2: Basins lowest part, medium to dark gray tone, nearly level relief and low river activity, this unit represents parcels of typical agricultural areas. The darker tones refer to intensive land use and/or clayey nature of soils or both. It includes some saline soil areas (abandoned) with very light gray tone.

Density Estimation of Hydromorphic Canals

Drainage density and irrigation canals frequency is done by topographic measures, this includes the definitions of the flood plain shape and the density of drainage and irrigation canals network or density, the ratio used is the total channel segment cumulated for all stream orders within a flood plain to the flood plain area, the channel frequency is defined as the summation of all segments in a drainage and irrigation canals of the flood plain by the flood plain area. [10,11].

$$\text{Density of hydromorphic channels} = \frac{\sum L}{A}$$

Where: L is channel length

A flood plain area

The distinction has been made between the thickness of main canals (0.5 mm) with its banks and secondary canals (branches 0.1 mm), main canals = 195 cm (measurements on A.P), secondary canals = 386 cm (measurements on A.P). The total = 581 cm, taking into consideration scale of (1:20 000) of Air photographs, the total area of the flood plain (A) is (21 Km²) and the total channel length (L) is (11.6 Km). The density of hydromorphic channels will be (55%).

RESULTS AND DISCUSSION

Landscape analysis reveals that irrigation-drainage problem is complicated in the region because of interaction of several factors contributing to moisture surplus which lead to the soil salinity and finally to abandoned arable land. Tigris activity in the flood plain continued erosion and deposition. Wind action have complicated the surface configuration of the area and hence the surface drainage. The presence of contrasting stratified soil material is a factor worth to mention in connection with internal drainage .The darker tone of the image is mostly fine texture (clay, clay loam) moist arable and, deposited in a basin by Tigris river and irrigation canal systems. The grayish tone indicates a dry arable land (not irrigated or fallow).The area has high water table(0.5-1m). Avast areas of arable land becomes saline and abandoned(very high gray tone)because of excessive irrigation practices. The collector drains should be located along the natural surface water flow lines. Large scale images would help in locating these lines. Detailed soil survey and topographic survey would help in locating the basin which need to be linked with main drain through appropriate interceptor drains.

The measurements of the drainage parameters tests should be located on representative sites of selected land type units. Soil samples required for particle size analysis and should be taken from soil horizons.

In essence more than half (55%) Of fertile arable land were changed with time in to remnants of irrigation and drainage ditches or waste land .The reason for that is the erroneous agricultural practices. the ancient practices of irrigation and drainage should be replaced by modern drip irrigation projects, The new generations of space remote sensing (IKONOS and Quick bird)are very promising , and should utilize for monitoring and exciting land survey

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Study of Some Changes in Spleen among Golden Hamsters Vaccinated with Killed *Leishmania tropica*

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الخلاصة

اختبرت في هذه الدراسة مجموعة من العوامل ذات العلاقة بالطحال (التغيرات النسيجية , معامل تضخم الطحال , طول الطحال , عدد الطفيليات , الطبقات ومزارع الطفيلي) وذلك في اربعة مجاميع من حيوانات الهامستر الذهبي التي حقنت بجرعة وجرعتين وثلاث جرعات من المستضدات المختلفة وكما يلي : المجموعة الأولى حقنت بعالق طفيلي اللشمانيا المقتولة بحرارة المؤصده , المجموعة الثانية حقنت بلقاح الـ BCG , المجموعة الثالثة حقنت بخليط اللقاحين السابقين اما المجموعة الرابعة فقد حقنت بمحلول دارئ الفوسفات الملحي واعتبرت كمجموعة سيطرة, وذلك لتقييم كفاءه اللقاحات سابقه الذكر في التمتع ضد خمج التحدي بأستخدام عزله ذات فوعه لطفيلي *Leishmania tropica* وباعتماد خمس فترات للمتابعة (90,75,60,45,30) يوما بعد الخمج. وقد كان خليط اللقاحين هو الأفضل في هذه الدراسة في تمنيعه لحيوان الهامستر ضد خمج لاحق باللشمانيا الجلدية , وذلك لأن الحيوانات التي حقنت به (بجرعة وجرعتين وثلاث جرعات) اظهرت النتائج الآتية مقارنة مع المجموعات التجريبية الأخرى:

- حدوث تغيرات نسيجية قليلة او متوسطة الشدة.
- اقل المعدلات لمعامل تضخم الطحال وبفرق معنوي (0.1 ± 1.36) ملغم/غم , (1.24 ± 0.08) ملغم / غم و (0.05 ± 1.21) ملغم/غم للمجاميع اعلاه على التوالي.
- اقل المعدلات لطول الطحال و بفرق معنوي (0.07 ± 24.4) ملم, (0.6 ± 23.7) ملم و (0.1 ± 23.4) ملم للمجاميع اعلاه على التوالي.
- اقل المعدلات في اعداد الطفيليات ولكن بفرق غير معنوي (0.01 ± 1.4) , (0.05 ± 1.32) و (0.03 ± 1.42) مليون طفيلي للمجاميع اعلاه على التوالي.
- سلبية نتائج مزارع الطفيليات ولغاية نهاية مده التجربه.

ABSTRACT

Different factors related with spleen (histopathological changes , spleen weight ratio , length , number of parasite , impression and culture of spleen) were screened in four groups of golden hamsters, inoculated with one , two and three doses of different antigens as following : Group 1 inoculated with autoclaved killed *Leishmania tropica* , Group 2 inoculated

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with BCG vaccine alone while Group 3 Inoculated with mixed vaccines (autoclaved killed *Leishmania* + BCG) and Group 4 inoculated with phosphate buffer saline which considered as control group , in order to evaluate the efficacy of the previous antigen against challenge infection with virulent *Leishmania tropica* isolate along five times follow up (30, 45, 60, 75, and 90) days after infection. Group 3 which inoculated with one , two and three doses of mixed vaccine, was considered as the best vaccine in this study because animal inoculated with this vaccine showed the following results compared with other antigens:

- Low or moderate histopathological changes.
- Less significant spleen weight ratio (1.36 ± 0.1) mg/gm , (1.24 ± 0.08) and mg/gm (1.21 ± 0.05) mg/gm respectively.
- Less significant spleen length (24.4 ± 0.07) mm , (23.7 ± 0.6) mm and (23.4 ± 0.1) mm respectively
- Less but no significant amastigote count (1.4 ± 0.01) , (1.32 ± 0.05) and (1.42 ± 0.03) million parasites respectively
- Negative spleen culture along 90 days of following up.

INTRODUCTION

Leishmaniasis is a group of diseases caused by over 20 known species of pathogenic protozoan parasites of the genus *Leishmania* with divers clinical features ranging from self-limiting cutaneous leishmaniasis to visceral disease(1,2). The various species of *Leishmania* are transmitted by sand flies, amastigotes, librated from host cells in the insect's gut, transform into promastigotes, which multiply there and finally introduced into a new hosts when sandfly again feed(3).The importance of *Leishmania* as a human pathogen has stimulated a large number of researches deal with immunization against Leishmaniasis especially in experimental animals (4, 5, 6).

The spleen is one of the organs that determine the severity of the *Leishmania* infection, because it contains a large proportion of paghocytic cells (7).

Evaluation the success of vaccines against Leishmaniasis is not so easy, investigators examined several parameters to measure immune response provoked by antigens used in immunization , such as the delayed type of hypersensitivity test (skin test) ,lymphocyte transformation , Interferon gamma production and following up of experimentally infected animal after immunization (8,9,10).In this paper we addressed the use of some changes in spleen to evaluate the success of vaccine against experimental infection

of *Leishmania tropica* using three different antigens with one, two and three doses for each antigens.

MATERIALS AND METHODS

Isolation of the *Leishmania* parasite

Leishmania tropica was isolated from a lesion in the left arm of a 21 years-old male at Baghdad teaching hospital / Baghdad according to method of Al-Aloussi, 1979 [11].

Media

1-Semi –Solid medium: This medium was prepared according to the method of Alder & Theodor, 1926 [12] and was used for parasite isolation from man and reclaim from the infected animal tissue.

2- Biphasic Medium: This media was prepared according the to method of Kagan & Normab, 1970 [13] and used for parasite cultivation in order to prepare vaccine antigens and for preparing injecting dose.

Autoclaved Killed *Leishmania* (AKL) Vaccine preparation

Moheballi, *et al*., (1998) method (14) was used in preparing *Leishmania tropica* vaccine with little modification according to AL-Warid, (15) as following:

1. Promastigote of *Leishmania tropica* was cultivated in Biphasic Medium at 26°C instated of RPMI-1640.
2. Promastigotes were harvested and concentrated using centrifuge at 3200 rpm.
3. The promastigotes were washed five times with phosphate buffer saline (PBS), and counted using Haemocytometer to get the final concentration of immunization dose which was 1×10^7 parasites / 0.2 ml.

The promastigotes were separated and transferred into several autoclavable containers and was put in autoclave at 121°C for 15 minutes, and then the containers were kept at 4°C.

BCG Vaccine

BCG vaccine was obtained from "The National Centre for Drug Control and Researches / Baghdad / Iraq", the vaccine was made by "Japan BCG Laboratory" each vial contained (0.5) mg of lyophilized vaccine and each 1 ml of vaccine contained 8.26×10^6 cells of *Mycobacterium bovis*.

Animals

One hundred eighty male of Golden hamsters (*Mesocricetus auratus*) aged (8-10) weeks were obtained from "The National Centre for Drug Control and Researches / Baghdad / Iraq". Animals were separated into four groups each group contained (45) animal which inoculated as following:

- 1- Group (1): inoculated with Autoclaved killed *Leishmania* (AKL) per 0.2 ml.

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- 2- Group (2): inoculated with 1.4×10^6 cell per 0.2 ml.
- 3- Group (3): inoculated with mixed inoculums of both (1×10^7 AKL /0.2 ml) and (1.4×10^6 unit of BCG / 0.2 ml).
- 4- Group (4): was considered as control group. Animals in this group were inoculated with 0.2 ml phosphate buffer saline.

One, two and three doses for each of the previous antigen were used with an interval of 15 days between each dose and the other.

All previous animals were inoculated intradermally in the left hind footpad using 1 ml sterile syringe for each animal. After 15 days of immunization, all animals were inoculated with (challenge dose) 5×10^7 promastigotes of virulent *Leishmania tropica* isolates / 0.2 ml .

Dissections

All animals of the four groups were dissected along five times of follow up (30, 45, 60, 75, and 90) days after challenge infection, the follow up of *L.tropica* infection was done using different parameters:

- 1- Histopathological of the spleen (5) ,for histopathological examinations a biopsy was taken at the site of infection fixed in 10% formalin in PBS, washed in water for 4 hours, dehydrated and embedded in paraffin, cut (3-4 μ m thick) and stained with hematoxylin and eosin for optical microscopic examination(16).
- 2- Spleen weight ratio (spleen weight (mg) / body weight (gm) (17)
- 3- Spleen length (7)
- 4- Estimated number of amastigote in spleen (18).
- 5- Impression and cultivation of spleen (17)

RESULTS AND DISCUSSION

Golden hamsters were used in this study because some investigators showed that these animals were the suitable host for *Leishmania tropica* experimental design (19). As well as gender and age of the hosts are also play an important role in the immune response stimulated by *Leishmania* (20, 21), so male aged 8-10 week was used in this study.

Promastigotes (infected stage of *Leishmania spp.*) were used as killed antigen, which were harvested in stationary phase, because the promastigote in stationary phase can be considered to be more virulent and immunogenic than promastigotes in log phase (22), as well as the second and third boosting dose of these antigens were administrated due to the recommendation of Goldsby *et al.* , 2000 who recommended to use more than one dose for killed vaccine(23).

Spleen showed sever histopathological changes in both control animals and animal administrated with BCG from the fifteen days post

infection till the end of the following up period, these changes represented by white pulp dilatation, infiltration of macrophage and lymphocytes , follicular hyperplasia , blood congestion and fibrosis , while both AKL and mixed vaccine administrated animal in different boosting dose showed low or moderate histopathological changes in their spleens (figure 1,2 and 3), this result agreed with other studies done in Iraq (24,25) who showed moderate histopathological changes in immunized animal with live attenuated vaccine when it compare with non immunized group. The moderate histopathological changes which showed in AKL and mixed vaccine administrated animal may due to high level of T-lymphocyte which produced interleukins that in turn activate macrophage which reduce the number of amastigote in spleen (9,15) .

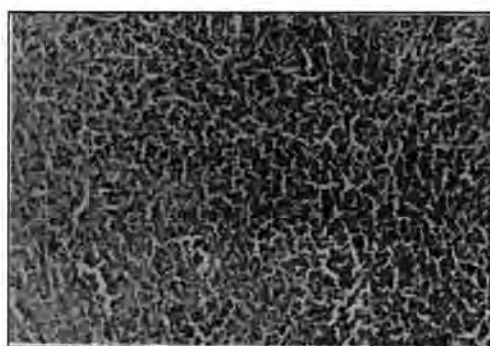


Figure 1: Section in spleen of mixed vaccine administrated group, showing white pulp dilatation after 60 days post infection , Hematoxylin - Eosine stain (400 X)



Figure 2: Section in spleen of BCG vaccine administrated group, showing hyperplasia and hyper trophy of spleen cells after 60 days post infection , Hematoxylin -Eosine stain (400 X)

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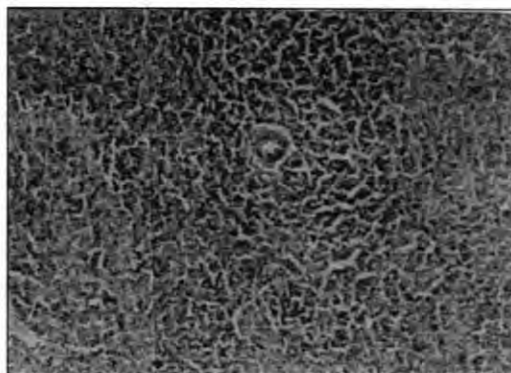


Figure 3: Section in spleen of Control group, showing white pulp dilatation, infiltration of macrophage and lymphocytes after 60 days post infection , Hematoxylin -Eosine stain (400 X)

Spleen weight ratio , spleen length and number of parasites in spleen were scored also during five times follow up (30, 45, 60, 75, and 90) days after challenge infection with virulent *Leishmania tropica* isolate, Statistical analysis showed that there was a significant differences ($p \leq 0.05$) among these parameters in experimented animal group following up intervals.

Animal inoculated with one, two and three doses of mixed vaccine showed less spleen ratio as their rat were (1.36 ± 0.1) mg/gm , (1.24 ± 0.08) and mg/gm (1.21 ± 0.05) mg/gm respectively , Animal inoculated with one , two and three doses of AKL showed the following spleen ratio respectively (2.31 ± 0.02) mg/gm , (1.73 ± 0.14) mg/gm and (1.69 ± 0.18) mg/gm , while the three control group showed high spleen weight ratio (4.04 ± 0.7) mg/gm, (4.3 ± 0.12) mg/gm and (4.73) mg/gm respectively. Animals inoculated with one , two and three dose of BCG vaccine showed the following spleen ratio (1.95 ± 0.07) mg/gm , (2.04 ± 0.12) mg/gm and (2.62 ± 0.31) mg/gm respectively after 75 day post infection (figure 4). Statistical analysis showed that was a significant differences ($p \leq 0.05$) among the experimented animal groups and this results agreed with Tonui & Titus (26) who showed that spleen weights in control mice increased over time, while spleen weights in mice immunized with *L. major* promastigote exogenous antigens(LmSEAgS) remained relatively constant.

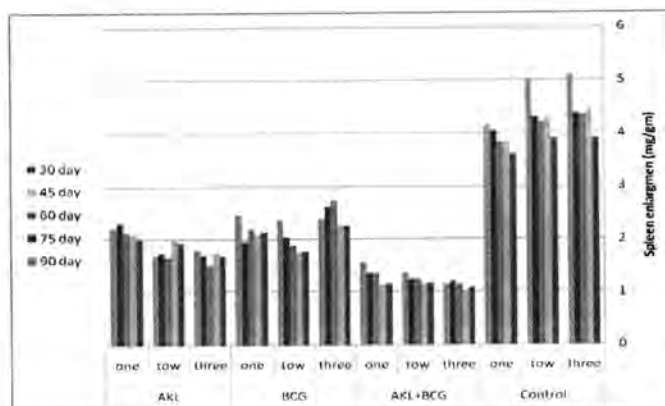


Figure 4: Graph showing the spleen weight ratio in four study groups at five successive follow up periods after challenge

Animal inoculated with one, two and three doses of mixed vaccine showed minimum spleen length as their values were (24.4 ± 0.07) mm, (23.7 ± 0.6) mm and (23.4 ± 0.1) mm respectively which were approximately equal to the normal value of spleen length (24.2 ± 0.33) mm, Animal inoculated with one, two and three doses of AKL showed the following spleen length (28.6 ± 0.1) mm, (28.5 ± 0.6) mm and (28.3 ± 0.59) mm respectively, while the three control group showed maximum spleen length (34.2 ± 0.14) mm, (34.3 ± 0.22) mm and (35.9 ± 2.7) mm respectively, followed by animals inoculated with one, two and three dose of BCG vaccine which showed the following spleen length (33.6 ± 0.46) mm, (31.11 ± 0.22) mm and (35.9 ± 2.7) mm respectively, after 75 day post infection (figure 5). Statistical analysis showed that was significant differences ($p \leq 0.05$) among the experimented animal groups. This result agreed with Al-Najjar who showed that both ultraviolet *Leishmania* vaccine and gamma *Leishmania* vaccine animal group had the lowest spleen length values compared with highest spleen length values in control groups.

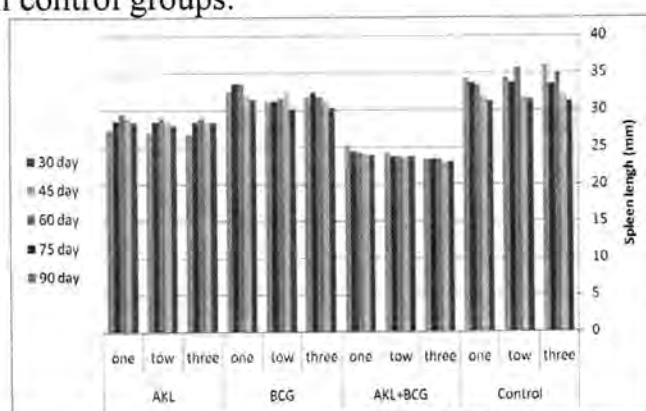


Figure 5: Graph showing the spleen length in four study groups at five successive follow up periods after challenge

Reductions in spleen weights and lengths in mixed antigen vaccinated hamsters with one, two and three doses were also accompanied by very low

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parasite burdens, where it reached (1.4 ± 0.01) , (1.32 ± 0.05) and (1.42 ± 0.03) million parasites respectively, Animals inoculated with one, two and three doses of AKL showed the following parasites number in spleen (2.31 ± 0.01) mm, (2.18 ± 0.01) , (2.4 ± 0.0) respectively, while the three control group showed maximum amastigote count (4.62 ± 0.18) mm, (5.2 ± 0.04) and (4.9 ± 0.9) million parasites respectively. Animals inoculated with one, two and three dose of BCG vaccine which showed the following amastigote count (3.5 ± 0.09) , (4.49 ± 0.22) and (3.2 ± 0.01) million amastigotes respectively, after 75 days post infection (figure 6). Although there were big differences in number of parasites, statistical analysis showed that there was no significant differences ($p \leq 0.05$) among the experimented animal groups

These results agreed with the result of Afrin & Ali (27) who noticed that increase in parasite burden in the control hamsters paralleled an increase in the weight of the spleen, similarly, the *Leishmania* Antigen-liposome-immunized group with significantly reduced parasite load had spleens comparable to those of normal, uninfected hamsters, and also agreed with Tonui & Titus (26) who noticed that there was very low parasite burdens, as much as a 4,913-fold reduction in parasite burden in *L. major* promastigote exogenous antigens (LmSEAg)-immunized mice compared with controls ($P < 0.001$). Furthermore other study showed significant lower parasite burdens in both spleens and livers compared with non-immunized mice or mice injected with adjuvant alone (28). The moderate changes (spleen weight ratio, spleen length and count of parasites) in spleens of immunized animals especially the mixed group and AKL vaccinated group can be discussed as both mixed and AKL antigens have the ability to provoke high level of T- lymphocyte which activate both macrophage and natural killer cells before reducing the number of parasite in spleen.

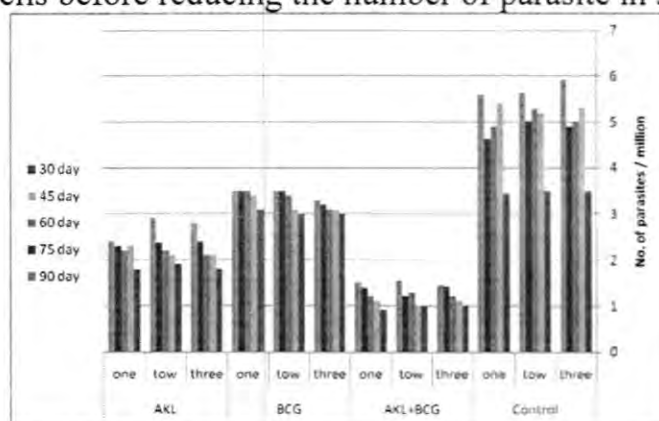


Figure 6: Graph showing the number of amastigote in four study groups at five successive follow up periods after challenge

Finally spleen impression and cultivation of spleen were scored during six times follow up (15, 30, 45, 60, 75, and 90) days after challenge infection with virulent *Leishmania tropica* isolate, results of spleen impressions were negative up to 15 days of infection in animals immunized with different dose of each (AKL) and (AKL+BCG). While spleen cultivation results were negative in the above mentioned animals along 90 days of follow up (table 1). These results may correlate with the high levels of lymphocytes and macrophages which induce different immunological factors that killed the parasites especially in spleen, which have large amount of macrophages (29). These factors can reduce or prevent the transforming of amastigotes to promastigotes in culture. This may be the reason of the negative cultivation results in the spleen belonging to the animals immunized with different doses of each (AKL) and (AKL+BCG).

Table 1: Impressions and parasite culture of spleen after challenge infection

SPLEEN									
No of dose	Days of infection /days	AKL		BCG		AKL + BCG		PBS	
		I	C	I	C	I	C	I	C
1	7	-	-	-	-	-	-	-	-
	15	-	-	+	+	-	-	+	+
	30	+	-	+	+	-	-	+	+
	45	+	-	+	+	+	-	+	+
	60	+	+	+	+	+	-	+	+
	75	+	-	+	+	+	-	+	+
	90	+	-	+	+	+	-	+	+
2	7	-	-	-	-	-	-	-	-
	15	-	-	-	+	-	-	+	+
	30	+	-	+	+	-	-	+	+
	45	+	-	-	+	+	-	+	+
	60	+	-	+	+	+	-	+	+
	75	+	-	+	+	+	-	+	+
	90	+	-	+	+	-	+	+	+
3	7	-	-	-	-	-	-	-	-
	15	-	-	+	+	-	-	+	+
	30	+	-	+	+	-	-	+	+

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	45	+	-	+	+	+	-	+	+
	60	+	-	+	+	+	-	+	+
	75	+	-	+	+	+	-	+	+
	90	+	-	+	+	-	+	+	+
I: Impression					C: Culture				
AKL : Autoclaved killed <i>Leishmania</i>					PBS: phosphate buffer saline				

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Certain Types of Separation Axioms in Intuitionistic Bitopological Spaces

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الخلاصة

يهدف البحث إلى دراسة بعض الأنماط الجديدة من بديهيات الفصل باستخدام المجموعة المفتوحة b - في الفضاءات التبولوجية الثنائية الحدسية.

ABSTRACT

The aim of this paper is to present and study some new separation axioms using the b -open sets in intuitionistic bitopological spaces.

INTRODUCTION

The concept of intuitionistic fuzzy set has been introduced by Atanassov in 1984. Later in 1996 Coker introduced the concept of intuitionistic set and intuitionistic topology as special case of intuitionistic topological spaces. In 1963 J.C.Kelly Introduced the concept of bitopological space on his work "Bitopological spaces" in 1996, Andrijevic [2] introduced b -open sets in topological spaces. In 1963 Levine [1], Introduced semi-open sets in topological spaces, and these semi-open sets were used to define three new separation axioms called semi- T_0 , semi- T_1 and semi- T_2 by Maheswari and Prasad in 1975. The purpose of this paper is to introduce some new separation properties by using the $(1,2)b$ -open sets, $(1,2)$ semi-open sets and $(1,2)$ pre-open sets in intuitionistic bitopological spaces and to investigate the relationships between them.

Preliminaries-2:

Definition 2-1:[6] A subset A of a space X is said to be:

- 1- Semi-open if $A \subseteq cl(int(A))$.
- 2- Pre-open if $A \subseteq int(cl(A))$.
- 3- b -open if $A \subseteq cl(int(A)) \cup int(cl(A))$.

Definition 2- 2: [3] Let X be a non-empty set, an intuitionistic set (IS's for short) A is an object having the form $A = \langle x, A_1, A_2 \rangle$ where A_1 and A_2 are disjoint subsets of X , the set A_1 is called the set of members of A while A_2 is called the set of nonmembers of A .

Definition 2-3: [3] Let X be a non-empty set, and let A, B be two IS's having the form $A = \langle x, A_1, A_2 \rangle$, $B = \langle x, B_1, B_2 \rangle$ and let $\{A_i : i \in I\}$ be an arbitrary family of IS's in X , where $A_i = \langle x, A_i^{(1)}, A_i^{(2)} \rangle$ then:

- 1- $\tilde{X} = \langle x, X, \phi \rangle$ and $\tilde{\phi} = \langle x, \phi, X \rangle$.

$$2- \quad A \subseteq B \text{ iff } A_1 \subseteq B_1 \text{ and } B_2 \subseteq A_2.$$

$$3- \quad A = B \text{ iff } A \subseteq B \text{ and } B \subseteq A.$$

4- The complement of A is denoted by \bar{A} and defined by $\bar{A} = \langle x, A_2, A_1 \rangle$.

$$5- \bigcup_{i \in I} A_i = \left\langle x, \bigcup_{i \in I} A_i^{(1)}, \bigcap_{i \in I} A_i^{(2)} \right\rangle \text{ and } \bigcap_{i \in I} A_i = \left\langle x, \bigcap_{i \in I} A_i^{(1)}, \bigcup_{i \in I} A_i^{(2)} \right\rangle$$

Remark 2-4: [4] Every crisp set A on a non-empty set X is obviously an IS having the form $\langle x, A, A^c \rangle$

Definition 2-5: [3] An intuitionistic topology (IT, for short) on a non-empty set X, is a family T of IS in X containing \emptyset and \tilde{X} and closed under arbitrary union and finitely intersection. In this case the pair (X,T) is called intuitionistic topological space (ITS, for short). Any IS in T is known as an intuitionistic open set (IOS, for short) in X. The complement of IOS is called intuitionistic closed set (ICS, for short).

Definition 2-6: [3] Let (X,T) be an ITS and let $A = \langle x, A_1, A_2 \rangle$ be an IS in X, then the interior and closure of A are denoted by $\text{int}(A)$ and $\text{cl}(A)$, respectively, and defined by:

$$\text{int}(A) = \bigcup \left\{ G_i : G_i \in T \text{ and } G_i \subseteq A \right\}$$

$$\text{cl}(A) = \bigcap \left\{ F_i : \bar{F}_i \in T \text{ and } A \subseteq F_i \right\}$$

So $\text{int}(A)$ is the largest IOS contained in A, and $\text{cl}(A)$ is the smallest ICS containing A.

Intuitionistic bitopological spaces -3

In [5] further definitions appear. In this section we introduce a new concept concerning intuitionistic bitopological spaces. First we recall the following definitions.

Definition 3.1: Let (X, T_1, T_2) be an intuitionistic bitopological space. A subset A of X is intuitionistic $T_1 T_2$ -open set if $A \in T_1 \cup T_2$ and intuitionistic $T_1 T_2$ -closed set if its complement in X is intuitionistic $T_1 T_2$ -open set. The intuitionistic

$T_1 T_2$ -closure of A is denoted by $T_1 T_2 - \text{cl}(A)$ and

$$T_1 T_2 - \text{cl}(A) = \bigcap \left\{ F : F \text{ is intuitionistic } T_1 T_2 - \text{closed set in } X \text{ and } A \subseteq F \right\}$$

Definition 3.2 : An intuitionistic topological space (X,T) is said to be R_0 if for each $G \in T, x \in G$ implies $T - \text{cl}(\{x\}) \subseteq G$ and it is R_1 if for each pair of points $x, y \in X$, such that $T - \text{cl}(\{x\}) \neq T - \text{cl}(\{y\})$ there are disjoint intuitionistic open sets U and V, such that $x \in U, y \in V$.

Definition 3-3: An intuitionistic bitopological space X is pair wise R_0 if for each $G \in T_i, x \in G$ implies $T_j - cl(\{x\}) \subset G$ for $i, j = 1, 2, i \neq j$ and pair wise R_1 if for $x, y \in X$, such that $T_j - cl(\{x\}) \neq T_i - cl(\{y\})$ there are T_i -intutionistic open set U and T_j -intutionistic open set V , such that $x \in U, y \in V$ and $U \cap V = \tilde{\phi}$, for $i, j = 1, 2$ and $i \neq j$.

Definition 3.4: An intuitionistic bitopological space X is pairwise- R_1 if for each $x, y \in X$, such that $x \notin T_i - cl(\{y\})$, there are T_i -intutionistic open set U and T_j -intutionistic open set V , such that $x \in U, y \in V$ and $U \cap V = \tilde{\phi}, i, j = 1, 2, i \neq j$

Definition 3.5: An intuitionistic subset A of X is called

- (i) a (1,2) intuitionistic b- open set [(1,2) IBOS, for short] if $A \subset T_1 - \text{int}(T_1 T_2 - cl(A)) \cup T_2 - cl(T_1 - \text{int}(A))$
- (ii) a (1,2) intuitionistic semi-open set [(1,2) ISOS for short] if $A \subset T_1 T_2 - cl(T_1 - \text{int}(A))$.
- (iii) a (1,2) intuitionistic pre- open set [(1,2) IPOS for short] if $A \subset T_1 - \text{int}(T_1 T_2 - cl(A))$.

The family of all (1,2) IBO (resp. (1,2) ISO, (1,2) IPO) sets of X is denoted by (1,2) IBO(X) (resp. (1,2) ISO(X), (1,2) IPO(X)).

The complement of a (1,2) IBO (resp. (1,2) ISO, (1,2) IPO) set in X is called (1,2) IBC (resp. (1,2) ISC, (1,2) IPC) sets in X .

(1,2) IBcl(A) (resp. (1,2) IScl (A), (1,2) Ipcl (A) denotes (1,2) b-closure (resp (1,2) semi- closure, (1,2) pre- closure) of A in X .

Proposition 3-6: Let X be an intuitionistic bitopological space .then:

$$(1,2) ISO (X) \cup (1,2) IPO (X) \subset (1,2) IBO (X).$$

Proof : The proof is obvious.

But the converse may be not true in general, for example.

Example 3.7: Let $X = \{a, b, c\}$,

$$T_1 = \left\{ \tilde{X}, \tilde{\phi}, \langle x, \{a\}, \{b, c\} \rangle, \langle x, \{b\}, \{c\} \rangle, \langle x, \{a, b\}, \{c\} \rangle, \langle x, \phi, \{b, c\} \rangle \right\}$$

$$T_2 = \left\{ \tilde{X}, \tilde{\phi}, \langle x, \{a\}, \{c\} \rangle \right\}, \text{ then :}$$

$$(1,2) ISO(X) = \left\{ \tilde{X}, \tilde{\phi}, \langle x, \{a\}, \{b, c\} \rangle, \langle x, \{a\}, \phi \rangle, \langle x, \{b\}, \{c\} \rangle, \langle x, \{c\}, \{b\} \rangle, \langle x, \{a, b\}, \phi \rangle, \langle x, \{a\}, \{b\} \rangle, \langle x, \{b\}, \phi \rangle, \langle x, \{a, b\}, \{c\} \rangle, \langle x, \{b, c\}, \phi \rangle, \langle x, \{a\}, \{c\} \rangle, \langle x, \{a, c\}, \{b\} \rangle, \langle x, \{a, c\}, \phi \rangle, \langle x, \phi, \{b, c\} \rangle \right\}$$

$$(1,2) IPO(X) = \left\{ \tilde{X}, \tilde{\phi}, \langle x, \{a\}, \{b, c\} \rangle, \langle x, \{a\}, \phi \rangle, \langle x, \{b\}, \{c\} \rangle, \langle x, \{a, b\}, \phi \rangle, \langle x, \{a\}, \{b\} \rangle, \langle x, \{a, b\}, \{c\} \rangle, \langle x, \{a\}, \{c\} \rangle, \langle x, \{a, c\}, \phi \rangle, \langle x, \phi, \{b, c\} \rangle \right\}.$$

Certain Types of Separation Axioms in Intuitionistic Bitopological Spaces

Hatim

$(1,2)IBO(X) = \{\tilde{X}, \tilde{\phi}, \langle x, \{a\}, \{b, c\} \rangle, \langle x, \{a\}, \phi \rangle, \langle x, \{b\}, \{c\} \rangle, \langle x, \{c\}, \{b\} \rangle, \langle x, \{c\}, \phi \rangle, \langle x, \{a, b\}, \phi \rangle, \langle x, \phi, \phi \rangle, \langle x, \{a\}, \{b\} \rangle, \langle x, \{b\}, \phi \rangle, \langle x, \{a, b\}, \{c\} \rangle, \langle x, \{b, c\}, \phi \rangle, \langle x, \{a\}, \{c\} \rangle, \langle x, \{a, c\}, \{b\} \rangle, \langle x, \{a, c\}, \phi \rangle, \langle x, \phi, \{b, c\} \rangle\}$.
 $\langle x, \{c\}, \phi \rangle \in (1,2)IBO(X)$ but $\langle x, \{c\}, \phi \rangle \notin (1,2)ISO(X)$ and $(1,2)IPO(X)$.

Proposition 3.8: An intuitionistic subset A of intuitionistic bitopological space X if
 $T_i - \text{int}(T_i T_2 - cl(A)) \subseteq T_i T_2 - cl(T_1 - \text{int}(A))$ or $T_1 T_2 - cl(T_1 - \text{int}(A)) \subseteq T_1 - \text{int}(T_1 T_2 - cl(A))$

then $(1,2)IBO(X) = (1,2)ISO(X) \cup (1,2)IPO(X)$.

Proof:

let $S \in IBO(X)$, If $T_1 - \text{int}(T_1 T_2 - cl(S)) \subseteq T_1 T_2 - cl(T_1 - \text{int}(S))$, then $S \subseteq T_1 T_2 - cl(T_1 - \text{int}(S))$

and so $S \in ISO(X)$. If $T_1 T_2 - cl(T_1 - \text{int}(S)) \subseteq T_1 - \text{int}(T_1 T_2 - cl(S))$, then $S \subseteq T_1 - \text{int}(T_1 T_2 - cl(S))$ and so $S \in IPO(X)$.

Intuitionistic ultra $b-T_i$ ($i = 0, 1, 2$) space. -4

Definition 4-1: An Intuitionistic bitopological space X is said to be intuitionistic ultra $b-T_0$ space (resp. Intuitionistic ultra semi- T_0 space and Intuitionistic ultra pre- T_0 space) if for $x, y \in X, x \neq y$ there exists $U \in (1,2)IBO(X)$ (resp. $(1,2)ISO(X)$ and $(1,2)IPO(X)$) such that

$x \in U, y \notin U$ or $x \notin U, y \in U$.

Example 4-2: let $X = \{a, b\}$ $T_1 = \{\tilde{X}, \tilde{\phi}, \langle x, \{a\}, \phi \rangle, \langle x, \phi, \{b\} \rangle\}$

$T_2 = \{\tilde{X}, \tilde{\phi}, \langle x, \{a\}, \{b\} \rangle, \langle x, \{a\}, \phi \rangle\}$

$(1,2)ISO(X) = \{\tilde{X}, \tilde{\phi}, \langle x, \{a\}, \phi \rangle, \langle x, \phi, \{b\} \rangle, \langle x, \{b\}, \phi \rangle, \langle x, \phi, \phi \rangle\}$

$(1,2)IPO(X) = \{\tilde{X}, \tilde{\phi}, \langle x, \{a\}, \{b\} \rangle, \langle x, \{a\}, \phi \rangle, \langle x, \phi, \{b\} \rangle\}$

$(1,2)IBO(X) = \{\tilde{X}, \tilde{\phi}, \langle x, \{a\}, \{b\} \rangle, \langle x, \{a\}, \phi \rangle, \langle x, \phi, \{b\} \rangle, \langle x, \{b\}, \phi \rangle, \langle x, \phi, \phi \rangle\}$

It is clear that X is Intuitionistic ultra $b-T_0$ space, Intuitionistic ultra semi- T_0 space, but not Intuitionistic ultra pre- T_0 space.

Definition 4-3: An Intuitionistic bitopological space X is said to be intuitionistic ultra $b-T_1$ space (resp. Intuitionistic ultra semi- T_1 space, Intuitionistic ultra pre- T_1 space) if for $x, y \in X, x \neq y$ there exists $U, V \in (1,2)IBO(X)$ resp. $(1,2)ISO(X), (1,2)IPO(X)$ s.t. $x \in U, y \in V, y \notin U, x \notin V$.

Example 4-4: let $X = \{a, b\}$ $T_1 = \{\tilde{X}, \tilde{\phi}, \langle x, \{b\}, \{a\} \rangle, \langle x, \{a\}, \phi \rangle\}$

$T_2 = \{\tilde{X}, \tilde{\phi}, \langle x, \{a\}, \phi \rangle\}$

$(1,2)ISO(X) = \{\tilde{X}, \tilde{\phi}, \langle x, \{b\}, \{a\} \rangle, \langle x, \{b\}, \phi \rangle\}$

$(1,2)IPO(X) = \{\tilde{X}, \tilde{\phi}, \langle x, \{a\}, \phi \rangle, \langle x, \{b\}, \phi \rangle, \langle x, \{b\}, \{a\} \rangle, \langle x, \phi, \phi \rangle\}$

$$(1,2)IBO(X) = \{\tilde{X}, \tilde{\phi}, \langle x, \{a\}, \phi \rangle, \langle x, \{b\}, \{a\} \rangle, \langle x, \{b\}, \phi \rangle, \langle x, \phi, \phi \rangle\}$$

Therefore X is Intuitionistic ultra $b-T_1$ space, Intuitionistic ultra pre- T_1 space but not Intuitionistic ultra semi T_1 space .

Example 4-5: see example 4-2, X is Intuitionistic ultra semi- T_1 space.

Remarks 4-6:

- 1- Every Intuitionistic ultra $b-T_1$ space is Intuitionistic ultra $b-T_0$ space.
- 2- Every Intuitionistic ultra semi- T_1 space is Intuitionistic ultra semi- T_0 space.
- 3- Every Intuitionistic pre- T_1 space is Intuitionistic ultra pre- T_0 space .

But the converse of remark4-6 is not true,

Example 4-7:see example 4-4 is Intuitionistic ultra semi- T_0 but not is Intuitionistic ultra semi- T_1 , and example 4-2 to explain X is Intuitionistic ultra pre- T_0 but not is Intuitionistic ultra pre- T_1 .

Definition 4-8:A Intuitionistic bitopological space X is said to be Intuitionistic ultra $b-T_2$ space (resp. Intuitionistic ultra semi- T_2 space, Intuitionistic ultra pre T_2 space) if for $x, y \in X, x \neq y$ there exists $U, V \in (1,2)IBO(X)$ (resp $(1,2)ISO(X), (1,2)IPO(X)$)

Such that $x \in U, y \in V, U \cap V = \tilde{\phi}$.

Remark 4-9: Every Intuitionistic ultra $b-T_2$ space (resp. Intuitionistic ultra semi- T_2 space and intuitionistic ultra pre- T_2 space) is Intuitionistic ultra $b-T_1$ space (resp. Intuitionistic ultra semi - T_1 space, Intuitionistic ultra pre- T_1 space).

Proposition 4-10:

- 1- Every Intuitionistic ultra semi- T_i space is Intuitionistic ultra $b-T_i$ space.
- 2- Every Intuitionistic ultra pre- T_i space is Intuitionistic ultra $b-T_i$ space, where
 $i = 0, 1, 2$

Proof: since

Every $(1,2)$ Intuitionistic semi- open set is $(1,2)$ Intuitionistic $b-$ open set and every

$(1,2)$ Intuitionistic pre- open set is $(1,2)$ Intuitionistic $b-$ open set.

The converse of proposition 4-10 is not true, see example 4-4, X is Intuitionistic ultra $b-T_i$ space but is not Intuitionistic ultra semi - T_i space, where $i = 0, 1$.

And example 4-2, X is Intuitionistic ultra $b-T_i$ space, but not Intuitionistic ultra pre- T_i space, where $i=0, 1$.

Theorem 4-11 : An intuitionistic bitopological space X is Intuitionistic ultra $b-T_1$ space if and only if $\langle x, \{a\}, \{a\}^c \rangle$ is (1,2) intuitionistic b -closed in X , for every $a \in X$.

Proof: if $\langle x, \{a\}, \{a\}^c \rangle$ is (1,2) intuitionistic b -closed in X , for $a, b \in X$ with $a \neq b$, $\langle x, \{a\}^c, \{a\} \rangle, \langle x, \{b\}^c, \{b\} \rangle$ are (1,2) Intuitionistic b -open sets such that $b \in \langle x, \{a\}^c, \{a\} \rangle$ and $a \in \langle x, \{b\}^c, \{b\} \rangle$. therefore, X is Intuitionistic ultra $b-T_1$ space.

Conversely, if X is Intuitionistic ultra $b-T_1$ space and $b \in X \setminus \{a\}$ such that $\{a\} = \langle x, \{a\}, \{a\}^c \rangle$, then $a \neq b$ therefore, there exist (1,2) Intuitionistic b -open sets U_a, V_b in X such that $a \in U_a, b \notin U_a$, and $b \in V_b, a \notin V_b$.

Let G be union of all such V_b then G is (1,2) Intuitionistic b -open set in X and $G \subset X \setminus \{a\} \subset X$, therefore, $X \setminus \{a\}$ is (1,2) Intuitionistic b -open set in X .

Intuitionistic ultra $b-R_i$ and Intuitionistic ultra semi- R_i space, $i = 0, 1-5$:

Definition 5-1: An Intuitionistic bitopological space X is said to be.

- 1- Intuitionistic ultra $b-R_0$ (resp. Intuitionistic ultra semi- R_0) if $(1,2)IBCl(\{x\}) \subset U$ [resp. $(1,2)IScl(\{x\}) \subset U$] whenever, $x \in U \in (1,2)IBO(X)$ [resp. $x \in U \in (1,2)ISO(X)$]
- 2- Intuitionistic ultra $b-R_1$ (resp. Intuitionistic ultra semi- R_1) if for $x, y \in X$ such that $x \notin (1,2)IBCl(\{y\})$ [resp. $(1,2)IScl(\{y\})$] there exist disjoint (1,2)IB- [resp. (1,2)IS-open] U, V in X such that $x \in U$ and $y \in V$
- 3- Intuitionistic weakly ultra $b-R_0$ (resp. Intuitionistic weakly ultra semi- R_0) if $\bigcap_{x \in X} (1,2)IBCl(\{x\}) = \tilde{\phi}$ [resp. $\bigcap_{x \in X} (1,2)IScl(\{x\}) = \tilde{\phi}$]

Example 5-2: : Let $X = \{a, b, c\}$

$$T_1 = \{ \tilde{X}, \tilde{\phi}, \langle x, \{a\}, \{b, c\} \rangle, \langle x, \{a, b\}, \{c\} \rangle \}$$

$$T_2 = \{ \tilde{X}, \tilde{\phi}, \langle x, \{b, c\}, \{a\} \rangle \}$$
 then

$$(1,2)IBO(X) = \{ \tilde{X}, \tilde{\phi}, \langle x, \{a\}, \{b, c\} \rangle, \langle x, \{a\}, \{b\} \rangle, \langle x, \{a\}, \{c\} \rangle, \langle x, \{a\}, \phi \rangle, \langle x, \{b\}, \{c\} \rangle, \langle x, \{b\}, \phi \rangle, \langle x, \{a, c\}, \{b\} \rangle, \langle x, \{c\}, \{b\} \rangle, \langle x, \{c\}, \phi \rangle, \langle x, \phi, \{a, c\} \rangle, \langle x, \{a, b\}, \{c\} \rangle, \langle x, \{a, b\}, \phi \rangle, \langle x, \{a, c\}, \phi \rangle, \langle x, \{b, c\}, \phi \rangle, \langle x, \phi, \{b, c\} \rangle, \langle x, \phi, \phi \rangle \}$$

$$(1,2)IBCl(\{a\}) = \langle x, X, \phi \rangle = \tilde{X}, (1,2)IBCl(\{b\}) = \langle x, \{b, c\}, \{a\} \rangle, \text{ and } (1,2)IBCl(\{c\}) = \langle x, \{c\}, \{a, b\} \rangle \text{ then}$$

$$\bigcap_{x \in X} (1,2)IBCl(\{x\}) = \langle x, \phi, X \rangle = \tilde{\phi}, \text{ therefore}$$

X is Intuitionistic weakly ultra $b-R_0$, but X is not Intuitionistic ultra $b-R_0$ since

$$(1,2)IBcl(\{a\}) = \tilde{X} \not\subset \langle x, \{a\}, \{b, c\} \rangle \in (1,2)IBO(X) \text{ for } a \in \{a\} = \langle x, \{a\}, \{b, c\} \rangle.$$

Proposition 5-3:

- 1- Every Intuitionistic ultra semi - R_0 is Intuitionistic ultra $b-R_0$.
- 2- Every Intuitionistic ultra semi - R_1 is Intuitionistic ultra semi- R_0 .

Proof : clear

Proposition 5-4 : If X is Intuitionistic ultra $b-R_1$ then it is Intuitionistic ultra $b-R_0$.

Proof: let X is Intuitionistic ultra $b-R_1$, $U \in (1,2)IBO(X)$ and $x \in U$ for each $y \in X \setminus U$ therefore, there exist $(1,2)$ IB-open sets U_x, V_y in X such that $x \notin (1,2)IBcl(\{y\})$ $x \in U_x, y \in V_y, U_x \cap V_y = \tilde{\phi}$, let $A = \bigcup \{V_y : y \in X \setminus U\}$ then

$X \setminus U \subset A$ and $x \notin A$ which is a $(1,2)b$ -open set so that

$$(1,2)IBcl(\{x\}) \subset X \setminus A \subset U.$$

Therefore, X is intuitionistic ultra $b-R_0$.

Theorem 5-5 :- An Intuitionistic bitopological space X is intuitionistic ultra $b-T_2$ if and only if it is intuitionistic ultra $b-T_1$ and intuitionistic ultra $b-R_1$.

Proof:

If X is intuitionistic ultra $b-T_2$ then it is intuitionistic ultra $b-T_1$ (by Remark 4-9). we prove X is intuitionistic ultra $b-R_1$.

If $x, y \in X$ such that $x \notin (1,2)IBcl(\{y\})$ then $x \neq y$. Therefore, There exist disjoint $(1,2)IB$ -open sets U, V in X such that $x \in U$ and $y \in V$. Therefore, X is

intuitionistic ultra $b-R_1$.

Conversely ; if X is intuitionistic ultra $b-T_1$ and intuitionistic ultra $b-R_1$ and $x, y \in X$ such that $x \notin (1,2)IBcl(\{y\})$ there exist disjoint $(1,2)IB$ open sets U, V in X such that $x \in U$ and $y \in V$. since X is intuitionistic ultra $b-T_1$, $(1,2)IBcl(\{y\}) = \{y\}$ (by theorem 4.11) Thus for $x \neq y$ and $V \in (1,2)IBO(X)$ such that $x \in U$ and $y \in V$, $U \cap V = \tilde{\phi}$.

Therefore, X is intuitionistic ultra $b-T_2$.

Corollary 5-6: An intuitionistic bitopological space X is intuitionistic ultra semi- T_2 if and only if it is intuitionistic ultra semi- T_1 and intuitionistic ultra semi - R_1 .

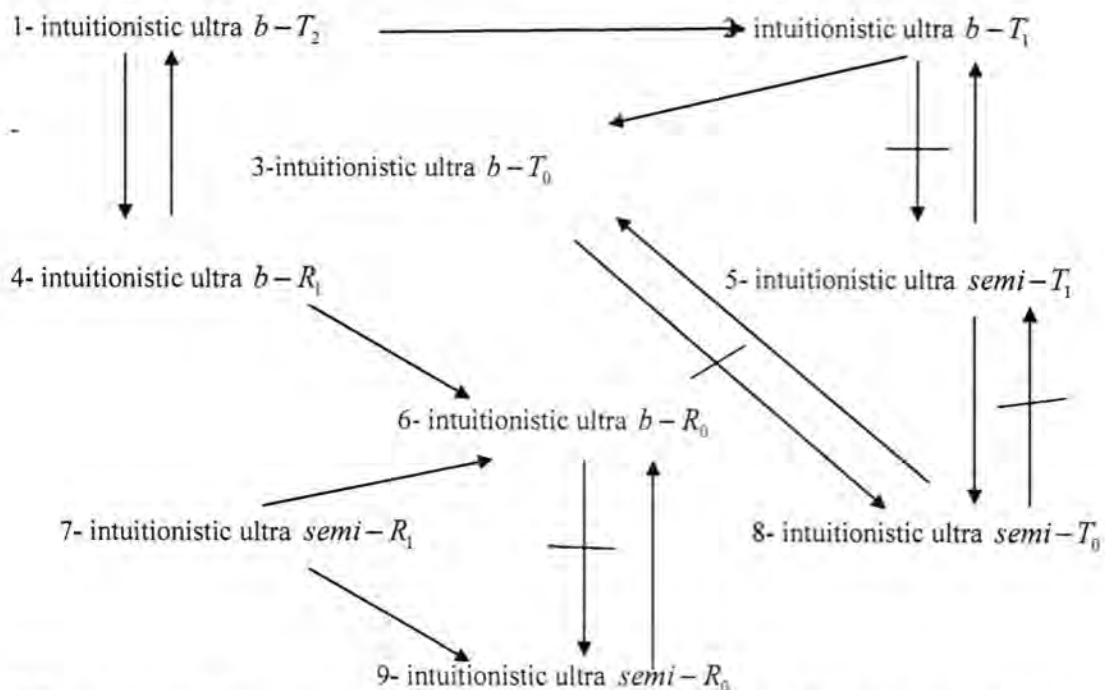
Proposition 5-7: Every intuitionistic weakly ultra semi - R_0 or intuitionistic weakly ultra pre - R_0 is intuitionistic weakly ultra $b-R_0$.

Certain Types of Separation Axioms in Intuitionistic Bitopological Spaces

Hatim

Proof: if X is intuitionistic weakly ultra semi- R_0 or intuitionistic weakly ultra pre- R_0 , $\bigcap(1,2)IScl(\{x\}) = \tilde{\phi}$ or $\bigcap(1,2)IPcl(\{x\}) = \tilde{\phi}$ there fore $\bigcap(1,2)IBcl(\{x\}) = \tilde{\phi}$.

We can explain the relation among the above concepts by following diagram over,



Where $A \rightarrow B$ (resp. $A \nrightarrow B$) represents that A implies B (resp. A does not imply B).

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Production of Pyrethrins in Tissue Cultures of Pyrethrum (*Chrysanthemum cinerariaefolium*)

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ABSTRACT

This study was carried out in an attempt to increase the production of pyrethrins in tissue cultures of pyrethrum (*Chrysanthemum cinerariaefolium*) on Murashige and Skoog's (MS) medium supplemented with different concentrations of plant growth regulators. Benzyl adenine (BA) and 2,4-dichlorophenoxy acetic acid (2,4-D) were tested for their potential in callus induction. Callus was induced on leaf explants using MS medium supplemented with 1 mg/l BA and 5 mg/l 2,4-D and on petal explants using 1 mg/l BA and 10 mg/l 2,4-D. those combinations were used for callus initiation and maintenance. Extracts of plant leaves, petals and callus tissues were prepared and investigated for pyrethrin content. Extracts contained flavonoids, terpenes, tannins, resins, essential oils and steroids. HPLC analysis was performed for detection of pyrethrins in the extracts. Results showed that pyrethrin concentration in callus culture extracts was higher than that of intact plant extracts. The concentration of pyrethrin significantly increased on a medium supplemented with 5 mg/l BA and 10 mg/l 2,4-D for leaf explants and 5 mg/l BA and 5 mg/l 2,4-D for petal explants.

الخلاصة

نفذت الدراسة الحالية كمحاولة لزيادة انتاج مركبات البايثرين في نبات الداودي (*Chrysanthemum cinerariaefolium*) عن طريق تقنية الزراعة النسيجية باستعمال الوسط الغذائي (MS) Murashige and Skoog والمجهز بتركيزات مختلفة من منظمات النمو النباتية، حيث تم اختبار إمكانية منظمي النمو Benzyl adenine (BA) و 2,4-dichlorophenoxy acetic acid (2,4-D) على إستحداث الكالس. أستحدث الكالس من أوراق وبتلات نبات الداودي ، وكذلك تمت إدامة الكالس على الوسط الغذائي MS المجهز بـ 1 ملغم/لتر من منظم BA و 5 ملغم/لتر من منظم 2,4-D بالنسبة للأوراق ، و 1 ملغم/لتر من منظم BA و 10 ملغم/لتر من منظم 2,4-D بالنسبة للبتلات ، والتي كانت من افضل التراكيز لنشوء وإدامة الكالس. حُضِرَت المستخلصات النباتية من أوراق و بتلات و مزارع الكالس لنبات الداودي وتم التحقق من إحتوائها على البايثرين. كذلك إحتوت مستخلصات الأوراق والبتلات على الفلافونويدات و التربينات والتانينات والراتنجات والزيوت الاساسية والستيرويدات. أستخدمت فحوصات كروماتوغرافيا السائل عالي الكفاءة للكشف عن البايثرين في المستخلصات، ولوحظ أن تركيز البايثرين في مزارع الكالس كان اعلى من تركيزه في

الاجزاء النباتية للنبات الاصلي. ولوحظت الزيادة المعنوية لتركيز البايثرين في الوسط الغذائي المجهز بـ 5 ملغم لتر BA و 10 ملغم لتر 2,4-D بالنسبة للأوراق ، و 5 ملغم لتر BA و 5 ملغم لتر 2,4-D بالنسبة للبتلات.

INTRODUCTION

Pyrethrins are widely used as natural insecticides produced by certain species of the pyrethrum plant. They offer all the advantages of chemical compounds, that is, rapidity of action, activity against a broad range of insects, low cost. They are characterized by their rapid biodegradability and low toxicity for mammals. The advent of strict environmental legislations and the mounting costs of industrial research and development costs of new chemical insecticides have encouraged the use of pyrethrins (1).

Pyrethrins target the central and peripheral nervous systems in vertebrates and invertebrates where they disrupt the signal transmission along the nerve axon. Pyrethrins bind to the sodium channel causing it to remain open, whereby the nerve continues to be stimulated uncontrollably causing tremors. This condition results in rapid knock down and muscular paralysis in target organism resulting in death. Pyrethrins enter the target organism via ingestion and physical contact (2).

Pyrethrum is highly poisonous to insects. It is used either as powder or as spray. It affords a protection against many agricultural pests (3).

The production of secondary metabolites *in vitro* is possible through plant tissue culture (4). Various factors are affecting the production of secondary metabolites in tissue culture. Initial growth and production of secondary metabolites are optimized by manipulating the physicochemical factors followed by selection of high-productive cells (5). Different strategies have been employed to increase secondary metabolite production such as components of the culture medium, plant growth regulators and physical factors. Khanna and Khanna (6) found that pyrethrin biosynthesis ability increased in callus cultures after the addition of exogenous ascorbic acid to the medium. In a study on pyrethrin formation by selected cell lines of *Chrysanthemum cinerariaefolium*, Pal and Dhar (7) found that the production of pyrethrins in callus cultures was influenced by the nature and concentration of growth regulators (auxins and cytokinins). Hitmi *et al.* (8) found that biomass yield and pyrethrin content in cell cultures were higher when they were grown in the light than in the dark.

This research work aims to:

1. Inducing callus cultures from plant leaves and petals on MS medium supplemented with different concentrations of plant growth regulators, and then selecting the best combination for callus induction.

2. Extracting pyrethrins from dried plant leaves, petals and callus tissues with petroleum ether and detecting the presence of pyrethrin compounds in plant leaf, petal and callus extracts by HPLC analysis.

MATERIALS AND METHODS

Callus cultures

(MS) medium (9) was prepared and used. Sucrose 30 g/l, myoinositol 100 mg/l and different concentrations of the auxin 2,4-D at the concentrations 0, 1, 5 or 10 mg/l and the cytokinin BA at the concentrations 0, 1, 5 or 10 mg/l were prepared and added. The pH was adjusted to 5.8, then 8 g/l of the agar type (agar-agar) was added to the medium, placed on a hot plate magnetic stirrer till boiling, then aliquots of 20 ml were dispensed into (8×6) cm culture vessels.

Culture medium was sterilized by autoclaving at 121 °C under 1.04 Kg/cm² pressure, for 15 min. Glassware and other instruments either autoclaved or placed in electric oven at 200 °C for 2 hrs. (5). Surface sterilized leaf and petal explants (1 cm) in diameter were inoculated into the culture vessels under aseptic conditions, placed in the incubator under 16 hrs. light / 8 hrs. dark photoperiod at 25°C.

Extraction

Leaves and petals of pyrethrum (*C. cinerariaefolium*) were air-dried in shade and callus tissues were oven dried at 40 °C for 24 hrs (10), and ground into fine powder using grinding machine. The extraction method of Barthomeuf *et al.*, (11) was followed with some modifications. Briefly, 2 grams of dried petals, leaves and callus initiated on leaves and petals were ground and soaked in 100 ml of petroleum ether for 24 hrs. The resulted dark yellow-greenish solutions were filtered through a Whatman No.1 filter paper. Anhydrous sodium sulphate 1/4 (v/fresh weight) were added to the extract solution for homogenization, and filtered again through a Whatman No.1 filter paper. The containers were sealed, to prevent evaporation, and covered with aluminum foil in order to prevent degradation of pyrethrins may be caused by ambient light.

The solvent was evaporated by using rotary evaporator and dried using freeze dryer. The extract powder was stored in a sealed container in dark at 4 °C until use.

HPLC Analyses

HPLC analyses were performed at a wave length of 225 nm using Agilent (1100 series) HPLC system (isocratic pumping system, variable wave length detector spectrophotometer), Hi Q sil C18 W column (4.6mm×250mm ID) and a solvent mixture of CH₃CN 20% : H₂O 80%. Equilibration at initial conditions for 40 min. The flow rate was 1.5 ml/min. Peak areas were compared with peak areas of the pyrethrin standard (analytical standard, Aldrich).

Detection of some active compounds

Pyrethrum leaf and petal crude extracts were analyzed for detection of alkaloids, flavonoids, essential oils, saponins, resins, tannins, coumarins, terpenes and steroids (12).

RESULTS AND DISCUSSION

Induction of callus cultures

Results in Table 1 explain the effect of different concentrations of BA and 2,4-D on callus fresh weight (mg) initiated on leaf explants. The concentrations of BA showed significant differences in callus induction, and the concentration of 5 mg/l BA significantly increased induction compared with the other concentrations, reached 320.06 mg of mean callus fresh weight on leaf explants. The concentrations of 2,4-D also showed significant differences, reached 327.47 mg of mean callus fresh weight on leaf explants at the concentration of 5 mg/l. The highest callus fresh weight for callus induction on leaf explants was achieved in a combination of 1 mg/l BA and 5 mg/l 2,4-D reached 416.89 mg callus fresh weight. While the lowest callus fresh weight was recorded in a combination of 0 mg/l BA and 0 mg/l 2,4-D reached 80.81 mg.

Table 1: The effect of different concentrations of BA and 2,4-D on callus fresh weight (mg) initiated on leaf explants of *C. cinerariaefolium* (n=12)

BA (mg/l)	2,4-D (mg/l)				Mean
	0	1	5	10	
0	80.81	174.41	195.13	156.20	159.88
1	168.71	249.85	416.89	395.70	307.78
5	184.33	324.30	385.28	386.36	320.06
10	217.13	307.40	312.60	287.90	281.25
Mean	170.99	263.99	327.47	306.54	---
LSD: 0.05	BA: 8.935 * , 2,4- D: 8.935 * , BA * 2,4 -D: 18.044 *				

* ($P \leq 0.05$).

Results in Table 2 show that the concentration of 5 mg/l BA significantly increased callus induction compared with the other concentrations, reached 263.66 mg of mean callus fresh weight on petal explants. While the concentrations of 10 mg 2,4-D significantly increased callus fresh weight compared with the other concentrations, reached 270.74 mg of mean callus fresh weight on petal explants. The highest callus fresh weight for callus induction on petal explants was achieved in a combination of

1 mg/l BA and 10 mg/l 2,4-D reached 378.84 mg callus fresh weight. While the lowest callus fresh weight was recorded in a combination of 0 mg/l BA and 0mg/l 2,4-D reached 71.87 mg.

Table 2: The effect of different concentrations of BA and 2,4-D on callus fresh weight (mg) initiated on petal explants of *C. cinerariaefolium* (n=12)

BA (mg/l)	2,4-D (mg/l)				Mean
	0	1	5	10	
0	71.87	104.24	140.15	176.30	123.14
1	98.16	179.38	343.30	378.84	249.92
5	182.59	270.60	300.38	301.08	263.66
10	194.45	206.89	227.80	226.74	213.97
Mean	136.76	190.27	252.90	270.74	---
LSD: 0.05	BA: 6.405 * , 2,4- D: 6.405 * , BA * 2,4 -D: 11.592 *				

* ($P \leq 0.05$).

These results are in agreement with Ramawat (5) who stated that callus induction in a number of plant species favors higher levels of auxins than cytokinins. According to the results stated above, callus was induced on leaf and petal explants then maintained on MS medium containing the same concentrations of BA and 2,4-D for induction. Induction and maintenance of callus cultures in *C. cinerariaefolium* seem to favor high level of 2,4-D and moderate level of BA. The increase of callus mass is important for the production of secondary metabolites since they are proportionally related (5). Callus induction and differentiation are influenced by many factors: medium components, type and concentration of plant growth regulators, plant physiological status, source of explants and environmental conditions (13).

Detection of some active compounds

Results in table 3 indicated the presence of flavonoides, resins, terpenes, steroids, tannins and essential oils in plant extracts. El-Shazly *et al.* (14) stated that the chemical constituents of the aerial parts of pyrethrum contain many sesquiterpenes and essential oils. Ahlem *et al.* (15) stated that the extracts from Chrysanthemum species showed the presence of various quantities of tannins and flavonoids.

Table 3: Secondary metabolites detected in leaf and petal extracts of *C. cinerariaefolium*

Type of secondary metabolite	Result of detection	
	Leaf Extract	Petal extract
Alkaloids	-ve	-ve
Flavonoids	+ve	+ve
Coumarins	-ve	-ve
Saponins	-ve	-ve
Terpenes	+ve	+ve
Tannins	+ve	+ve
Resins	+ve	+ve
Essential oils	+ve	+ve
Steroids	+ve	+ve

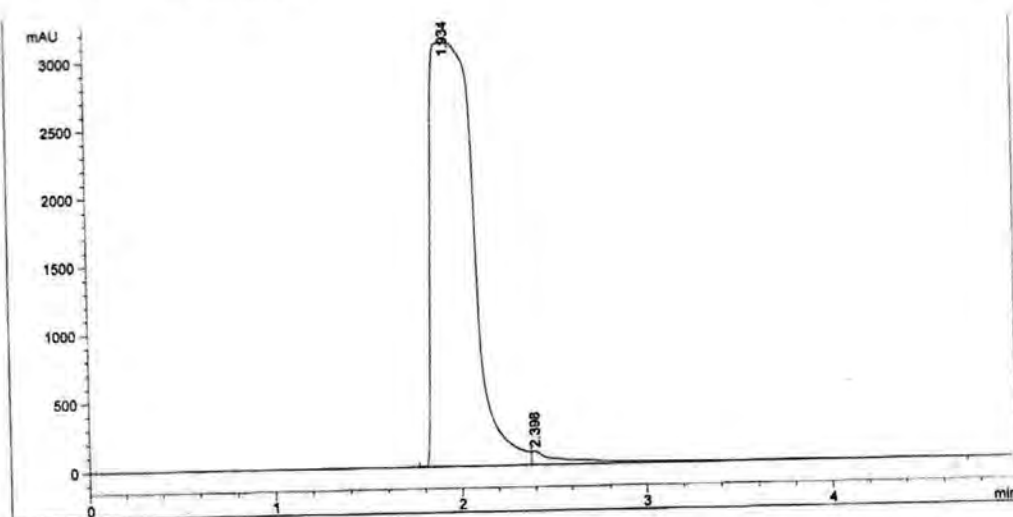
+ve indicates the presence of secondary metabolite.

-ve indicates the absence of secondary metabolite.

HPLC analysis of leaf, petal and callus tissue extracts

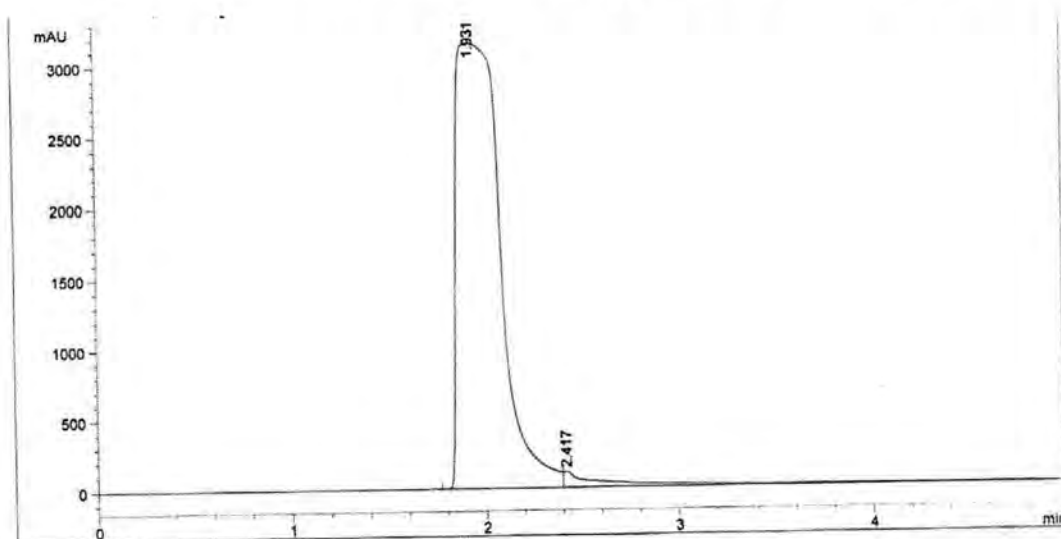
Results showed in Fig. 1, 2, 3, 4 confirm that the retention time of leaf, petal and callus extracts is compatible with the retention time of the analytical standard (Fig. 5), which was 1.9 min.

The concentration of pyrethrin in the extracts was estimated according to the area percentage of the peaks appeared on the chromatograms. The area of the peak is proportional to the concentration of the analyte (16). The callus induced from pyrethrum leaves and petals showed higher peaks than the intact leaf and petal extracts. The concentration of pyrethrin in the callus cultures was higher than that found in intact pyrethrum leaves and petals. The standard showed the highest area percentage (99.93%). All chromatograms showed the same peak which represents pyrethrin I. Other contents which not appeared may due to their insolubility in petroleum ether or require different conditions during analysis with HPLC.



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	1.934	VV	0.2350	4.95301e4	3116.53125	96.6536

Figure 1: HPLC chromatogram for pyrethrum petals extract



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	1.931	VV	0.2330	4.91020e4	3106.49658	95.6991

Figure 2: HPLC chromatogram for pyrethrum leaves extract

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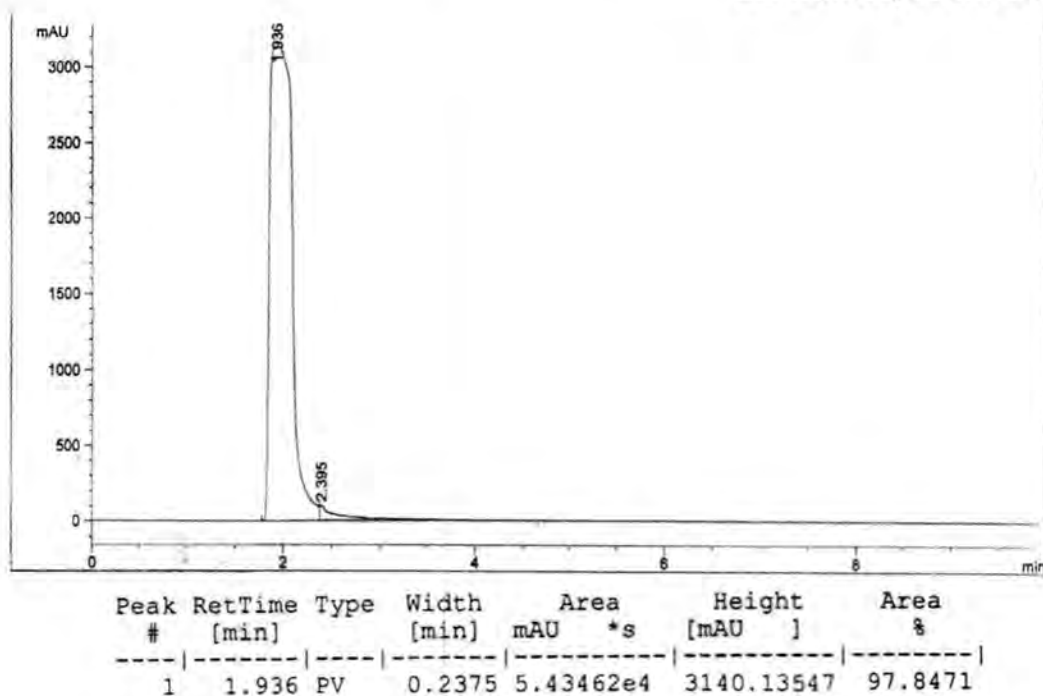


Figure 3: HPLC chromatogram for callus induced from pyrethrum petals

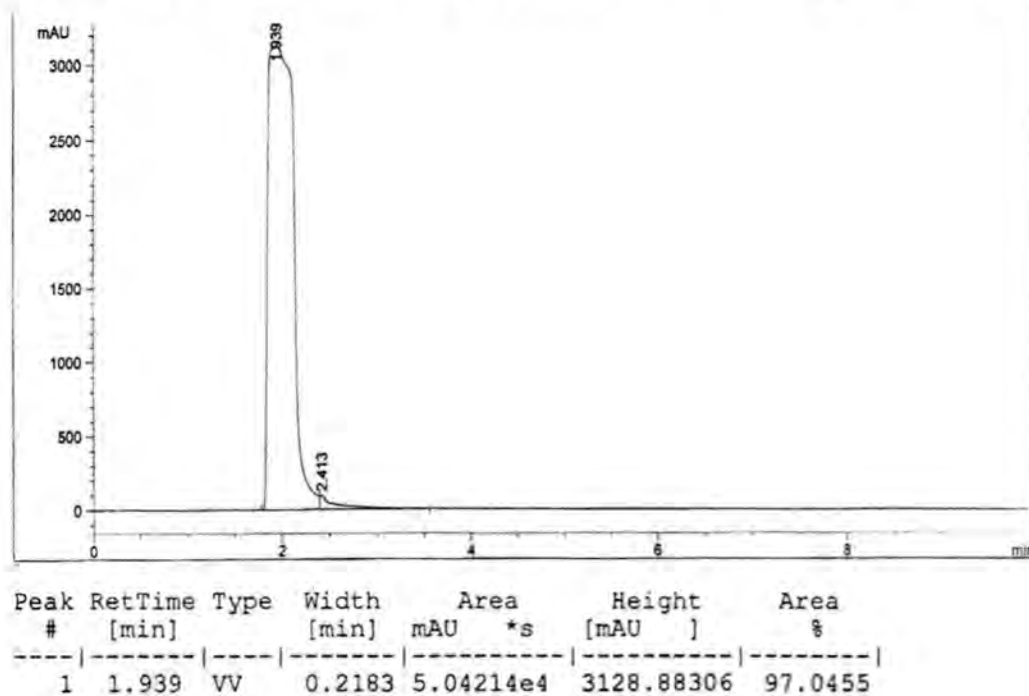


Figure 4: HPLC chromatogram for callus induced from pyrethrum leaves

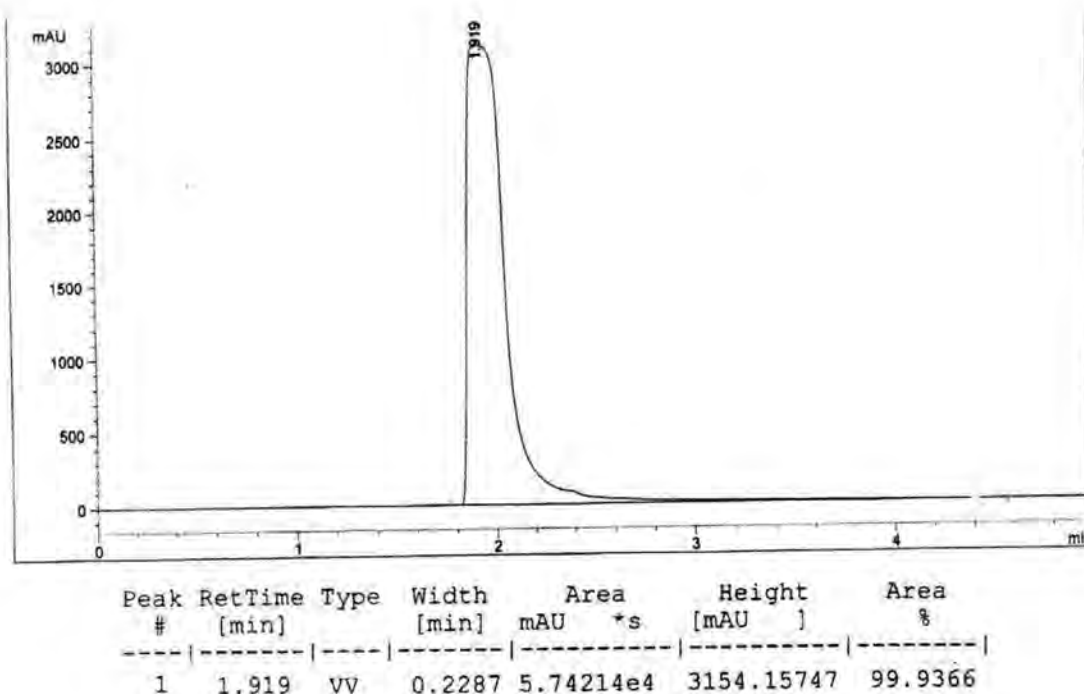


Figure 5: HPLC chromatogram for the pyrethrum standard

CONCLUSION

Callus cultures of *C. cinerariaefolium* can be induced and maintained on MS medium supplemented with 1 mg/l BA and 5 mg/l 2,4-D for leaf explants and 1 mg/l BA and 10 mg/l 2,4-D for petal explants. The concentration of pyrethrin in callus cultures (97.84% area percentage for callus induced from petals and 97.04% area percentage for callus induced from leaves) is higher than that in the intact pyrethrum leaves (95.69% area percentage) and petals (96.65% area percentage). The concentration of pyrethrin in petals is higher than that in leaves in the cases of dried leaf, petal explants and callus cultures.

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Certain Type of Lie Algebra Action

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الخلاصة

الهدف الاساس من هذه الدراسة هو البحث عن فعل مهم بصفات جديدة من بديهية Schure التي تبين ان الفعل على الجداء التتسوري لتمثيلات جبرلي يحمل صفات مهمة، اذ ان احد التمثيلات عادي والثاني ثنائي للحصول على نتائج جديدة، يربط الجداء التتسوري مع التمثيلات الثنائية لتمثيلات عادية، هدفنا الرئيسي لهذا العمل هو لاعطاء تمثيل جبرلي بتوأمة (ضمنيه) هذه الافعال (التمثيلات).

ABSTRACT

The main aim in this study is to look for an interesting action with new properties from a Schure's lemma, which states that the action of the tensor product of Lie algebras representations has interesting property. Putting in mind that one of the two representations is usual and the other is the dual we obtain some results by relating the tensor product of dual representations with usual representations. Our main work here is to give a representation of Lie algebra by intertwine these actions (representations).

INTRODUCTION

A Lie algebra is a finite-dimensional vector space which is naturally endowed with a bilinear operation, Lie algebras can then be studied using purely algebraic tools, a part from the intrinsic interest, the theory of Lie algebras and its representations is used in various parts of mathematics, A representation of a group G is a homomorphism of the group G onto a group of linear map acting on vector space Ω , the tensor product of vector spaces Ω_2 and Ω_1 is a vector space $\Omega_2 \otimes \Omega_1$, for which there exists bilinear map $\delta : \Omega_2 \times \Omega_1 \rightarrow \Omega_2 \otimes \Omega_1$ which satisfies the following property. Whenever $\varphi : \Omega_2 \times \Omega_1 \rightarrow \Omega$ is any bilinear map, there exists a unique linear map

$\theta : \Omega_2 \otimes \Omega_1 \rightarrow \Omega$, such that $\theta \cdot \delta = \phi$, and this property is called universal property.[1], [2].

Our main interest in this thesis is to give a representation of Lie algebra by give the definition of Lie algebra action on tensor product and the natural action and intertwining these actions.

1. The action of Lie algebra on Hom. And tensor.

Definition, (1.1), [3]: Let \mathbb{A} be a non empty set and let G be a group with neutral element $e \in G$, a left action of G on \mathbb{A} is a map $\phi : G \times \mathbb{A} \rightarrow \mathbb{A}$ such that satisfies the following $\phi(e, x) = x$ and $\phi(g, \phi(h, x)) = \phi(gh, x)$, for all $x \in \mathbb{A}$ and $g, h \in G$.

Definition, (1.2), [4]: Let $(\hat{g}_1, [,])$ and $(\hat{g}_2, [,])$ be two Lie algebras over the same field \mathcal{F} , a homomorphism of Lie algebras from \hat{g}_1 into \hat{g}_2 is a linear map $\Omega : \hat{g}_1 \rightarrow \hat{g}_2$, such that

$\Omega[x, y] = \Omega(x) \cdot \Omega(y) - \Omega(y) \cdot \Omega(x)$, for all $x, y \in \hat{g}_1$, and for simply we denote it by $\Omega[x, y] = \Omega(x)\Omega(y) - \Omega(y)\Omega(x)$, if in addition Ω is a one-to-one and onto then Ω is called a Lie algebra isomorphism. A Lie algebra isomorphism of a Lie algebra with itself is called a Lie algebra automorphism. A representation of the Lie algebra \hat{g} is a (finite-dimensional) real or complex vector space Ω together with a homomorphism $\hat{g} \rightarrow gl(\Omega)$ of Lie algebra.

Definition, (1.3), [5]: Let $\rho_{N_1} : \hat{g} \rightarrow gl(N_1)$ and $\rho_{N_2} : \hat{g} \rightarrow gl(N_2)$ be two representations of a Lie algebra \hat{g} , a homomorphism (or intertwining map) $\psi \cdot (\rho_{N_1}(x)) = (\rho_{N_2}(x)) \cdot \psi$ is a linear map which commutes with the action of \hat{g} , a homomorphism ψ is said to be an isomorphism of representations if it is an isomorphism of vector space. If ψ is the intertwining map of representations and in addition is invertible then ψ said to be an equivalence of representations.

Definition, (1.4), [5]: Let \hat{g}_1 and \hat{g}_2 be two Lie algebras and let Ω_1 and Ω_2 be representations of \hat{g}_1 and \hat{g}_2 acting on spaces N_1 and N_2 respectively. Then the tensor product of Ω_1 and Ω_2 denoted by $\Omega_1 \otimes \Omega_2$ is a representation of $\hat{g}_1 \times \hat{g}_2$ acting on $N_1 \otimes N_2$ defined by:

$\Omega_1 \otimes \Omega_2(x, y) = \Omega_1(x) \otimes I + I \otimes \Omega_2(y)$ where I is the identity map, for all $x \in \hat{\mathfrak{g}}_1, y \in \hat{\mathfrak{g}}_2$.

Example, (1.5): Let $\Omega_1 : \mathfrak{sl}(2, \mathbb{R}) \rightarrow \mathfrak{gl}(N)$ be a representation of $\mathfrak{sl}(2, \mathbb{R})$ such that:

$$\Omega_1(h) = a = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & -2 \end{pmatrix}, \Omega_1(e) = b = \begin{pmatrix} 0 & 0 & 1 \\ -2 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad \Omega_1(f) = c = \begin{pmatrix} 0 & -1 & 0 \\ 0 & 0 & 0 \\ 2 & 0 & 0 \end{pmatrix};$$

Where $\{h, e, f\}$ is basis for $\mathfrak{sl}(2, \mathbb{R})$

And let $\{f_1, f_2, f_3\}$ be abasis for $\mathfrak{so}(3)$, Where $f_1 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix}, f_2 =$

$$\begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ -1 & 0 & 0 \end{pmatrix}, f_3 = \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \text{ with relations } [f_1, f_2] = f_3, [f_2, f_3] = f_1, [f_3, f_1] = f_2.$$

And let $\Omega_2 : \mathfrak{so}(3) \rightarrow \mathfrak{gl}(N)$ be a representation, Such that: $\Omega_2(f_1) = y_1 =$

$$\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix}, \Omega_2(f_2) = y_2 = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ -1 & 0 & 0 \end{pmatrix}$$

$\Omega_2(f_3) = y_3 = \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$, then the tensor product of these representations is:

$$\begin{aligned} \Omega_1 \otimes \Omega_2(h, f_1) &= \Omega_1(h) \otimes I + I \otimes \Omega_2(f_1) \\ &= \begin{pmatrix} 0 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & -2 \end{pmatrix} \otimes \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} + \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \otimes \\ &\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix} \end{aligned}$$

$$= \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 2 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 2 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -2 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -2 & -1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & -2 \end{pmatrix}_{9 \times 9}.$$

Definition, (1.6), [4]: Let Ω be a representation of Lie algebra \hat{g} acting on a finite dimensional vector space \mathcal{N} , then the dual representation of Ω is the representation of \hat{g} acting on \mathcal{N}^* given by $\Omega^*(x) = -(\Omega(x))^t$, the dual representation is also called contragradient representation.

2. The dual action of Lie algebra on Hom. and tensor.

Schure's lemma, (2.1.) [5]: Suppose that Ω_1 and Ω_2 are representations of Lie algebra \hat{g} acting on finite-dimensional vector spaces \mathcal{N}_1 and \mathcal{N}_2 , respectively.

Define an action of \hat{g} on $\text{Hom}_{\mathcal{F}}(\mathcal{N}_2, \mathcal{N}_1)$ by $\psi : \hat{g} \rightarrow \text{gl}(\text{Hom}_{\mathcal{F}}(\mathcal{N}_2, \mathcal{N}_1))$, $\psi(x)\vartheta = \Omega_1(x)\vartheta - \vartheta\Omega_2(x)$ for all $x \in \hat{g}$ and $\vartheta \in \text{Hom}_{\mathcal{F}}(\mathcal{N}_2, \mathcal{N}_1)$ and:

$\text{Hom}_{\mathcal{F}}(\mathcal{N}_2, \mathcal{N}_1) \cong \mathcal{N}_2^* \otimes \mathcal{N}_1$ as equivalence of representations.

Proposition, (2.2): Let $\Omega : \hat{g} \rightarrow \text{gl}(\mathcal{N})$ be a representation of Lie algebra \hat{g} on to \mathcal{F} -finite dimensional vector space \mathcal{N} , then $\Omega^* : \hat{g} \rightarrow \text{gl}(\mathcal{N}^*)$ is the dual representation on \mathcal{N}^* which is given by $\Omega^*(x) = \rho^* \Omega(x)$, for all $x \in \hat{g}$, where $\rho : \mathcal{N} \rightarrow \mathcal{F}$.

proof

Since Ω is a linear map that satisfies $\Omega([x, y]) = [\Omega(x), \Omega(y)]$

then Ω^* is a linear map that satisfies $\Omega^*([x, y]) = [\Omega^*(x), \Omega^*(y)]$

and for all basis $\omega_j \in \mathcal{N}$ there exist basis $\omega_i^* \in \mathcal{N}^*$ where $i = 1, 2 ; j = 1, 2$

such that: $\omega_i^*(\omega_j) = \begin{cases} 1 & \text{if } i = j \\ 0 & \text{if } i \neq j \end{cases}$ then ω_i^* is called the dual basis of ω_j .

But in terms of matrices and linear map,

$$\text{gl}(\mathcal{N}_2) \cong \text{gl}(m, \mathcal{F}) \text{ and } \text{gl}(\mathcal{N}_1) \cong \text{gl}(n, \mathcal{F})$$

we have the matrix representations: $\Omega_2 : \hat{g} \rightarrow \text{gl}(m, \mathcal{F})$, $\Omega_1 : \hat{g} \rightarrow \text{gl}(n, \mathcal{F})$ and

$\Omega_2^* : \hat{g} \rightarrow \text{gl}(m, \mathcal{F})$ defined by $\Omega_2^*(X) = -(\Omega_2(X))^t$

Ω_2^* is a Lie algebra homomorphism of Lie algebra \hat{g} into $gl(m, \mathcal{F})$ since:

$$\begin{aligned}\Omega_2^*([X, Y]) &= -(\Omega_2[X, Y])^t \\ &= -([\Omega_2(X), \Omega_2(Y)])^t \\ &= -(\Omega_2(X)\Omega_2(Y) - \Omega_2(Y)\Omega_2(X))^t \\ &= (\Omega_2(X))^t(\Omega_2(Y))^t - ((\Omega_2(Y))^t(\Omega_2(X))^t) \\ &= [-(\Omega_2(X))^t, -(\Omega_2(Y))^t] \\ &= [\Omega_2^*(X), \Omega_2^*(Y)], \text{ for all } X, Y \in \hat{g}.\end{aligned}$$

The following diagram shows that Ω_2^* is a Lie algebra homomorphism.

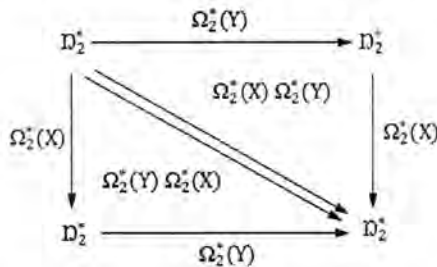


Figure 1

Remark (2.3): Let Ω_1 and Ω_2 be two representations of Lie algebras acting on vector spaces $\mathcal{D}_1, \mathcal{D}_2$ respectively, and let $\text{Hom}_{\mathcal{F}}(\mathcal{D}_2, \mathcal{D}_1)$ be the \mathcal{F} -vector space of all linear maps from \mathcal{D}_2 onto \mathcal{D}_1 , define $\psi: \hat{g} \rightarrow gl(\text{Hom}_{\mathcal{F}}(\mathcal{D}_2, \mathcal{D}_1))$ by:

$$\psi(x)\vartheta = \Omega_1(x)\vartheta - \vartheta\Omega_2(x), \text{ for all } x \in \hat{g}, \vartheta \in \text{Hom}_{\mathcal{F}}(\mathcal{D}_2, \mathcal{D}_1)$$

$$(\psi(x)\vartheta)(v) = \Omega_1(x)\vartheta(v) - \vartheta(\Omega_2(x)(v)) \text{ for all } x \in \hat{g}, \vartheta \in \text{Hom}_{\mathcal{F}}(\mathcal{D}_2, \mathcal{D}_1) \text{ and } v \in \mathcal{D}_2.$$

Thus ψ is a homomorphism of Lie algebras \hat{g} into $gl(\text{Hom}_{\mathcal{F}}(\mathcal{D}_2, \mathcal{D}_1))$.

The following diagram shows that the action of Lie algebra \hat{g} on $\text{Hom}_{\mathcal{F}}(\mathcal{D}_2, \mathcal{D}_1)$ as follows:

$$\psi(x)\vartheta = \Omega_1(x)\vartheta - \vartheta\Omega_2(x).$$

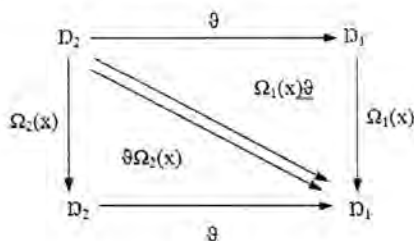


Figure 2

Now to prove ψ is a representation of Lie algebra, we must prove that ψ is a homomorphism of Lie algebras \hat{g} into $gl(\text{Hom}_{\mathcal{F}}(\Omega_2, \Omega_1))$.

By definition of Lie algebra homomorphism we must prove that ψ is a linear map and satisfy the following $\Omega([x, y]) = \Omega(x)\Omega(y) - \Omega(y)\Omega(x)$, for all $x, y \in \hat{g}$.

ψ is a linear map since $\psi(\alpha x + \beta y) \vartheta = \alpha \psi(x) \vartheta + \beta \psi(y) \vartheta$

Now to prove $\psi([x, y])\vartheta = \psi(x)(\psi(y)\vartheta) - \psi(y)(\psi(x)\vartheta)$

$$\begin{aligned} \text{The left hand side is } \psi([x, y])\vartheta &= \Omega_1([x, y])\vartheta - \vartheta\Omega_2([x, y]) \\ &= (\Omega_1(x)\Omega_1(y) - \Omega_1(y)\Omega_1(x))\vartheta - \vartheta(\Omega_2(x)\Omega_2(y) - \Omega_2(y)\Omega_2(x)) \\ &= (\Omega_1(x)\Omega_1(y))\vartheta - (\Omega_1(y)\Omega_1(x))\vartheta - \vartheta(\Omega_2(x)\Omega_2(y)) + \vartheta(\Omega_2(y)\Omega_2(x)) \\ &= (\Omega_1(x)\Omega_1(y))\vartheta - \vartheta(\Omega_2(x)\Omega_2(y)) - \\ &\quad ((\Omega_1(y)\Omega_1(x))\vartheta - \vartheta(\Omega_2(y)\Omega_2(x))). \end{aligned}$$

And the right hand side is:

$$\begin{aligned} \psi(x)(\psi(y)\vartheta) - \psi(y)(\psi(x)\vartheta) &= \Omega_1(x)(\psi(y)\vartheta) - (\psi(y)\vartheta)\Omega_2(x) - (\Omega_1(y)(\psi(x)\vartheta) - (\psi(x)\vartheta)\Omega_2(y)) \\ &= \Omega_1(x)(\Omega_1(y)\vartheta - \vartheta\Omega_2(y)) - (\Omega_1(y)\vartheta - \vartheta\Omega_2(y))\Omega_2(x) \\ &\quad - (\Omega_1(y)(\Omega_1(x)\vartheta - \vartheta\Omega_2(x)) - (\Omega_1(x)\vartheta - \vartheta\Omega_2(x))\Omega_2(y)) \\ &= (\Omega_1(x)\Omega_1(y))\vartheta - \vartheta(\Omega_2(x)\Omega_2(y)) - ((\Omega_1(y)\Omega_1(x))\vartheta - \vartheta(\Omega_2(y)\Omega_2(x))). \end{aligned}$$

The following diagram shows that ψ is A Lie algebra homomorphism.

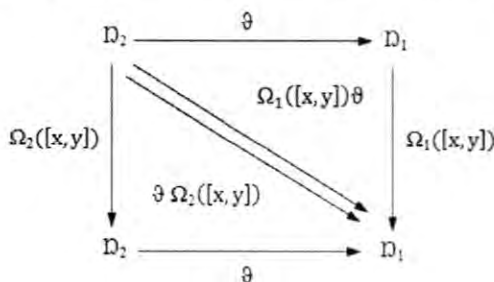


Figure 3

Remark, (2.4) : The map ψ above is called action of Lie algebra on $\text{Hom}_{\mathcal{F}}(\Omega_2, \Omega_1)$.

Example, (2.5): Let $\Omega_1 : \mathbb{R} \rightarrow \mathfrak{so}(3, \mathbb{R}) \subset \mathfrak{gl}(3, \mathbb{R})$ and $\Omega_2 : \mathbb{R} \rightarrow \mathfrak{o}(3, \mathbb{R}) \subset \mathfrak{gl}(3, \mathbb{R})$ are two representations of Lie algebra \mathbb{R} , where $(n = m = 3)$ and Ω_1 is the \mathbb{R} -vector space of dim.3 and so is Ω_2 , such that:

$$\Omega_1(a) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -x \\ 0 & x & 0 \end{pmatrix}, \Omega_2(a) = \begin{pmatrix} 0 & 0 & x \\ 0 & 0 & 0 \\ -x & 0 & 0 \end{pmatrix}, \text{ for all } a \in \mathbb{R}.$$

The representation ψ of \hat{g} on $\mathfrak{gl}(\text{Hom}_{\mathbb{R}}(\Omega_2, \Omega_1))$ is

$\psi : \mathbb{R} \rightarrow \mathfrak{gl}(\text{Hom}_{\mathbb{R}}(\Omega_2, \Omega_1)) \cong \mathfrak{gl}(M, (3, \mathbb{R}))$ such that

$$(\psi(a)\vartheta)(v) = \Omega_1(a)\vartheta - \vartheta(\Omega_2(a)(v))$$

$$\begin{aligned} &= \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -x \\ 0 & x & 0 \end{pmatrix} \vartheta - \vartheta \left(\begin{pmatrix} 0 & 0 & x \\ 0 & 0 & 0 \\ -x & 0 & 0 \end{pmatrix} (v) \right) \\ &= \vartheta \left(- \begin{pmatrix} 0 & 0 & -x \\ 0 & 0 & 0 \\ x & 0 & 0 \end{pmatrix} + \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -x \\ 0 & x & 0 \end{pmatrix} \right) = \begin{pmatrix} 0 & 0 & x \\ 0 & 0 & -x \\ -x & x & 0 \end{pmatrix}. \end{aligned}$$

Remark, (2.6): According to the remarks (3.1.3) and (3.1.4) that given above:

Let $\psi : \hat{g} \rightarrow \mathfrak{gl}(N_2^* \otimes N_1)$, which is a representation of \hat{g} acting on the vector space $N_2^* \otimes N_1$ and defined by :

$$\psi(x)(\omega_2^* \otimes \omega_1) = (\Omega_2^*(x) \otimes I + I \otimes \Omega_1(x))(\omega_2^* \otimes \omega_1)$$

$$\psi(x)(\omega_2^* \otimes \omega_1) = \Omega_2^*(x)\omega_2^* \otimes \omega_1 + \omega_2^* \otimes \Omega_1(x)\omega_1$$

$$(\psi(x)(\omega_2^* \otimes \omega_1))(v) = \Omega_2^*(x)\omega_2^*(v) \otimes \omega_1 + \omega_2^*(v) \otimes \Omega_1(x)\omega_1$$

Since $(\omega_2^* \otimes \omega_1) : N_2 \rightarrow N_1$ then $(\omega_2^* \otimes \omega_1)(v) = \omega_2^*(v)\omega_1$

and we define $\Omega_2^*(x)\omega_2^*(v) \otimes \omega_1 = -\omega_2^*(\Omega_2(x)(v))\omega_1$

then the representation of Lie algebra on $N_2^* \otimes N_1$ becomes

$$(\psi(x)(\omega_2^* \otimes \omega_1))(v) = -\omega_2^*(\Omega_2(x)(v))\omega_1 + \omega_2^*(v)\Omega_1(x)\omega_1$$

for all $x \in \hat{g}$, $v \in \Omega_2$.

The following diagram shows that the action of Lie algebra \hat{g} on tensor product as follows:

$$\psi(x) (\omega_2^* \otimes \omega_1) = (\Omega_2^*(x) \otimes I + I \otimes \Omega_1(x)) (\omega_2^* \otimes \omega_1)$$

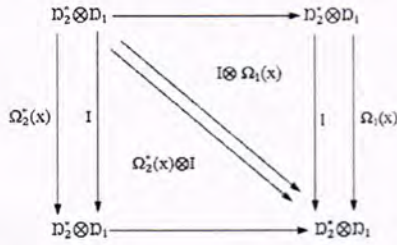


Figure 4

To show that ψ is a representation of \hat{g} acting on $gl(N_2^* \otimes N_1)$

where Ω_2 and Ω_1 are two representations of \hat{g} acting on N_2 and N_1 respectively.

$\psi(x) (\omega_2^* \otimes \omega_1)$ is a linear map since:

$$(\psi(\alpha x + \beta y)) (\omega_2^* \otimes \omega_1) = (\alpha \psi(x)) (\omega_2^* \otimes \omega_1) + (\beta \psi(y)) (\omega_2^* \otimes \omega_1)$$

And:

$$\psi([x, y]) (\omega_2^* \otimes \omega_1) = \psi(x) (\psi(y) (\omega_2^* \otimes \omega_1)) - \psi(y) (\psi(x) (\omega_2^* \otimes \omega_1))$$

thus, the left hand side is:

$$\begin{aligned} \psi([x, y]) (\omega_2^* \otimes \omega_1) &= ((\Omega_2^*([x, y]) \otimes I) + (I \otimes \Omega_1([x, y]))) (\omega_2^* \otimes \omega_1) \\ &= ((\Omega_2^*(x)\Omega_2^*(y) - \Omega_2^*(y)\Omega_2^*(x)) \otimes I) + I \otimes \Omega_1(x)\Omega_1(y) \\ &\quad - I \otimes \Omega_1(y)\Omega_1(x)) (\omega_2^* \otimes \omega_1) \\ &= (\Omega_2^*(x)(\Omega_2^*(y)\omega_2^*)) \otimes \omega_1 - (\Omega_2^*(y)(\Omega_2^*(x)\omega_2^*)) \otimes \omega_1 + \\ &\quad \omega_2^* \otimes (\Omega_1(x)\Omega_1(y)\omega_1) - \omega_2^* \otimes (\Omega_1(y)\Omega_1(x)\omega_1) \\ &= (\Omega_2^*(x)(\Omega_2^*(y)\omega_2^*)) \otimes \omega_1 + \omega_2^* \otimes (\Omega_1(x)\Omega_1(y)\omega_1) - \\ &\quad (\Omega_2^*(y)(\Omega_2^*(x)\omega_2^*)) \otimes \omega_1 + \omega_2^* \otimes (\Omega_1(y)\Omega_1(x)\omega_1) \end{aligned}$$

And the right hand side is $\psi(x) (\psi(y) (\omega_2^* \otimes \omega_1)) - \psi(y) (\psi(x) (\omega_2^* \otimes \omega_1))$

$$\begin{aligned} &= \Omega_2^*(x) (\psi(y) \omega_2^* \otimes \omega_1) + (\psi(y) \omega_2^* \otimes \omega_1) \Omega_1(x) - \Omega_2^*(y) (\psi(x) \omega_2^* \otimes \omega_1) \\ &\quad - (\psi(x) \omega_2^* \otimes \omega_1) \Omega_1(y) \\ &= \Omega_2^*(x) (\Omega_2^*(y) \omega_2^* \otimes \omega_1 + \omega_2^* \otimes \Omega_1(y) \omega_1) \\ &\quad + (\Omega_2^*(y) \omega_2^* \otimes \omega_1 + \omega_2^* \otimes \Omega_1(y) \omega_1) \Omega_1(x) \\ &\quad - \Omega_2^*(y) (\Omega_2^*(x) \omega_2^* \otimes \omega_1 - \omega_2^* \otimes \Omega_1(x) \omega_1) \\ &\quad - (\Omega_2^*(x) \omega_2^* \otimes \omega_1 - \omega_2^* \otimes \Omega_1(x) \omega_1) \Omega_1(y) \\ &= (\Omega_2^*(x) (\Omega_2^*(y) \omega_2^*)) \otimes \omega_1 + \omega_2^* \otimes (\Omega_1(x) (\Omega_1(y) \omega_1)) \\ &\quad - ((\Omega_2^*(y) (\Omega_2^*(x) \omega_2^*)) \otimes \omega_1 + \omega_2^* \otimes (\Omega_1(y) (\Omega_1(x) \omega_1))). \end{aligned}$$

Then the left hand side is equal to the right hand side, this means that $\psi([x, y]) (\omega_2^* \otimes \omega_1)$ a Lie algebra homomorphism and then it is a representation of Lie algebra.

Now if ψ is a matrix representation, then:

$$\psi(X) (\omega_2^* \otimes \omega_1) = (\Omega_2^*(X) \otimes I + I \otimes \Omega_1(X)) (\omega_2^* \otimes \omega_1)$$

$$\psi(X) (\omega_2^* \otimes \omega_1) = \Omega_2^*(X) \omega_2^* \otimes \omega_1 + \omega_2^* \otimes \Omega_1(X) \omega_1$$

$$\begin{aligned} (\psi(X) (\omega_2^* \otimes \omega_1))(v) &= (\Omega_2^*(X) \omega_2^*)(v) \omega_1 + \omega_2^*(v) \Omega_1(X) \omega_1 \\ &= -\omega_2^*(\Omega_2(X)(v)) \omega_1 + \omega_2^*(v) \Omega_1(X) \omega_1 \\ &= (\Omega_2^*(X) \otimes \Omega_1(X)) (\omega_2^* \otimes \omega_1). \end{aligned}$$

Proposition, (2.7): Let Ω_1 and Ω_2 be representations of \hat{g} acting on \mathcal{F} -finite dimensional vector spaces Ω_1 and Ω_2 , respectively. Then the action of lie algebra of \hat{g} on $\text{Hom}_{\mathcal{F}}(N_2, N_1)$ is equivalent to the action of Lie algebra \hat{g} on $(N_2^* \otimes N_1)$.

Proof:

To show that $\Phi : N_2^* \times N_1 \rightarrow \text{Hom}_{\mathcal{F}}(N_2, N_1)$ is a bilinear map.

let Φ defined by:

$$\Phi(\omega_2^*, \omega_1) = \vartheta, \text{ for all } \omega_2^* \in N_2^*, \omega_1 \in \Omega_1,$$

where $\vartheta : N_2 \rightarrow N_1$ is a linear map, defined by:

$$\vartheta(v) = \omega_2^*(v) \omega_1$$

for all $\omega_2^*, \omega_2'^* \in N_2^*, v \in N_2, \alpha, \beta \in \mathcal{F}, \omega_1 \in N_1$

$$\begin{aligned} \Phi(\alpha \omega_2^* + \beta \omega_2'^*, \omega_1) &= (\alpha \omega_2^* + \beta \omega_2'^*)(v) \omega_1 \\ &= \alpha \omega_2^*(v) \omega_1 + \beta \omega_2'^*(v) \omega_1 \\ &= \alpha \Phi(\omega_2^*, \omega_1) + \beta \Phi(\omega_2'^*, \omega_1). \end{aligned}$$

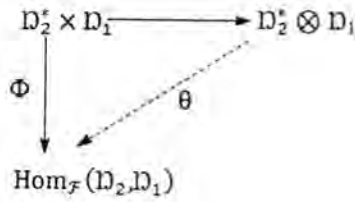
For all $\omega_1, \omega_1' \in N_1, \omega_2^* \in N_2^*$

$$\begin{aligned} \Phi(\omega_2^*, \alpha \omega_1 + \beta \omega_1') &= \omega_2^*(v) (\alpha \omega_1 + \beta \omega_1') \\ &= \omega_2^*(v) (\alpha \omega_1) + \omega_2^*(v) (\beta \omega_1') \\ &= \alpha \omega_2^*(v) \omega_1 + \beta \omega_2^*(v) \omega_1' \\ &= \alpha \Phi(\omega_2^*, \omega_1) + \beta \Phi(\omega_2^*, \omega_1') \end{aligned}$$

So $\Phi : N_2^* \times N_1 \rightarrow \text{Hom}_{\mathcal{F}}(N_2, N_1)$ is a bilinear map.

Thus by using the tensor and the universal property of this tensor product, we get a unique linear map θ , see figure (5).

Such that for all $\omega_2^* \in N_2^*, \omega_1 \in \Omega_1$ we have $(\theta(\omega_2^* \otimes \omega_1))(v) = \omega_2^*(v) \omega_1$

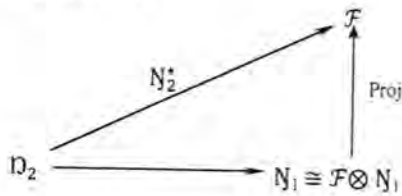

Figure 5

So, by the universal property of tensor product $N_2^* \otimes N_1$, there exists a unique linear map $\theta : N_2^* \otimes N_1 \rightarrow \text{Hom}_{\mathcal{F}}(N_2, N_1)$, this makes the above diagram commutative.

Consider the composition of linear maps, where $\omega_2^*(v)$ is defined as follows:

$$\vartheta(v) = \omega_1, \exists! f \in \mathcal{F} \text{ such that } \omega_1 \rightarrow (f, \omega_1)$$

Since all maps are linear and f is unique, put $\omega_2^*(v) = f$ related to ω_1 , see figure (6).


Figure 6

Define $\mathcal{L} : \text{Hom}_{\mathcal{F}}(N_2, N_1) \rightarrow N_2^* \otimes N_1$ by $\mathcal{L}(\vartheta') = \omega_2^*(v)\omega_1$.

Define $\omega_2^* : N_2 \rightarrow \mathcal{F}$, by $\omega_2^*(v) = f$, where f is given by:

$\mathcal{L}(\vartheta'(v)) = (f, \vartheta'(v))$, we can show that ω_2^* is linear.

Put $\vartheta'(v) = \omega_1$, for all $\omega_2^* \in N_2^*$, $\omega_1 \in D_1$, $\vartheta' \in \text{Hom}_{\mathcal{F}}(N_2, N_1)$ and is related to ω_1

$$\begin{aligned} \vartheta'(\alpha v_1 + \beta v_2) &= \alpha \vartheta'(v_1) + \beta \vartheta'(v_2) \\ &= \alpha f_1 + \beta f_2 \\ &= \alpha \omega_2^*(v_1) + \beta \omega_2^*(v_2), \text{ for all } v_1, v_2 \in D_2 \end{aligned}$$

Where:

$$\omega_2^*(v_1) = f_1 \rightarrow \omega_2^*(\alpha v_1) = \alpha f_1$$

$$\omega_2^*(v_2) = f_2 \rightarrow \omega_2^*(\beta v_2) = \beta f_2$$

$$\omega_2^*(\alpha v_1 + \beta v_2) = \alpha f_1 + \beta f_2$$

Clear ϑ' is a linear and $\mathcal{L}^{-1} = \theta$, thus \mathcal{L} is a linear map.

Now to verify that θ is an intertwining map for the actions of \hat{g} on $N_2^* \otimes N_1$ and on $\text{Hom}_{\mathcal{F}}(N_2, N_1)$.

Let Ω_1 and Ω_2 be two representations of \hat{g} acting on vector spaces N_1 and N_2 , respectively and consider the homomorphism $\Omega_2^* \otimes \Omega_1$ of Lie algebra \hat{g} into the Lie algebra $\text{gl}(N_2^* \otimes N_1)$ defined by:

$$\begin{aligned} ((\Omega_2^* \otimes \Omega_1)(x))(\omega_2^* \otimes \omega_1) &= (\Omega_2^*(x) \otimes I + I \otimes \Omega_1(x))(\omega_2^* \otimes \omega_1) \\ &= \Omega_2^*(x)\omega_2^* \otimes \omega_1 + \omega_2^* \otimes \Omega_1(x)\omega_1 \text{ where } x \in \hat{g}, \omega_2^* \end{aligned}$$

$\in N_2^*, \omega_1 \in N_1$.

And apply the resulting map to the vector $v \in N_2$ we get:

$$(((\Omega_2^* \otimes \Omega_1)(x))(\omega_2^* \otimes \omega_1))(v) = -\omega_2^*(\Omega_2(x)(v))\omega_1 + \omega_2^*(v)\Omega_1(x)\omega_1$$

Now let φ be the homomorphism of \hat{g} into $\text{gl}(\text{Hom}_{\mathcal{F}}(N_2, N_1))$ corresponding to $\Omega_2^* \otimes \Omega_1$ under the isomorphism θ for a map ϑ of the form (1).

$$\begin{aligned} (\varphi(x)\vartheta)(v) &= \varphi(x)\theta(\omega_2^* \otimes \omega_1)(v) \\ &= \theta((\Omega_2^* \otimes \Omega_1)(x)(\omega_2^* \otimes \omega_1))(v) \\ &= \theta(-\Omega_2(x))^t \omega_2^* \otimes \omega_1 + \omega_2^* \otimes \Omega_1(x)\omega_1(v) \\ &= -\omega_2^*(\Omega_2(x)(v))\omega_1 + \omega_2^*(v)\Omega_1(x)\omega_1 \\ &= -\vartheta(\Omega_2(x)(v)) + \Omega_1(x)\vartheta(v). \end{aligned}$$

Thus θ intertwines the actions of \hat{g} on elements of the form $\omega_2^* \otimes \omega_1$.

Since every element of $N_2^* \otimes N_1$ is a linear combination of elements of this form, we conclude that θ is an intertwining map.

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Isolation of Multi Antibiotic Resistance *Serratia marcescens* and the Detection of *AmpC* & *GES* β L Genes by Polymerase Chain Reaction Technique

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ABSTRACT

A total of (420) specimens were collected from Welfar teaching hospital of pediatrics and Al-Kindi hospital, during the period from November, 2007- February, 2008, from patient with ages of (2-120 years and include (300) clinical specimens (which include wound swabs, Sputum, urine and blood specimens), and (120) environmental specimens. Fifty were positive cultures, the identification of microorganism revealed that 21% of the positive cultures were *Serratia marcescens*. The most frequent isolation was from urinary tract infection, followed by wound, respiratory tract infection and blood sepsis. For identification, these isolates cultured on DTC (Deoxyribonucleic acid, Toluidin blue, Cefalotin) agar were used and the typical colonies formed red halo for several millimeters around it. During the identification of *S. marcescens* species *Pseudomonas* spp. were occasionally present and were easily differentiated by weak or negative DNase reaction, positive oxidase test and forming green colonies on the above culture medium. Multiple antibiotic resistances by the strains are an important subject to be considered of high virulence. Accordingly, isolates in this study were multiple resistances to more than one antibiotic and said to be multidrug resistance. 13 isolates were resistant to (11-12) antibiotics while 12 of the isolates were resistant to (8-10) antibiotics. Molecular method was carried out for detection of *AmpC* and *GES* encoded gene, results showed that among (5) isolates carry the *AmpC* gene which is a type of ES β LS that gives resistance to the bacterium whereas no isolate carrying *GES* gene and this genotyping method for detection ensured the phenotyping method used for ESBL detection as in this method, no isolate gave positive result.

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الخلاصة

تم خلال الدراسة جمع (420) عينة، موزعة ما بين (300) عينة سريرية و (120) عينة بيئية من مستشفيات الكندي و مستشفى حماية الأطفال التعليمي (لأطفال تتراوح أعمارهم ما بين 2-12 سنة). تضمنت العينات السريرية مسحات الجروح، الإدرار، عينات الدم والقشع، و تم جمع (120) عينة بيئية لدراسة تلوث بيئة المستشفيات بهذه البكتيريا والتي تم جمعها من مناطق مختلفة. أعطى (50) منها نتيجة موجبه بعد زراعتها على الأوساط الزرعيه، 21% منها كان يعود لجنس *Serratia*. كانت أكثر نسبة عزل لهذه البكتيريا من عينات الإدرار تليها عينات الجروح، القشع والدم. شخّصت العزلات أولاً على وسط DTC بعدها شخّصت المستعمرات المثاليه المتميزه بتكوينها هاله حمراء حولها. رافقت عملية التشخيص وجود بكتريا *Ps.aeruginosa* وكان من السهولة تمييزها لكونها تعطي نتيجة سالبة على وسط DTC وكونه موجب لفحص الاوكسيدز وتعطي مستعمرات خضراء على الوسط السابق. المقاومة المتعددة للمضادات الحيوية من الأمور المهم اخذها بنظر الاعتبار لأنها تعتبر دليل على الضراوة العالية لبكتريا *S.marcescens*. أظهرت الدراسة ان 13 عزلة لبكتريا *S.marcescens* كانت مقاومة ضد (12-11) مضاداً، في حين اظهرت 12 عزلة لبكتريا *S.marcescens* مقاومة ضد (10-8) مضاداً. اعتمدت الطرق الجزيئية لتحديد جينات *AmpC* و *GES* اذ اعتمد فحص PCR والذي كان له مواصفات عاليه من حيث السرعة و الحساسية و الخصوصية العالية. وظهرت النتائج ان من بين جميع العزلات كان هناك فقط 5 تحمل أنزيم *AmpC* ولم تظهر أي من العزلات امتلاكها الجين المشفر لإنتاج *GES* وهذه النتيجة قد توافقت مع نتيجة فحص انتاج ESBL مظهرياً بواسطة طريقة الأقراص المتاخمة.

INTRODUCTION

Serratia marcescens is an aerobic Gram-negative bacillus which can survive well in moist environments (1). *S. marcescens* has been reported to cause variable infections, including respiratory tract, urinary tract, and wound infections and bacteremia (2). *S. marcescens* often develops multidrug resistance and tends to spread rapidly in the nosocomial environment, and has been implicated in outbreaks of nosocomial infection both in neonates and adults. *S. marcescens* is more likely to colonize the respiratory and urinary tracts of hospitalized adults but the gastrointestinal tract in neonates (3).

The high resistance noticed an alternative agents for the prevention and treatment of *S.marcescens* infection is urgently needed (4). *S.marcescens* have been found to be resistant to Gentamicin ,Ofloxacin ,Ampicillin, Chloromphenicol and Amikacin (5), While Chen *et al.* (6) referred that this microorganism shows intrinsic resistance to many antimicrobial agents. *S. marcescens* shows intrinsic resistance to wide variety of antimicrobial agent (multi drug resistance), multi drug efflux pumps are often involved in multi drug resistance in *S. marcescens* (6). Matsuo *et al.* (7) referred that drug efflux pumps is a major cause of multi drug Resistance and has been found to play a major role in intrinsic resistance of *S. marcescens*. Yu *et al.* (8) showed resistance of *S. marcescens* is usually mediated by overproduced *AmpC* cephalosporeinase.

Study of epidemiologic markers is important in an attempt to trace the source of contamination or to prevent patient-to-patient spread (9) . The phenotypic ESBL detection methods described above provide only presumptive identification of an ESBL producer. An alternative approach is to detect the β -lactamase gene. The easiest and most common molecular method used to detect the presence of a β - lactamase is nucleic acid amplification with oligonucleotide primers. PCR with oligonucleotide primers that are specific for a β -lactamase gene is the easiest and most common molecular methods used to detect the prescence of a β -lactamase belonging to a family of enzymes (10).

MATERIAL AND METHOD

Sample collection and isolation of organism:

A collection of 420 samples were divided into: **A:**300 clinical specimens were obtained from patients with different infections (included wound swabs, urine and blood samples) referred to (Welfare teaching hospital of pediatrics and Al-Kindi hospital). Beginning of November,2007 until the end of Fabruary,2008 ,for children with (2-12) years. **B:** 120 swabs from different sites of hospital environments included (Welfare teaching hospital of pediatrics,Al-Kindi hospital).which include (operation room, instruments and furnitures, patient beds, wall and floor of hospitals).

All the specimens were streaked on MacConky agar and incubated aerobically overnight at 37C° to detect *S. marcescens*. Non lactose

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fermenting colonies were picked up with sterile loop and incubated on to DTC :(Deoxyribonucleic acid, Toluidine blue, Cefalotin), and gelatin agar. The colonies of each representative isolates were then characterized using standard bacteriological methods earlier described (11)

Antibiotic susceptibility:

Antibiotic susceptibility test for isolated microorganisms was performed by disc diffusion and broth dilution method.(12) .

β-lactams : detected by two standard method (Iodometric method and Capillary tube method) according to (13).

Disk antagonism test (DAT): The disk antagonism test was used to detect the inducibility of β-lactamase. Disks of inducing agent amoxicillin/clavulanic acid (Am/CA) and cephalosporins (ceftazidime and cefotaxime) were placed on the surface of the test bacterial lawn on MHA plates on a lawn of bacterial culture of the suspected inducible AmpC β-lactams producers separated by 15 mm. The plates were examined after overnight incubation at 37⁰C. If blunting of the cephalosporin disks adjacent to the amoxicillin/clavulanic acid disks occurred, the organisms were considered to produce inducible AmpC β-lactams. (14).

oligonucleotide primers used in PCR. The sequences of the primers used in the PCR are listed in below :

Primer	Sequences	Reference
<i>AmpC</i>	CCTGCAACCTAAGAGCTTCT	15
<i>AmpC</i>	GCGCCTGGATGATGTGGTAA	15
<i>GESIF</i>	AAAGCAGCTCAGATCGGTGT	16
<i>GESIR</i>	TCATGTGTCCCGATGGTAGA	16

PCR procedure. Template DNAs were prepared from each strain as described previously (9). PCR amplification was performed in a 50-ml volume with the TC-5000 PCR system (USA) thermal cycler. Reaction mixtures contained 2μl (each) primer, PCR master mix 25μl , approximately 3 μl of template DNA and completed with 18μl Nuclease Free Water . PCR steps programmed for AmpC & GESβL performed according to Mahlen et al.,2003 and De Vires et al.,2006 respectively. After agarose gel electrophoresis, the ethidium bromide-stained PCR products were visualized under UV light. In the amplification of the intI3 gene, the

annealing step was carried out at 578C. For more rapid and convenient template DNA extraction, the supernatant of a bacterial culture suspension boiled for 10 min was applied as described previously(17)

Results and discussion

A total of (420) specimen was included in this study of these. There were (300) clinical specimens, and (120) environmental specimens. The (300) clinical specimens comprises, wound swabs, urine and blood specimens resulted in (50) positive cultures and the identification of microorganism revealed that 21(%) of the positive culture was *Serratia* spp. (table 1).

Table1: Number and frequency of *Serratia marcescens* isolated from different clinical specimens

Clinical specimens	No. of specimen	No. of isolates	% of isolation from specimen	% of isolation from total isolations
Urinary tract infection	150	12	8	57.14
Wound infection	75	5	6.6	23.8
Respiratory tract infection	40	2	5	9.52
Bacteraemia	35	2	5.7	9.52
Total	300	21		100

S. marcescens isolated from urinary tract infections in frequency of (57.14%) was the most frequent, followed by wounds and respiratory tract infections, blood sepsis (23.8%) respectively. Wound cultures showed mixed infection with *Pseudomonas* spp., while one of the positive blood cultures was *S. liquificans* and has been excluded from this study. Contamination of hospital environment was detected in (120) specimens collected from different sites including walls, floors, and hospital beds (table 2). (18) revealed that *S. marcescens* was rarely isolated from clinical specimens. Study results matched with (19), who could isolate 23 clinical isolates referred to *S. marcescens* from different sites of the body and this

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also matched with (20), who obtained 6 isolates of *S.marscecens* from total number of 32 different Gram negative isolates mostly from urine, pus, throat swabs and blood specimens. The highest frequency of isolation of *S.marscecens* was from UTI (57.14%) from total *S.marscecens* isolates, this result matched with the findings of (21), who stated that *S.marscecens* tend to colonize urinary tract of adults in patients.

Most of the isolates responsible for hospital environment contamination were Gram negative bacilli, the most frequent isolates were *Pseudomonas* spp., Gram positive bacteria were also observed as a source of hospital environment contamination. This result supported by (22) study which showed that the environmental screening yielded 4 strains of *S.marscecens*. That matched with (23), who reported that environmental cultures were positive for *S.marscecens* in 1.4% and confirmed that *S.marscecens* was endemic in neonatal intensive care unit and belonged to one genotype.

Table2: Number and frequency of *Serratia marcescens* isolated from different environmental specimens

Environmental specimens	No. of specimen	No. of isolates	% of isolation from specimen	% of isolation from total isolations
Walls and floors	40	2	5	50
Patient beds	40	1	2.5	25
Hospital equipments	40	1	2.5	25
Total	120			100

Identification

Strains of *S. marscencens* formed typical colonies on DTC agar forming red halo for several millimeters around the colony. Colonies of *Pseudomonas* spp. were occasionally present, but these were easily differentiated because of their weak or negative DNase reaction, positive oxidase test and usually forming green colonies on the above culture medium. After 24 hrs. Of incubation *S. marscencens* colonies appeared as circular, opaque, convex, with 2-15 mm diameter, it's color ranging from dark red to white. The use of MacConky agar supplemented with sorbitol

for primary isolation improved considerably the isolation rate of *S. marscecens* and detection from clinical specimens easier and time and cost efficient. (24) referred that Deoxyribonuclease (DNase) produced by *S. marscecens* is characteristic feature which is useful in distinguishing this organism from closely related members of Enterobacteriaceae.

Antibacterial susceptibility testing:

Revealed that all strains of *S. marscecens* showed 100% sensitivity to 4 antibiotics that were Imipineme, Aztereonam, Meropenem and Ciprofloxacin. On the other hand the *S. marscecens* strains were 100% resistant to 10 antibiotics which were Cephatoxin, Cephradine, Cephtazidime, Cefixime, Cephalothin, Penicilline, and were less resistance to 3 antibiotics that were. Amoxacilline, Erythromycine, Tetracycline 96%, 92%, 68% respectively (fig.1) In addition, *S. marscecens* strains are variably sensitive to Vancomycin, Gentamicin and Amikacine. As shown in (fig.1) the most sensitive isolates were those which isolated from one of the two blood cultures (B24) as it showed sensitivity to (9) different antibiotics followed by wound isolates (W21) UTI isolate (U12) and one environmental isolate (E1) they were sensitive to 8 different antibiotics. The third isolate in sensitivity was environmental isolate (E2) which was susceptible to (7) different antibiotics the next isolate (E3, E4) environmental isolates (U5, U6, U8, U10, U11, U13, U16, U17, U19, U20) are UTI isolates and one blood isolates B25 showed sensitivity to 6 different antibiotics U7 and R23 were sensitive to 5 antibiotics U9 and U14 were sensitive only 4 antibiotics from above results we can notice that the most sensitive isolate was blood culture isolate by being sensitive to 9 antibiotics and the most resistant isolates were urinary tract isolates by being sensitive to only 4 antibiotics and resisting 14 antibiotics. This result was supported by the study of (25), who was indicated that all *S. marscecens* isolates are sensitive to ciprofloxacin, also the result matched with (26) who was noted that *S. marscecens* is resistant to most of the antibiotics except carbapenems. As well as (27) indicated that *S. marscecens* was generally susceptible to imipenem, followed by ciprofloxacin and ofloxacin by Agar diffusion susceptibility testing.

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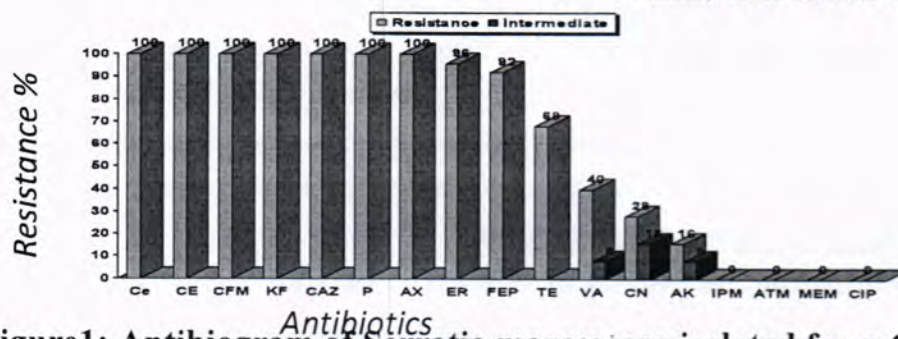


Figure1: Antibiotogram of *Serratia marcescens* isolated from Clinical and environmental specimens

Multiple antibiotic resistances:

Multiple antibiotic resistances are an important subject to be considered, since it has a role in controlling and directing the remedy policy in bacterial infections. Moreover, multiple resistances are a sign of higher virulence. In this study most of the isolates of *S. marcescens* showed multiple resistances to more than one antibiotic table (5).

S. marsceceus isolated from the clinical and environmental sources were divided In to tow groups (A and B) depending on the antibiotics they resist (table 6) Accordingly, the above table shows that group (B) was the dominant group in regard to antibiotic resistance, where 13 (52%) isolates were resistant to (11-12) antibiotics while group (A) 12 of the isolates were resistant to (8-10) antibiotics A collective result obtained out of table (6) indicates that the dominant pattern of resistance among *S. marsceceus* isolates of all groups was the resistance to all 11-12 antibiotics. (28) described an outbreak of multi drug resistant *S. marsceceus* Infection and colonization involving adults admitted to surgical intensive care unit. (6) *S. marsceceus* shows intrinsic resistance to awide variety of antimicrobial agent (multi drug resistance) multi drug efflux pumps are often involved in multi drug resistance in *S. marsceceus*.

Table3: Multi- drug resistance of *Serratia marcescens*

Isolates symbol	No. of isolates	% of isolates	No. of antibiotics resistat by isolates
S ₁	1	4	8
E ₂ /E ₃ /U ₆ /B ₁	4	16	9
E ₁ /E ₄ /W ₂ /U ₅ /U ₇ /U ₈ /U ₉	7	28	10
W ₁ /W ₃ /W ₄ /W ₅ /U ₂ /U ₃ /U ₄ /U ₁₁ /B ₂ /S ₂	10	40	11
U ₁ /U ₁₀ /U ₁₂	3	12	12

Table 4: Classification of *S. marscecens* according to number of antibiotic resistant

Group	No. of antibiotics resistat by isolates	No. of isolates	% of isolates
A	8-10	12	48
B	11-12	13	52

 β -lactamase detection: A-Capillary tube method

To detect the ability of *S. marscecens* isolates to produce β -lactamase enzyme depending on pencilloic acid production as a result of β -lactamase enzyme action. This method is considered one of the rapid in testing the of β -lactamase. Out of (25) isolates 5(20%) were β -lactamase producers, one (4%) isolate gave result after (10) minutes. While 4(16%) isolates gave result after (5) minutes. Whereas 20(80%) isolates were β -lactamase negative (table 7).

Table 5: β -lactamases production by Capillary tube method from *S. marscecens*

Result	No. of isolates	% of isolates
+++	-	-
++	1	4
+	4	16
-	20	80

+++ Through 5-10 min ++ Through 10-15 min + After 15 min - No production

B-Iodometric method:

Iodometric method is important in primary investigation for β -lactamase enzymes production. The method depends on the reaction between Iodine and starch to form blue or dark violet complex, while during β -lactamase enzyme production it will hydrolyse penicilline G and produce inactive penicilloic acid that reduce Iodine to Iodide, the last have no ability to react with starch, so color will be changed to white, (table 8) shows that 6(24%) isolates out of 12 isolates were able to produce β -lactamase enzyme,

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one isolate gave rapid positive result that indicate its ability to produce large amounts of β -lactamase enzyme.

Table 6: β -lactamases production by Iodometric method from *Serratia marcescens*

Result	No. of isolates	% of isolates
Positive	6	24
Negative	19	76

From the above, noticed slightly difference between Iodometric & Capillary tube method. Six isolates of *S.marscegens* produced β -lactamase enzyme by Iodometric method, but only 5 isolates of *S.marscegens* produced β -lactamase enzyme by Capillary tube method. As shown in (figure 2) .

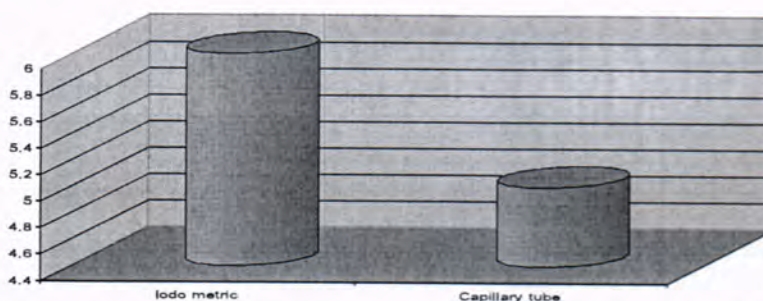


Figure 2: Difference between two methods (Iodometric & Capillary tube) for β -lactamases production

(29) pointed that the production of β -Lactamase enzyme may be insufficient which may be found in the periplasmic space, as the presence of enzyme in this site one of the causes that leads to difficulties in detecting it. Results also showed difference in the time of production the enzyme, and this result is similar to (30) result which showed that the difference in the time of production the enzyme may belong to the difference in the enzyme concentration in periplasmic space , in addition to the presence of stimulatory factors for producing factor which the antibiotic have a role in decreasing or increasing the enzymatic activity.

Extended Spectrum β -Lactamase production:

With the spread of AmpC and ESBLs producing strains all over the world, it is necessary to know the prevalence of these strains in hospitals. Detection of resistant isolates would allow doctors to formulate a policy of empirical therapy in high-risk units where infections due to resistant organisms. The method that used in this study to detect ESBL producing bacteria was the disk approximation test. All the (25) bacterial isolates used in the study have no synergy zone of inhibition between β -lactam antibiotic and Amoxicillin /Clavulanate which mean that they are no ESBL producers. The test done by using different antibiotics which where Augmentin (Clavulanic acid /Amoxicillin), Cefotaxime, Ceftazidime and Aztreonam. The result of this study was in agree with the findings of (31) which showed that from 24 isolates of *S.marscecens* non susceptible to Cefotaxime ,only one ESBLs producer was found by using ESBLs screen test. The result of this study was in agreement with the finding of Cheng *et al.* (2006) finding that showed 5(12%) ESBLs producers were identified out of 123 non repetitive isolates of *S.marcescens* and they recommended that the detection and report of ESBLs production by *S.marcescens* in clinical laboratories must be made mandatory. in the same way (15) showed that *S.marcescens* isolates are AmpC type β -lactamase Producers that indicate by imipinem and cefoxitin .

Polymerase chain reaction:

After all the *S.marcescens* isolates were tested for its ability to produce β -Lactamase enzyme two phenotypic methods (Iodometric and Capillary) were carried out and there were different results of production the enzyme .After that two tests of detection the extended Spectrum β -Lactamase was done by double disks diffusion method. All (25) isolates didn't show any ability to produce the GESBLs, while (5) isolates showed ability to produce Extended Spectrum β -Lactamase type AmpC by PCR as shown in fig4-3. Because all of that genetic method was adapted using specific primers to detect the presence of the genes in the bacteria, (25) isolates were tested and the results showed that there is no presence of GESBL n all of them, while 5 isolates showed the genes encoded for AmpC enzyme and this result agreed with sensitivity test results as they was the most resistant isolates to β -Lactamase enzymes antibiotics (multiple drug resistant).The environmental isolates of *S.marscecens* didn't seem to have

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genes encoded for *GESβL* and *ampC*, whereas among (10) clinical isolate (5) was carrying *ampC* gene and this indicates its pathogenicity as it hold the chromosomal gene that encoding for resisting the antibiotics. The 5 isolates that was holding the *AmpC* gene encoding for β -lactamase enzyme production was those which were collected from urinary tract U5, U9, U14 and U6 and one isolate from respiratory tract R 23. These Five isolates exhibited either resistance or reduced susceptibility to Augmentin, Cefixime and Cefepime with MICs 1024 $\mu\text{g/ml}$ for each of them except U6 which have MIC of 512 $\mu\text{g/ml}$ to Cefixime and U5 which have MIC of (256) $\mu\text{g/ml}$ to Cefepime. On the other hand the isolates were susceptible to Ciprofloxacin and Imipenem with MIC of 4 $\mu\text{g/ml}$ for each one except U6 that exhibited MIC of for Imipenem and MIC of 2 $\mu\text{g/ml}$ to Ciprofloxacin by all (5) isolates. This result agree with (32) found five *S.marcescens* isolated from UTI were positive for chromosomal *AmpC*. And agree with (15) which showed the amplified DNA segment (*AmpC* gene) have molecular weight near to 1100 base pair. While the other (20) *S. marcescens* is a lots were negative for chromosomal *AmpC*, Indication that another mechanism, in addition to the *AmpC* is also involved in the determination of the resistance phenotype of *S. marcescens* strains. (33) referred that *S. marcescens* strains poses different mechanism of resistance to the expanded spectrum Cephalosporin, beside *AmpC* expression, Acquisition of Ambler class A extended spectrum β -lactamase (*ESβLs*) or class B metalo β -lactamase also confers resistance cephalosporin's (34).The different phenotype resistance pattern of *S. marcescens* may be due to, regulation of the *AmpC* expression occurs at multiple levels, which might be involved in the mechanism(s) that determines the differing *AmpC* activity of *S. marcescens* strains (15). The process that results in the emergence of these β -lactamase resistant *S. marcescens* strains in the hospital is unclear, but frequent use of extended spectrum cephalosporin's could result in the emergence of resistance strains producing a chromosomal *AmpC* in fact based on in vitro antibiotic selection experiments, (35) proposal that increased use of extended spectrum cephalosporin's may eventually, leading to the emergence of extended-spectrum cephalosporin's-resistant strains. Our isolates were tested for primary detection of β -lactamase enzymes prescens .Among (25) isolates of *S.marcescens* only 4 gave positive result that shows its ability to produce β -lactamase enzyme. Number of studies pointed that *S. marcescens* have the ability to produce chromosomal β -

lactamase enzymes that stimulated by the antibiotic which have β -lactam ring. (36) found that all *S.marcescens* isolates (77) were AmpC producers that chromosomally encoded. (37) showed of 72 isolates, 16 isolates were de repressed AmpC and 22 isolates produced extended spectrum β -lactamase, the most prevalent ES β Ls were CTX-M enzyme followed by TEM-S2 SHV-12. (2) referred that ES β Ls production occurred in about 19% of *S.marcescens* isolates. Not all ES β L producers universally resistant to any of ESBLs. They vary in their substrates specificity and may not phenotypically express resistance to its own substrate. (38). The coexistence of both ES β Ls and AmpC-type β -lactamase may result in false negative tests. AmpC type β -lactamase resists inhibition by clavulnate and hence obscures the synergistic effect of clavulnate and cephalosporin against ES β Ls (10).

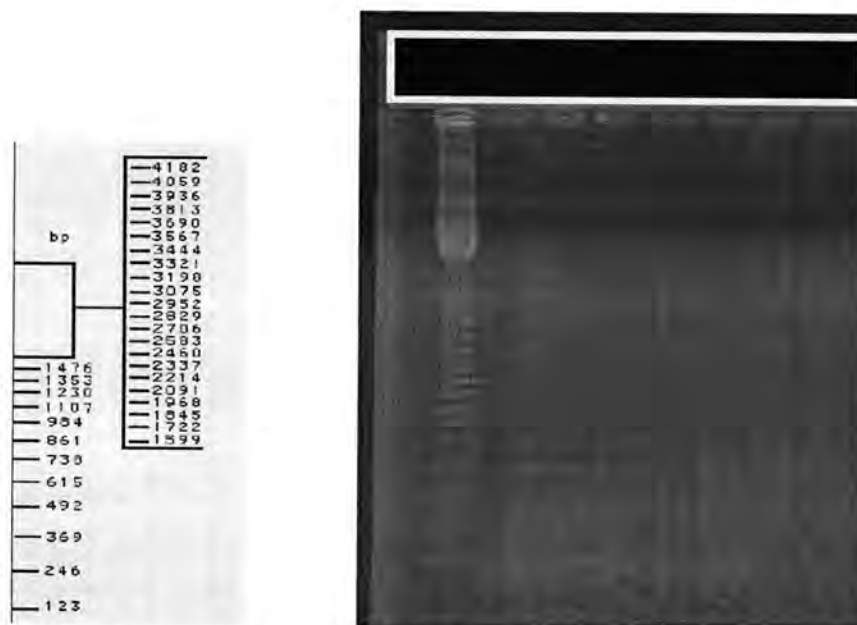


Figure 3: Agarose gel electrophoresis and Ethidium bromide staining. to detect GES β L gene Lane M, molecular size DNA ladder (123 bp DNA Ladder); lanes 1-5, DNAs isolated from *S. marcescens* samples and all of these showed Negative PCR bands; lanes 6-7, negative control; The PCR was carried out in duplicate. The photocomposition of the figure was obtained with Gel documentary Camera.

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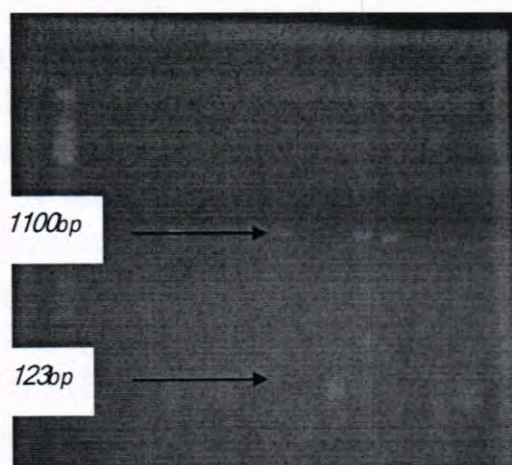


Figure 4: Agarose gel electrophoresis and ethidium bromide staining. To detect AmpC gene, Lane M, molecular size DNA ladder (123 bp DNA Ladder); lanes 1-14, DNAs isolated from *S.marcescens* samples and only lanes 4,7,8,11,12 showed Positive PCR bands; lanes 15, negative control; The PCR was carried out in duplicate. The photocomposition of the figure was obtained with Gel documentary Camera.

This survey showed that PCR is comparable in respect to the discrimination and reproducibility for epidemiological studies of *S. marcescens* strains in nosocomial outbreaks.

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Study of Plasma Malondialdehyde, Albumin and Bilirubin Levels in Asthmatic Patients as Markers of Oxidative Stress

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الخلاصة

الربو هو مرض مزمن يصيب المجاري التنفسية الواقعة تحت تأثير الالتهاب والجهد التأكسدي. مستوى المالونديالدهيد (MDA) - ناتج فوق اكسدة الدهن - يزداد في الأمراض الالتهابية ويستعمل كمؤشر عام للجهد التأكسدي. الألبومين والبروتين هما من مكونات النظام الدفاعي لمنع الأكسدة. إن هدف هذه الدراسة هو تقدير الجهد التأكسدي كمكون في عملية الربو وذلك بقياس MDA (كمؤشر أكسدة)، البروتين والألبومين (كمؤشرات حيوية لنظام دفاع منع الأكسدة) في المرضى المصابين بالربو. الدراسة تضمنت سبعة وثلاثون مريضاً مصاباً بالربو (20 أنثى و 17 ذكر) تم مقارنتهم ب 37 من الأصحاء كمجموعة سيطرة. حلت عينات البلازما لقياس MDA الكلي، وكذلك الألبومين والبروتين. كانت نتائج الدراسة كالتالي: تركيز MDA في البلازما ازداد بشكل ملحوظ ($p < 0.05$) بينما تركيز كل من الألبومين والبروتين في البلازما نقصاً بشكل ملحوظ ($p < 0.05$) في المرضى المصابين بالربو مقارنة بمجموعة السيطرة (الأصحاء). وهو ما يؤدي إلى الاستنتاج بأن المستويات المرتفعة ل MDA في بلازما المرضى المصابون بالربو تشير إلى المستوى العالي للجهد التأكسدي في هؤلاء المرضى. تناقص تركيز كل من الألبومين والبروتين هو بسبب إستهلاكهما مما يشير إلى دورهما كجزئيات مانعة للأكسدة في المرضى المصابين بالربو.

ABSTRACT

Asthma is a chronic disorder of the airways with underlying inflammation and oxidative stress. Malondialdehyde (MDA) - the lipid peroxidation product- level increases in inflammatory diseases and used as a common oxidative stress marker. Albumin and bilirubin are components of antioxidant defense system. The aim of this study are, Evaluating oxidative stress as a component of asthma process by measuring MDA (as an oxidative marker), albumin and bilirubin (as biomarkers of antioxidant defense system) in asthmatic patients. Thirty seven asthmatic patients (20

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females and 17 males) were involved compared with 37 healthy controls. Plasma samples analyzed for total MDA, albumin and bilirubin. The results of underlying study are: plasma MDA was significantly increased ($p < 0.05$) while plasma albumin and bilirubin were significantly decreased ($p < 0.05$) in asthmatic patients compared to control group. Which lead to conclude that elevated levels of MDA in plasma of asthmatic patients indicate high level of oxidative stress in these patients. Decreasing plasma albumin and bilirubin is due to their consumption and indicate their role as antioxidant species in asthmatic patients.

INTRODUCTION

Asthma is a worldwide disease. It is defined as a chronic inflammatory disorder of the airways. The inflammation also causes an associated increase in airway responsiveness to a variety of stimuli (1).

Lungs are organs with large epithelial surface area that is at risk for oxidant-mediated attack. The tracheobronchial tree and the alveolar spaces are exposed to reactive oxidizing species in the form of inhaled airborne pollutants, tobacco smoke and product of inflammation. Disequilibrium, either through increased oxidant stress or decrease antioxidant resources, can result in a series of pathophysiological events in the lungs that culminate in cellular death and pulmonary dysfunction(2). It has been shown that inflammation driven by increased oxidative stress (defined as imbalance between the production of reactive oxygen species (ROS) and a biological system's ability to readily detoxify the reactive intermediates) occurs in the airways of patients with asthma (3,30).

Malondialdehyde (MDA) is produced as a by-product of polyunsaturated fatty acid peroxidation and is the principal and most studied product of polyunsaturated fatty acid peroxidation (4). MDA is one of the most frequently used indicators of lipid peroxidation(5).

Human serum albumin (HSA) is an abundant multi functional non-glycosylated, negatively charged plasma protein, with ascribed ligand-binding, transport properties and antioxidant functions (6). Many antioxidant activities of albumin result from its ligand-binding capacities. Hydroxyl radicals released from Fenton reaction are mostly directed to the protein, sparing more important targets (7). Another indirect antioxidant activity of albumin comes from its ability to transport bilirubin. Such albumin-bound bilirubin was shown to act as an inhibitor of lipid

peroxidation its as well as protection of alpha-tocopherol from damage by peroxy radicals (8). Human serum albumin (HSA) contains one reduced cysteine residue (Cys34) which, due to the large amount of albumin in plasma, constitutes the largest pool of thiols in the circulation. Through the reduced Cys34, albumin is able to scavenge hydroxyl radicals (7).

Bilirubin (BR) is the yellow breakdown product of normal heme catabolism (9). Bilirubin contains an extended system of conjugated double bonds and a reactive hydrogen atom and thus could possess antioxidant properties. Depending on these ideas Stocker et al indicate that bilirubin at micromolar concentrations can scavenge the chain-carrying peroxy radical

$$LOO\cdot + BR \rightarrow LOOH + BR\cdot$$

BR· may then react with either another peroxy radical to give rise to a nonradical product, or oxygen as below (10,29):



In serum J. Neuzil & R. Stocker demonstrate that lipoprotein-associated and albumin-bound BR can efficiently protect lipid from such peroxidation (8).

Aim of the study

Study the behavior of some oxidative stress markers in asthmatic patients and compare them with healthy control group.

MATERIALS AND METHODS

Thirty seven asthmatic patients (20 females and 17 males) were evaluated in this study. Diagnosis of asthma was made by a respiratory physician. The study was carried out in Baghdad Teaching Hospital.

The exclusion criteria were (i) age less than 15y (ii) vitamin supplements taken in the last 4 weeks, (iii) presence of other diseases known to be associated with elevated oxidative stress (cancer, diabetes, arthritis, etc.). A matching group of 37 healthy volunteer subjects (21 male and 16 female) were considered as a control group.

Each plasma sample was analyzed for total malondialdehyde (MDA), albumin and bilirubin. Plasma albumin and bilirubin were measured by colorimetric method using kits supplied by bioMaghrab Company. MDA lipid peroxidation end product measured spectrophotometrically after adding thiobarbituric acid under acidic conditions (28).

RESULTS AND DISCUSSION

Number and percentage (according to gender) of subjects who's involved in this study are given in Table 1.

Table 1: distribution of study participants according to their health status and gender

Gender	Study Group					
	Asthmatic		Control		Total	
	N	%	N	%	N	%
Male	17	45.9%	21	56.0%	38	51.3%
Female	20	54.1%	16	44.0%	36	48.7%
Total	37	100.0%	37	100.0%	74	100.0%

MDA concentration in the plasma of asthmatic group was significantly higher than the control group ($12.6 \pm 0.82 \mu\text{mol/l}$ and $4.50 \pm 0.33 \mu\text{mol/l}$ respectively), $p < 0.01$ as shown in table -2.

Table 2: plasma malnodialdehyde concentration ($\mu\text{mol/l}$) in asthmatic patients compared to control subjects

Groups	N	MDA* $\mu\text{mol/l}$ Mean \pm SEM	P
Control	37	4.50 ± 0.33	---
Asthmatics	37	12.6 ± 0.82	<0.01

*MDA= Malnodialdehyde

The mean (\pm SEM) values of plasma albumin levels in 37 healthy controls and 33 asthmatics one are listed in table-3. Data in this table showed that albumin concentration in the plasma of asthmatic group was significantly lower compared with control group ($40.29 \pm 1.24 \text{ g/l}$ and $45.17 \pm 1.54 \text{ g/l}$ respectively), $p < 0.05$.

Table 3: plasma Albumin (g/l) In asthmatic patients compared to control subjects

Groups	N	Albumin g/l Mean \pm SEM	P
Control	37	45.17 \pm 1.54	---
ashmatics	33	40.29 \pm 1.24	<0.05

The mean (\pm SEM) values of plasma bilirubin levels in 37 healthy controls and 31 asthmatics one are listed in table-4. Data in this table showed that bilirubin concentration in the plasma of asthmatic group was significantly lower ($p < 0.05$) compared with that of the control group (0.58 ± 0.04 mg/dl).

Table 4: plasma bilirubin concentration (mg/dl) in asthmatic patients compared to control subjects

Groups	N	Bilirubin mg/dl Mean \pm SEM	P
Control	37	0.58 \pm 0.04	---
ashmatics	31	0.41 \pm 0.05	<0.05

Asthma is an inflammatory disease with hyperresponsivness. Both of these characteristics produce an oxidative stress situation which is believed to contribute to pathophysiology of asthma. Reactive molecules (particularly free radicals) produced from oxidative stress. These reactive molecules in addition to causing tissue damage by oxidation of biomolecules like DNA, lipids, proteins and sugars (11,12). Malondialdehyde, MDA, is a highly reactive three carbon dialdehyde produced as a byproduct of polyunsaturated fatty acid peroxidation (a process of fatty acids oxidation in cell membrane lipids, termed as lipid peroxidation) (13). MDA one of the most frequently used indicators of lipid peroxidation(14).

Table 2 illustrates significant increase in the plasma MDA levels of asthmatic patients compared to control. Similar findings were reported by Ozaras et al, Jacobson et al. and sharma A. et al. ,all of them, found that MDA was higher in plasma of asthmatic patients compared to controls(15-17).

The increase in the MDA concentration indicates the increased peroxidation of lipids (i.e. oxidative stress) in the asthma disease, where the oxidative stress is involved in asthma pathogenesis and symptoms (18).

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High levels of MDA itself is involved in many harmful effects of inflammation (13, 19).

Reactive oxygen species (ROS) production (which cause oxidative stress situation when increased) is strictly regulated by antioxidant defense that protect organism against the potentially destructive effects of ROS. Albumin and bilirubin are members of body defense systems(20).

Table-3- illustrates significant decreasing in the plasma albumin levels of asthmatic patients compared to control. Albumin is found to have an antioxidant properties (7,8). So the decrease in plasma albumin level obtained in the present study could be explained by that albumin antioxidant activity. The results obtained in the present study agree with Vural, et al and Picado, et al , both of them reported a decrease serum albumin level in asthmatic patients (21,22).

Table-4- illustrates significant decrease in the plasma bilirubin levels of asthmatic patients compared to control. Bilirubin is a molecule with effective antioxidant properties due to its structure (10); therefore it is not strangely to exhibit its antioxidative properties that leads to the consumption of this molecules and hence, the low plasma levels.

The result of bilirubin levels in the present study is agree with results obtained by Misso, et al who found a low plasma bilirubin concentration in severe asthma(23) and also with Ohru T. *et al* who found remission of asthmatic patients who develop jaundice (24). Neuzil & Stocker demonstrate that lipoprotein-associated and albumin-bound bilirubin can efficiently protect lipid from peroxidation (8).

Many studies stated low bilirubin levels as biomarker of many diseases' pathology. In peripheral vascular disease, bilirubin levels are lower than in the normal population (24). Hopkins et al compared familial coronary artery disease patients with control subjects. The diseased individuals displayed substantial lower serum bilirubin levels than the control subjects (25). Levinson S. also observed an inverse relationship between bilirubin levels and severity of ischemic heart disease⁽²⁶⁾. In meta-analysis of 11 studies, Novotny & Vitek found elevated bilirubin levels associated with diminished risk of atherosclerosis (27).

In conclusion, according to this study it is obvious that oxidative stress is an important feature of asthma pathphysiology because of significant elevation of MDA, which is a well-known oxidative stress marker. Also the decreased

plasma albumin and bilirubin levels clearly indicate the antioxidant activities for these molecules.

So we recommend use of MDA, albumin and bilirubin measurements as an aid for asthma severity.

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الخلاصة

التحليل الكيماوي أجريت لتقييم التوليد الهيدروكربوني لنماذج صخور لها هذه الخصائص وشخصت بالطريقة الكيماوية كونها إحدى الوسائل المؤدية إلى تقييم الصخور المصدرية والمأخوذة من التكوينات الجيولوجية (سيكانيان، ساركلو، ناوكليكان، سارمورد) (جيا كارة) (الجوراسي المتوسط إلى الأعلى - الطباشيري الأعلى). ويمثل طباقه العراق وهي الصخور المصدرية المأخوذة من الآبار الاستكشافية (بطمه 15) (عجيل 8) (محول 2) (قرة جوق 1) (قرة جوق 2) و(طق طق 1) والتي يقع معظمها في الجزء الشمالي من العراق، ومقارنتها مع النماذج المأخوذة من المكاشف وبالتحديد الموقع المثالي لقبة سورداش وأيضا في مكاشف أخرى التي توضح مقاطع من صخور الجوراسي في قريه بانك شمال زاخو. أن معظم التحاليل الكيماوية تستنتج التطور الحاصل حاليا والذي له قوة لاثبات التوليد لهذه الصخور المصدرية ويعطي لنا أيضا الكميات الهائلة للنفوط والغازات المصاحبة الواعدة أكثر من التوقعات السابقة لتكوين حقول نفطية عملاقة وحقول غاز حرارية. أن قيمة دلائل الانتاج تحدد بأن نظام النفط بالعراق الذي لا يختلف كثيرا عن الأحواض بالدول المجاورة للعراق. وعلى هذا الأساس يعتبر العراق كحوض ينفرد بخصوصيته في جميع الأحواض النموذجية من ناحية إجمالي النفط الكلي الذي يبين نموذجية الصخور المصدرية التي تم تحديدها ضمن قياسات إجمالي الكربون العضوي والنضج الحراري كدلائل مصاحبة مع درجة الحرارة القصوى والتي تشير بوضوح إلى دليل الهيدروجين والأكسجين والذي يقودنا لتحديد مولدات النفط والغاز والذي يفتح لنا أفقا للتطبيقات الحالية ورؤية جديدة يمكن الاعتماد عليها.

ABSTRACT

Chemical analysis were carried out to evaluate the potentiality of rock samples having hydrocarbon characteristics, identified by chemical method as one of the approaches to evaluate the source rocks encountered from ,Sehkanian, Sargelu, Naokelekan, Sarmord, Ghia Kara of (Middle to

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Upper Jurassic-Lower cretaceous) stratigraphic sequence of Iraq, representing source rocks, which are recovered from exploratory wells (Bm-15, Aj-8, Mk-2, Qc-1, Qc-2 and Taq-1), located almost all at the northern part of Iraq, and as comparable with the outcropped samples defiantly at the type locality in Surdash Anticline and also in other exposed and clear section of the Jurassic rocks is Banik village. The bulk of chemical analysis includes the development which is currently have its own strength to approve the potentiality of the source rocks, giving rise to generating enormous amounts of oil and subordinate gas promising more than ever before predictions to form super giant oil and thermogenic gas fields. The value of the production indices determine that the system of the oil in Iraq which is not widely differ from the depocenters of the surrounding countries. Accordingly, Iraq is considered as a unique and specified basin that have the systematic events through the total petroleum system, that shows typical source rocks determined by the remarkable total organic carbon, and maturation evidences accompanied with maximum temperature, indicating obviously the Hydrogen and Oxygen Index, that lead to determine the oil and gas prone opening horizons for more current applications and dependable version.

INTRODUCTION

The sequence of the studied formations, represents the ideality, and formative rock packages, characterizing the whole scope of the source rocks, extended through wide spread areas of Iraqi outcrops and oil exploratory wells (figure -1). The stratigraphic sequences (figure-2), expresses the promising areas for generating oil and gas, and giving rise to more explanations to the most productive basins, by means of rate of sedimentation of the material covering the burial particulates causing increasing in thermal history of each basin, and causes typical oil and gas prone by the thermal maturation. Expresses the promising areas for generating oil and gas, and giving rise to more explanations to the most productive basins, by means of rate of sedimentation covering the burial particulates causing increasing in thermal history of each basin, and causes typical oil and gas prone by the thermal maturation. The hydrocarbon potential sourced rock packages evaluated by chemical analytical data reflect the whole scope of the prolific well sites extended through Iraqi

Mesopotamian basin lead to the expectations for generating oil and/or gas, thus giving rise to extensive explanations for the most productive, generative and remarkable basins as well. The rate of sedimentation process to burry that particulates (living bio organisms) writing a historical record for each basin shown by the specified palynomorphs, that subjected to thermal maturation processes, throughout geologic past Eras, to release biomarkers detected by chemical analysis using modern specific methods, and techniques to prove the type of hydrocarbon prolific well sites as well as the conditions, and state of the environmental deposition media. This research is mainly enhance the role of chemical analysis among other approaches [1], palynological analysis, visual (optical), biomarker parameters and how to set up models of various dimensions making use of the input data that can serve the complementary fashion that enable to perform the upstream sector [2]. Chemical analysis certainly acts as the aid to resolve so many problems and reduces certainly the risk assessments for the most expensive well drilling sites.

Screening for core and cutting samples should be followed in any successful exploring programs to cancel less than 0.5 % TOC samples.

Total Petroleum System of Jurassic –Cretaceous Period:

Passive margin conditions along the Arabian plate during the Jurassic through late Cretaceous periods produced abroad stable shelf environment. Flooding of this warm plate form in warm equatorial latitudes allowed for continued deposition of shallow marine carbonates over the Greater Arabian Basin (Murriss-1980, Al-Husseini-1997). In particular Jurassic geologic conditions of the Arabian subcontinent resulted in deposition of the following ideal sequence of Primary Petroleum System elements: thick oil prone source rocks, extensive reservoir facies, and excellent seals. Wide spread, early and middle Jurassic marine transgression deposited a thick sequence of shallow – marine shelf carbonates and plate form evaporates. Late Jurassic (Oxfordian and early Kimmeridgian) differential subsidence and sea level rise resulted in the formation of broad, intra- shelf sub-basins. These were the depocenters for the main Jurassic source rocks Late Jurassic (Tithonian) eustatic variations of the Arabian plate form resulted in dominant reservoirs and cap-rocks(Arab Formation carbonates and Arab Formation and Hith Formation evaporate seal rocks) . In the north most Arabian Gulf and sourced within the Jurassic Gotina sub-basin , oil and gas

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accumulated in the Middle to Upper Jurassic, high energy calcarenites and oolites of bar or shelf-margin origin. These reservoirs are cyclic and interbedded with organic rich (2-5 TOC %), muddy lime rock source that were deposited under anoxic and dysoxic condition sign the restricted, intra-shelf Gotina sub-basin/Barsarin/Sargelu/Najmah TPS, is identified in the northern area and consists of the following two assessment units:

- 1- The proven platform Horst/Graben- Related oil assessment unit.
- 2- The hypothetical basinal oil and gas assessment.



Figure 1: The map of the exploration fields, extends northern part of Iraq (Lexique) [8].

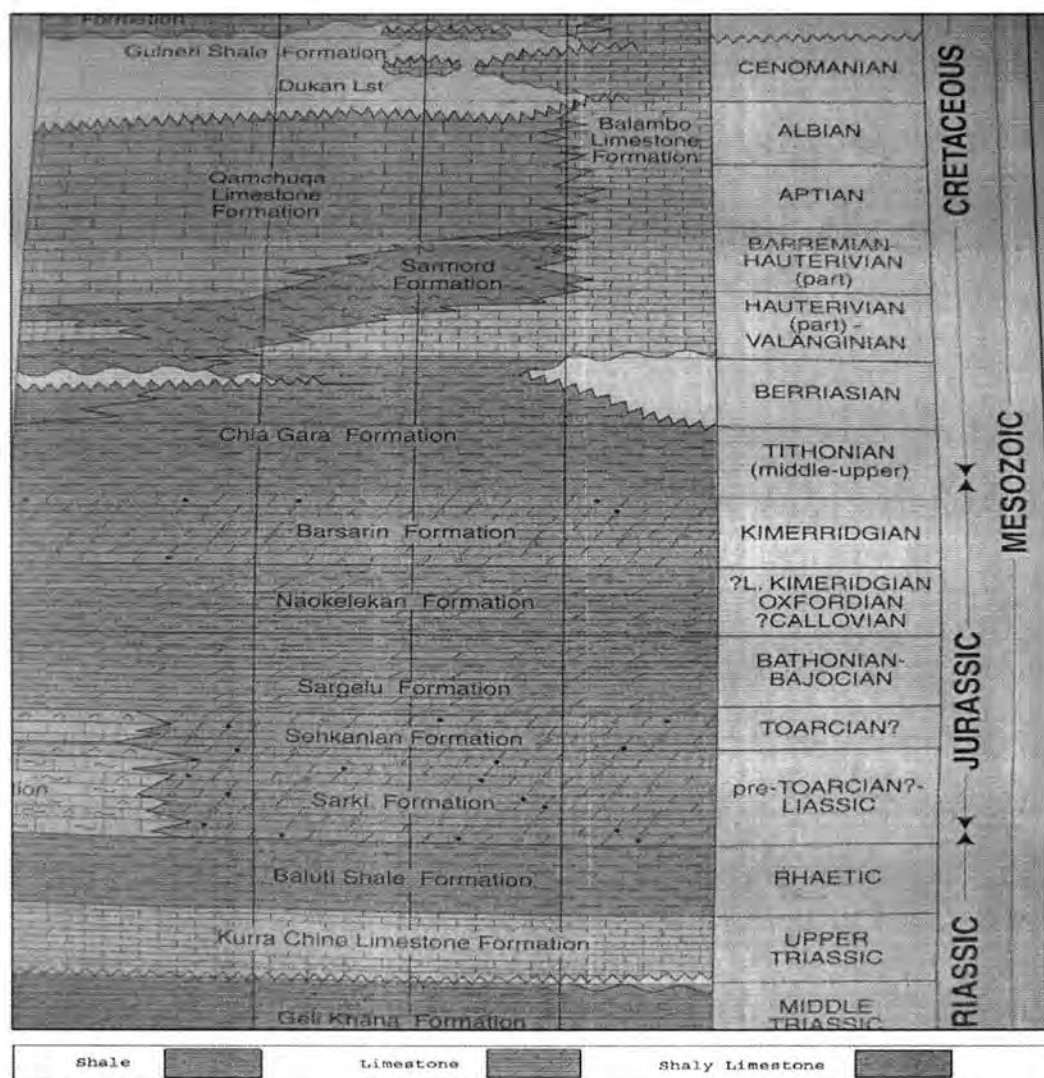


Figure 2: The stratigraphic section (Lexique)

MATERIALS AND ANALYTICAL SCHEMES

Source rocks and cuttings was conducted on forty samples, chemical technique employed in the undertaken study include Rock Eval Pyrolysis to determine S_1 , S_2 and S_3 peaks and maximum temperature alteration (T_{max}) Hydrogen index (HI), Oxygen index (OI), production index as well as total organic carbon percent (TOC) by Leco and Rock - Eval pyrolyser table 1 (a & b) determine the chemical analysis

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Table 1: a- Rock Eval Pyrolysis

	Well Name	Formation	Depth (m)	TOC	S1	S2	S3	Tmax °C	Cal. %Ro	HI	OI	PI
1	Aj-8	Sargelu & Naokelekan	3242	11.81	5.57	45.53	0.95	449	0.92	386	8	0.11
2	Aj-8		3253	3.00	1.85	6.33	0.49	439	0.74	211	16	0.23
3	Aj-8		3268	1.05	0.47	1.87	1.16	446	0.87	178	110	0.20
4	Aj-8		3273	1.03	1.50	2.82	0.44	437	0.71	274	43	0.35
5	Aj-8		3283	0.83	0.60	1.75	0.44	444	0.83	211	53	0.26
6	Aj-8		3299	1.42	1.19	2.33	1.09	439	0.74	164	77	0.34
7	Aj-8		3301	1.26	1.02	1.79	0.62	447	0.89	142	49	0.36
8	Aj-8		3312	0.66	0.57	1.32	0.49	441	0.78	200	74	0.30
9	Bm-15	Sargelu & Sarmord	2030	0.34	0.20	1.00	0.10	443	0.81	294	29	0.17
10	Bm-15		2031	0.35	0.26	0.89	0.16	444	0.83	254	46	0.23
11	Bm-15		2232	1.91	0.53	5.44	0.17	443	0.81	285	9	0.09
12	Bm-15		2233	0.22	0.35	0.70	0.10	439	0.74	318	45	0.33
13	Bm-15		2234	0.10	0.18	0.30	0.04	439 *	0.74	300	40	0.38
14	Bm-15		2235	0.24	0.20	0.59	0.07	439	0.74	246	29	0.25
15	Bm-15		2236	0.45	0.24	1.69	0.13	442	0.80	376	29	0.12
16	Mk-2	Sargelu & Naokelekan	2260	20.69	2.53	80.51	0.76	440	0.76	389	4	0.03
17	Mk-2		2263	16.09	2.48	66.95	1.39	439	0.74	416	9	0.04
18	Mk-2		2264	13.68	2.02	78.77	0.80	440	0.76	576	6	0.03
19	Mk-2		2267	13.04	0.99	50.81	0.86	439	0.74	390	7	0.02
20	Mk-2		2454	4.04	1.41	35.50	0.60	442	0.80	879	15	0.04

Table 1: b

	Well Name	Formation	Depth (m)	TOC	S1	S2	S3	Tmax °C	Cal. %Ro	HI	OI	PI
21	Surdash 1 [#]	Sargelu & Naokelekan & Chia Gara	0	0.57	0.01	0.17	0.47	502 *	1.88	30	82	0.06
22	Surdash 2 [#]		0	0.32	0.05	0.21	0.14	504 *	1.91	66	44	0.19
23	Surdash 3 [#]		0	0.30	0.10	0.23	0.04	458 *	1.08	77	13	0.30
24	Surdash 4 [#]		0	0.90	0.10	0.27	0.57	512 *	2.06	30	63	0.27
25	Qc-1	Naokelekan	2667	2.47	0.94	2.82	0.20	445	0.85	114	8	0.25
26	Qc-1		2671	6.97	2.78	11.58	0.49	448	0.90	166	7	0.19
27	Tq-1	Sargelu & Sehkian & Chia Gara	3309	1.73	0.11	0.01	0.26	472 *	1.34	1	15	0.92
28	Tq-1		3309	0.88	0.02	0.02	0.22	473 *	1.35	2	25	0.50
29	Tq-1		3307	0.16	0.00	0.02	0.03	479 *	1.46	13	19	0.00
30	Tq-1		3306	0.00	0.00	0.01	0.11	396 *	-1.00	-1	-1	0.00
31	Tq-1		3306	2.18	0.10	0.03	0.04	472 *	1.34	1	2	0.77
32	Tq-1		3307	0.78	0.01	0.01	0.13	438 *	0.72	1	17	0.50
33	Tq-1		3306	2.02	0.10	0.03	0.29	486 *	1.59	1	14	0.77

34	Qc-2	Sargelu & Sehkanian & Naokelkan	1562	0.85	0.35	5.77	0.11	438	0.72	679	13	0.06
35	Qc-2		1567	0.69	0.24	4.82	0.27	435	0.67	699	39	0.05
36	Qc-2		1589	0.42	0.32	4.53	0.23	435	0.67	1079	55	0.07
37	Qc-2		1601	0.88	0.27	4.96	0.22	440	0.76	564	25	0.05
38	Qc-2		1622	0.39	0.18	2.14	0.03	437	0.71	549	8	0.08
39	Qc-2		1637	0.77	0.22	4.78	0.04	438	0.72	621	5	0.04
40	Qc-2		1651	0.50	0.20	2.86	0.09	436	0.69	572	18	0.07

Notes:

* Tmax data not reliable due to poor S2 peak

TOC = weight percent organic carbon in rock

S1, S2 = mg hydrocarbons per gram of rock

S3 = mg carbon dioxide per gram of rock

Tmax = °C

HI = hydrogen index = $S2 \times 100 / TOC$

OI = oxygen index = $S3 \times 100 / TOC$

S1/TOC = normalized oil content = $S1 \times 100 / TOC$

PI = production index = $S1 / (S1+S2)$

Cal. %Ro = calculated vitrinite reflectance based on Tmax

Measured %Ro = measured vitrinite reflectance

Outcrop samples

Chemical Analysis:**The Technique of Rock –Eval Pyrolysis**

Determination of the elemental composition of kerogen is a relatively time-consuming process. Development of the rock Eval technique for alternative method for determination of two indices that could be used to replace the H/C against O/C parameters. This technique is a pyrolysis method where by a sample is exposed to a temperature programmed pyrolysis from ambient to 600°C and the pyrolysis products detected immediately and without any chromatographic separation [3] the result is basically three peaks:

S1, S2 and S3 (modern versions of the rock Eval technique produce some additional peaks but, for the purpose of this discussion, the presence of the three mentioned peaks is sufficient).

S1 corresponds to the material, which is normally solvent extracted from a source rock.

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S2 corresponds to the products formed from the thermal break down of the kerogen.

S3 is derived from oxygen-containing parts within the kerogen. From these three parameters, plus the total organic carbon content of the sample, two important parameters are developed, namely, the so-called HI, which is the S2 peak normalized to the TOC and the oxygen index (OI), which is the S3 peak normalized to the TOC, it has been shown that HI and OI are directly proportional to the H/C and O/C ratios and, therefore, a plot of HI to OI can be used to replace the H/C against O/C values (figure -3) on the Tissot-Welte diagram as it was performed in both (Oklahoma University and Geomark Research, Inc. Houston, Texas) for our current study and it was obviously declared in figures attached the analyses.

There are several indicators available that can be used to estimate the relative maturity of a source rock. The traditional method is measuring the maturity of vitrinite. The chemical composition of the maceral vitrinite, derived from higher plant debris. Changes as the level of maturity increases. With increasing maturity the ability of vitrinite to reflect light increases and hence a vitrinite reflectance scale has been developed which correlates the degree of reflectance with maturity. Maturity changes of vitrinite have been studied by coal chemists for long period of time [4]. A similar approach was adopted by the petroleum geochemists [5].

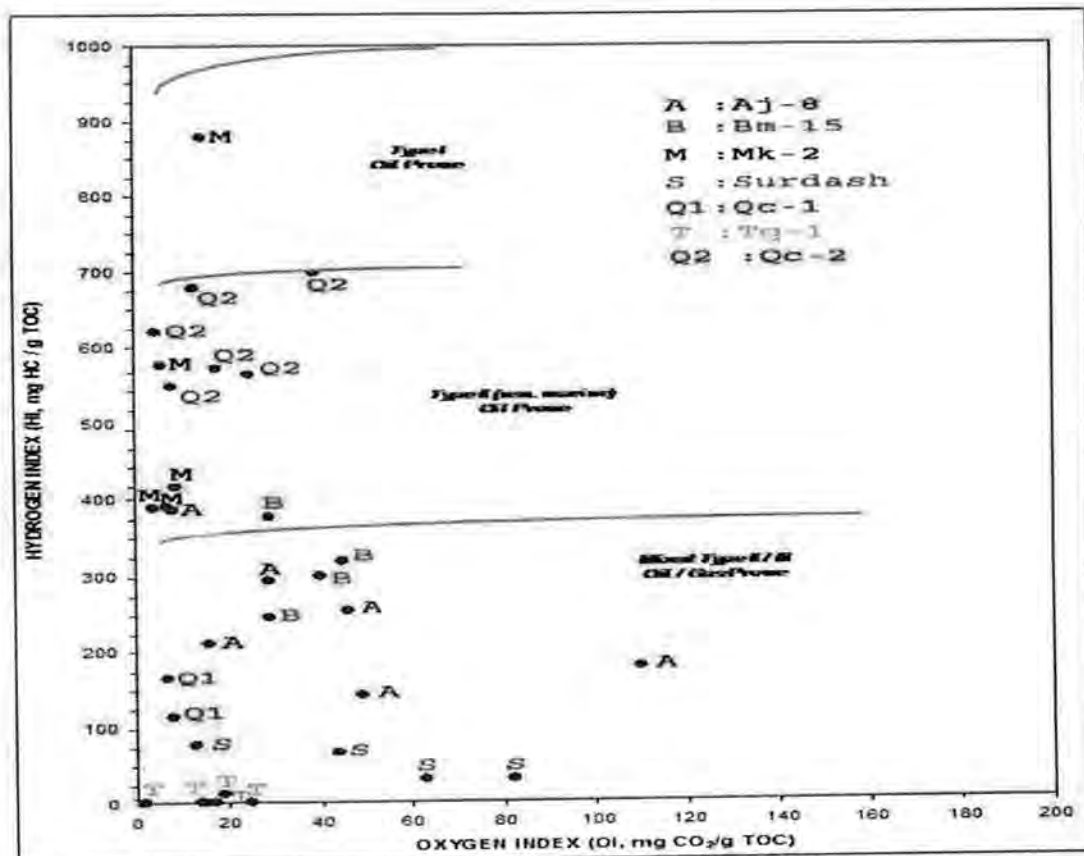


Figure 3: Determination of Kerogen type and potentiality by (HI versus OI)

Another extremely important feature related to the generation of oil or gas is the maturity level of the source rock. Organic matter has to reach a certain level of maturity before it starts too thermally and is converted into liquid or gaseous hydrocarbons. The threshold level for oil generation varies depending upon kerogen type. For example the type IIs kerogen enriched in sulfur generates oil at lower temperature than type II kerogen that is not enriched in sulfur. Information such as this critical in any exploration study and for modeling basin [6]. Determination of maturity levels is critical to the success of any exploration program. Recovery of immature, but organic-rich, source rocks would indicate good source potential for such rocks if buried more deeply in other parts of the basin. At the other extreme, an over mature source rock would indicate a mature part of the basin not capable of generating additional liquid hydrocarbons, but possibly gas.

Kerogen Type and Maturity

Based on T_{max} indicates that almost all samples is located within oil window of kerogen type I, II, III at temperature around 430-460°C, above 460°C only two samples located within condensate-wet gas window, and four sample located within dry gas window at temperature exceeds 585°C with very low HI figure(4) , and about T_{max} (cal.vitrinite reflectance %) so the calculated vitrinite reflectance equivalent (cal.v ref) around (0.60-1.00)that almost all types of kerogen relatively varied in HI is located within oil window approximately six samples located within condensate gas window, meantime increasing in (cal.veq), only three samples located within dry gas window Fig (5). So this distribution of maturation zone could be illustrated as contour lines indicated the increasing of maturation east world, and separates immature zone than the mature zone.

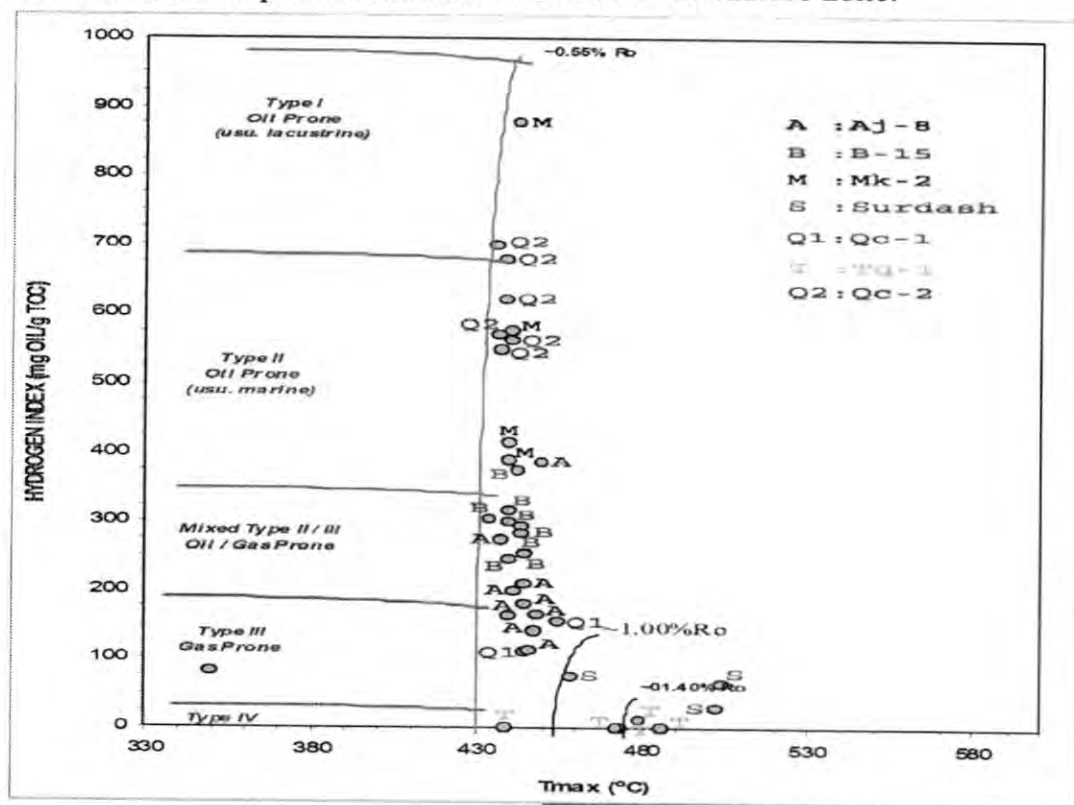


Figure 4: Kerogen type and maturation

Oil window shows concentration of almost all samples within the range of PI (0.08-0.4), higher values are often due to migrating hydrocarbons or contaminate , whereas maturity (calculated vitrinite reflectance) from T_{max} illustrated that the whole samples located within oil zone fig (6) calculated

%Ro indicate maturity shows that within depth (500m) the majority of the samples located within oil zone, and from the depth of (620-700)m still within oil zone while the increasing in depth up to (1km) conversion toward condensate zone and thermal maturity increased with depth according. The depth bounded between (3317-3340) m in Taqtaq-1 oil well indicates the migrated oil that the PI is equal to 1 mgHc/g TOC, Tmax decreases to (-1C°) and TOC increases to more than 1.5.

Kerogen Conversion and Maturity

Based on Tmax versus production index (PI),

(figure-6) or transformation ratio (TR) which is typically climbs from 0.1-0.4, from the beginning to the end of the oil-generation window, but many PI versus-depth plots show considerable variation owing to different kerogen types, migrated oil effects, and anomalously high number when S2 is too low. Because of measurement errors, the PI is meaningless if the S2 is below 0.2 many high PI values above 1 mgHc/gTOC indicate migrated oil, especially if the Tmax decreases and TOC increases at the same time (figure -7) [7].

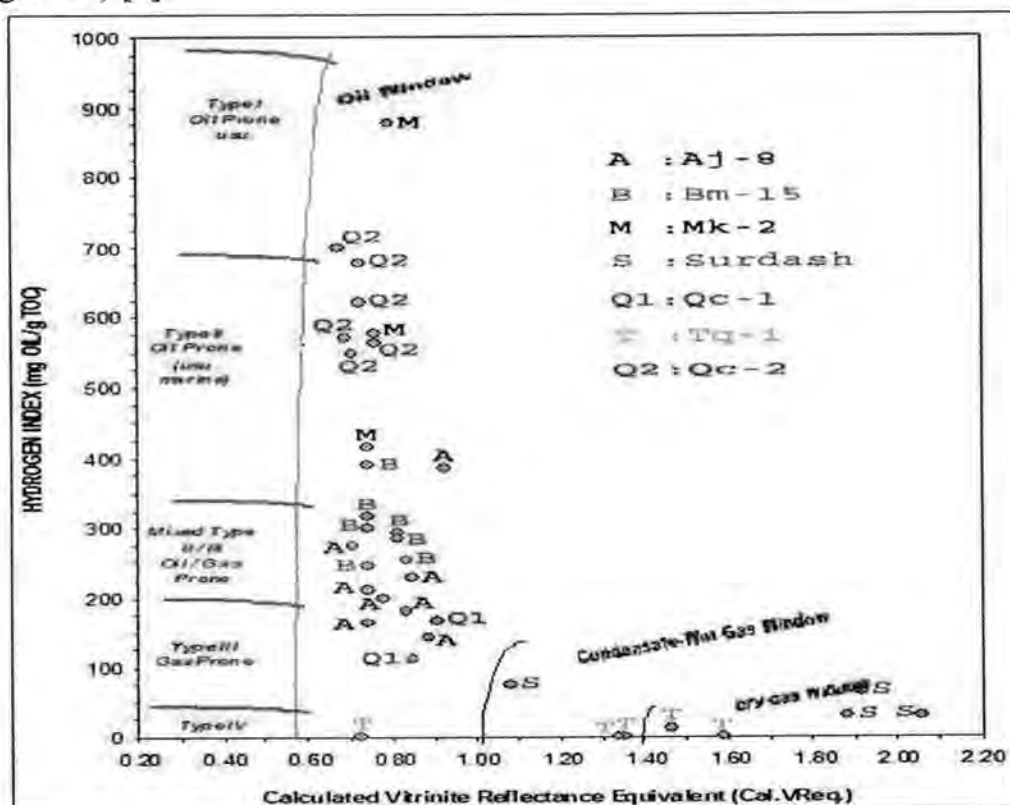


Figure 5: Kerogen type determined by cal.vit. Reflectance

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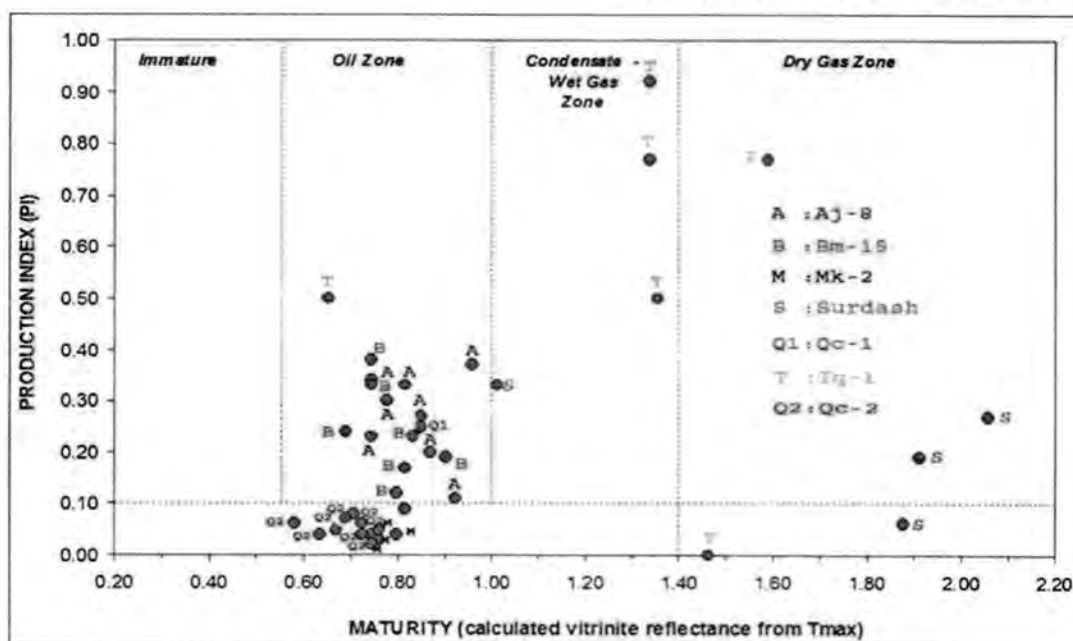


Figure 6: Production index referring to ideal zone according to maturity (based on Tmax)

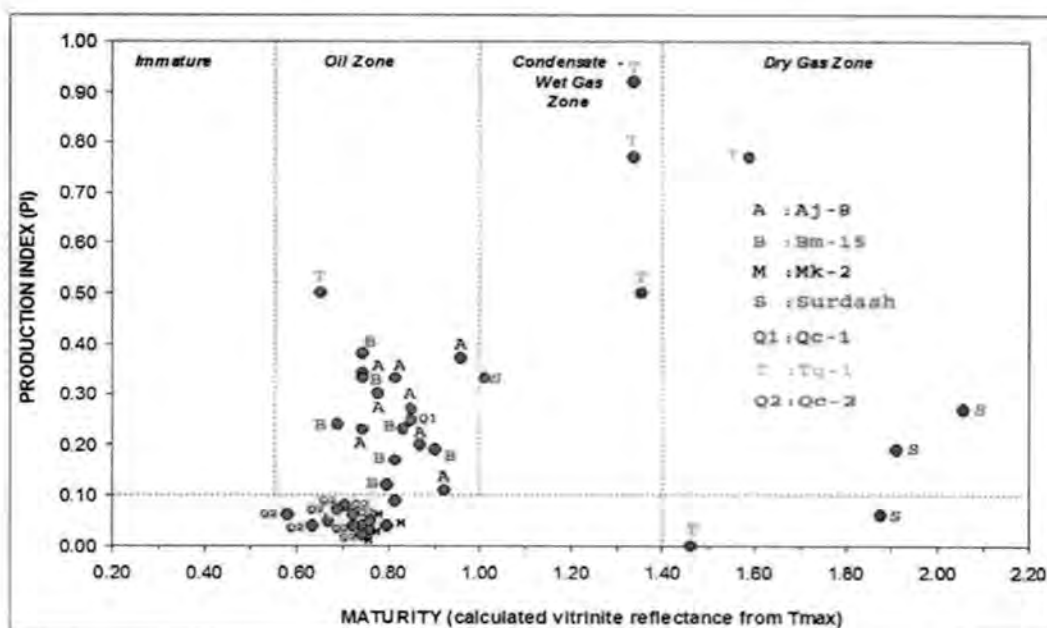


Figure 7: Production index determined via maturity based on cal.vit.R0 from Tmax

RESULTS AND DISCUSSION

It is obviously declared, that the results of the chemical analysis are very formative referring as a comparison study, among the encountered formations and the locality of the studied wells, which all the formations are good to very good source rocks, but not all the locations of the same formations show the same oil or gas prone. Qara chuq 1 &2, Makhul -2, Ajeel -8, Bm-15 are defiantly indicating the potentiality to oil prone, otherwise Taqtaq-1 show potentiality to gas prone with the campaign of the outcropped samples, so the dependable parameters used in chemical analysis done by our team and declared by means of schematic sections, are systematic and matched with optical (palynological) analysis which is performed previously [2] a sure and fix the suitable approach to determine the promising oil and gas fields.

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**Applications of Chemical Analysis to Evaluate Jurassic Hydrocarbon Potentiality
Northern Iraq**

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The shadow effect on solar water heater

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الخلاصة

في هذا البحث درسنا تأثير الظل على درجة حرارة السخان الشمسي والتي قد تصل الى 50% اعتمادا على درجة شدة الظل تم اجراء هذا البحث في الشهر الثاني شباط 2010

ABSTRACT

In this search we study the shadow effect on solar water heater temperature which may be reached more than 50% dependent on shadow illumination degree ,this search down in February 2- 2010

INTRODUCTION

The solar radiation incident on the surface of the earth can be conveniently utilized for the benefit of human society. One of the popular devices that harness the solar energy is solar water heating system (SWHS). Solar Water Heating is a Renewable Technology which can be used to meet the hot requirement in domestic, Commercial and Industrial Sector.^[1,2,3]

The choice of system depends on heat requirement, weather conditions, heat transfer fluid quality, space availability, annual; solar radiation, etc. The SHW systems are economical, pollution free and easy for operation in warm countries

Evacuated Tube Collector is made of double layer borosilicate glass tubes evacuated for providing insulation. The outer wall of the inner tube is coated with selective absorbing material. This helps absorption of solar radiation and transfers the heat to the water which flows through the inner tube.

Solar energy radiation permeates outer glass tubes to heat water in the vacuum tubes. Since cold water has higher specific gravity and hot water has lower specific gravity, cold water flows downwards and hot water rises upwards in the inner tubes, this gradually raises water temperatures in the hot water tank. The black part on the outer walls of inner tubes is selectively coated and serves as the medium for light to

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heat conversion in ETC. Sun's rays reach the absorber coating through the outer glass tubes. The coating absorbs the visible light and near infrared rays of sun's rays to convert light energy into heat energy. This raises the water temperature in the inner tubes.

The selective absorption coating, made of Al-N/Al, is currently the most widely used coating. This coating is capable of absorbing 93% solar energy and reflects back 6%. A vacuum inter-space between the outer tube and the inner tube reduces the heat loss, preserving heat, and thus promoting thermal collection efficiency. [1, 2, 3, 4 and 5]

The collector must be installed without any shadow because the shadow will decrease the solar radiation incident on the surface of the collector solar water heater therefore decrease the output of it .

MATERIALS AND METHODS

Evacuated Tube :- figure (1) show two evacuated tube chooses for this experiment as elements for solar water hater and make simulation shadow by wood barrier and both Evacuated tubes was full in water

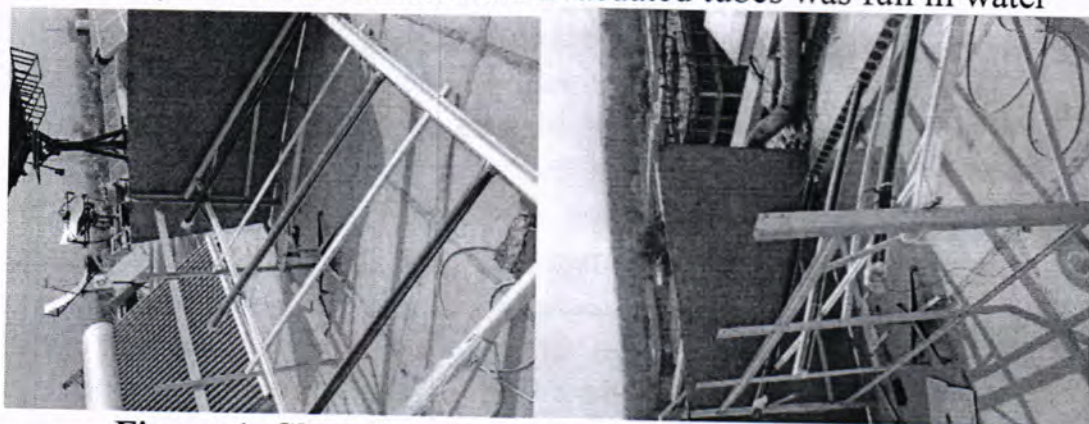


Figure 1: Show the evacuated tubes and wood barrier

We read solar radiation and air temperature form weather station (watch dog type) this reading for solar radiation in (w/m^2) and air temperature in ($^{\circ}\text{C}$), show in figure (2) , this reading with time to long day hours to know how much can evacuated tubes produce the heat follow to incident solar radiation temperature background.

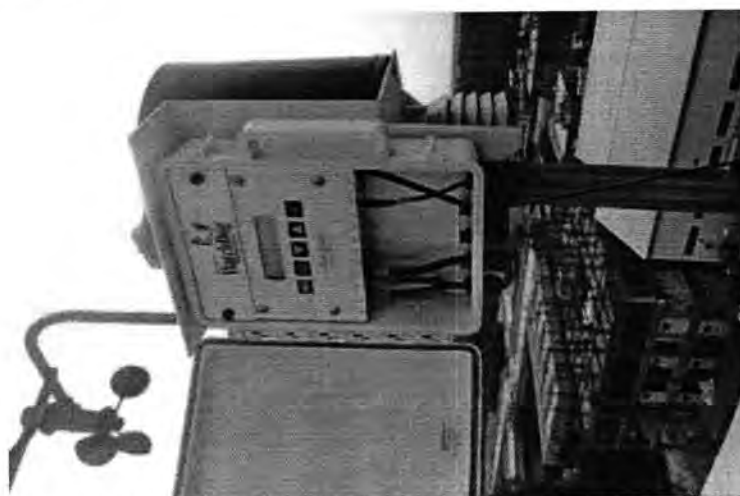


Figure 2: Show the weather station with Data logger type watch dog

We read water temperature the Figure (3) show the thermocouple type (k) with reader to measure water temperature in ($^{\circ}\text{C}$) with time in (hour)

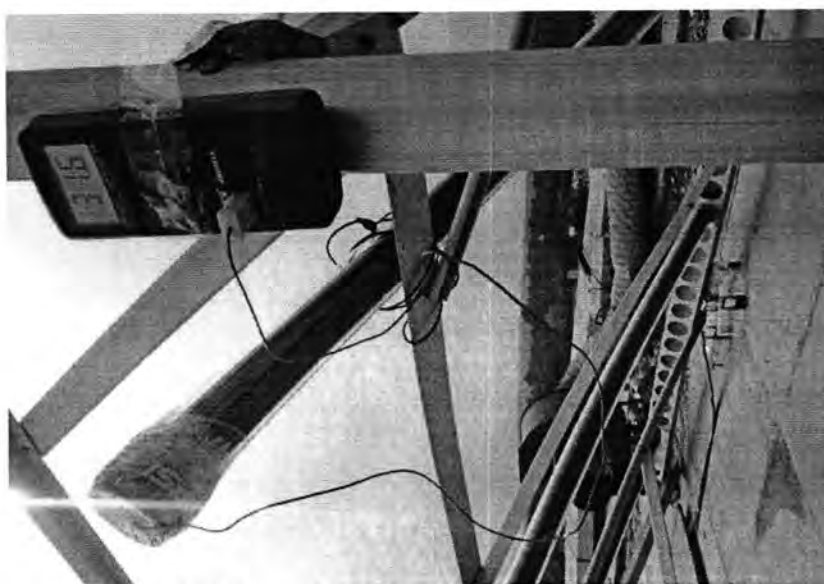


Figure 3: Show the thermocouple with reader

RESULTS AND DISCUSSION

The records was be the solar radiation with time for long day through the weather station to camper the behavior an amount of solar radiation with the time for long day from 8; p.m. to 2; a. m. from the figure (4) we notice an amount of solar radiation be arise with time to reach a peak in 11.45 p.m. because the sun altitude in the sky and an

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amount of solar radiation be bigger that in the morning and begin to decay after this time because the sun be go down

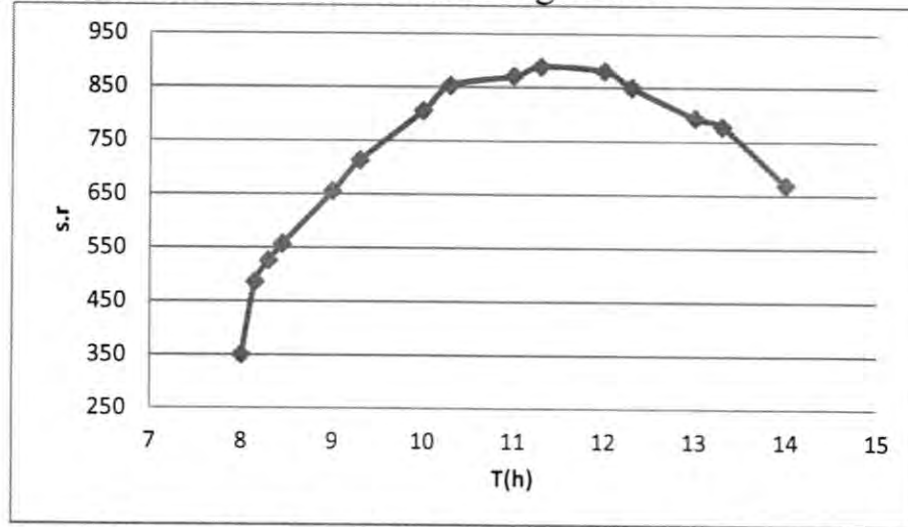


Figure 4: Show the solar radiation with time

We read the air temperature in ($^{\circ}\text{C}$) with time in (hour) through the weather station show in figure (5) because effect the air temperature in evacuated tube by an amount of infrared radiation in background, raise the air temperature that mean an amount of infrared radiation in background be bigger and can be the evacuated tube absorb an amount of infrared radiation.

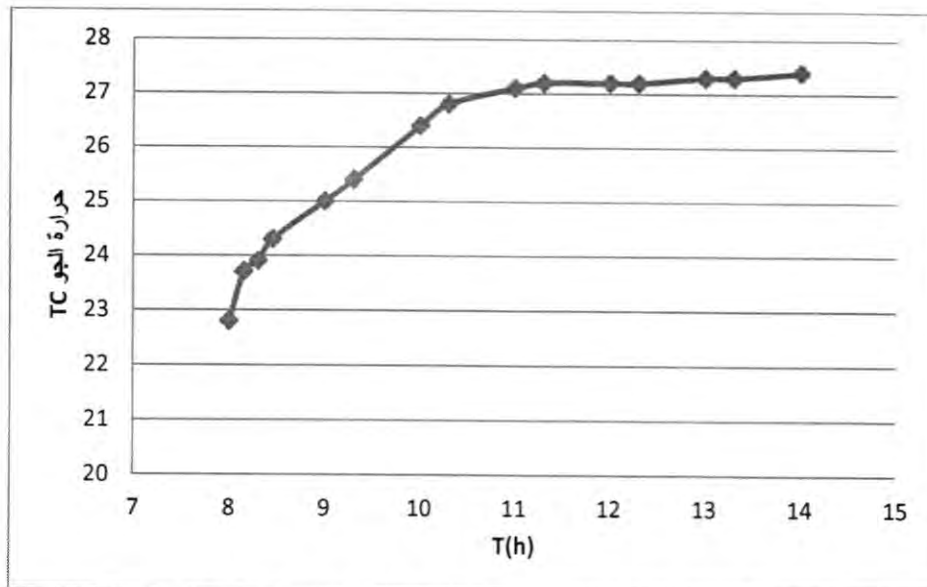


Figure 5: Shows the air temperature with time

And read the two evacuated tube temperatures with shadow and without shadow to camper between them from the readings show in

figure (6) and we see the effect shadow on evacuated tube temperature because cover the solar radiation to reach to evacuated tube and take long time to raise solar water heater temperature. We must take care when installation solar water heater far the shadow likes buildings, trees and dust.

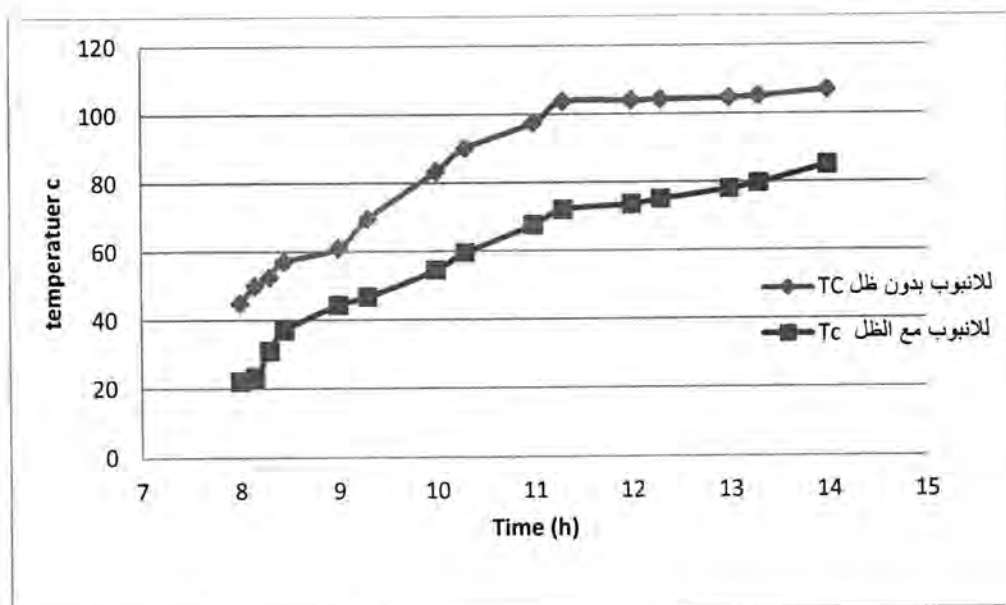


Figure 6: Show the two evacuated tube temperatures with shadow and without shadow with time

The shadow affect on all the solar energy applications special this technical (solar water heater) because the shadow will be cover the solar radiation and forbidden it to reach to solar water heater the decrease ratio in this search will be 35 – 40 % .

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Adsorption of 2,4-Dichlorophenoxyacetic acid onto coconut activated carbon: Kinetics and equilibrium studies

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ABSTRACT

The adsorption equilibrium and kinetics of 2,4-Dichlorophenoxy acetic acid (2,4-D) onto coconut activated carbon (CAC) were examined at 30 °C. Adsorption isotherm of the 2,4-D on the activated carbon was determined and correlated with common isotherm equations. The equilibrium data for 2,4-D adsorption well fitted to the Langmuir equation, with maximum monolayer adsorption capacity of 476.2 mg/g. Two simplified kinetic models including pseudo-first-order and pseudo-second-order equation were selected to follow the adsorption processes. The adsorption of 2,4-D could be best described by the pseudo-second-order equation.

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INTRODUCTION

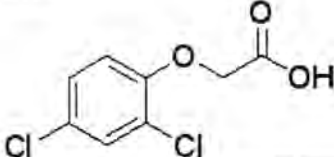
The increasing use of pesticides in agricultural activities has given rise to the contamination of surface and ground waters. This contamination occurs mainly through surface run-off, leaching, deposition from aerial applications and industrial wastewater discharges [1]. The herbicide, 2,4-dichlorophenoxyacetic acid (2,4-D) is one of the most extensively applied pesticide for the control of broad-leaved weeds in fields worldwide [2]. It is considered as moderately toxic and maximum allowable concentration is 0.1 mg/L in drinking water [3]. The uncontrolled use of pesticides over the past 50 years has led to the contamination of hydrological systems and the awareness of organic contaminants in drinking water has paved way for the development of various techniques for the removal of pollutants from water. Several methods either independently or in concert, have been used for the removal of pesticides including chemical oxidation [4], photo degradation [5], combined ozone and UV irradiation [6], Fenton degradation [7], biological degradation [8], ozonation [9], membrane filtration [10] and adsorption [11]. Adsorption technology has been widely used to remove toxic compounds from polluted waters and is presently the most viable option being employed for the removal of pesticides from wastewaters [12]. Activated carbon (AC) or other highly porous materials, such as synthetic resins, are commonly utilized as adsorbents. AC is a widely used adsorbent in the treatment of wastewater and drinking water because it is properties including good mechanical strength, chemical stability in diverse media, and large pore size distribution in addition to its extensive specific surface area [13]. The focus of this research was to evaluate the adsorption isotherm and kinetic information for the adsorption of 2,4-D onto coconut activated carbon.

MATERIALS AND METHODS

2,4-Dichlorophenoxyacetic acid

Technical grade 2,4-D supplied by Sigma-Aldrich was used as adsorbate. Distilled water was used in the preparation of all solutions. The physical properties and molecular structure of 2,4-D are given in Table 1.

Table 1: Physicochemical properties and molecular structure of 2,4-D

Chemical formula	$C_8H_6Cl_2O_3$
Formula weight	221.04
Solubility in water (mg/L)	900
UV absorption, λ_{max} (nm)	284
Chemical structure	

Batch equilibrium studies

Adsorption tests were performed in a set of Erlenmeyer flasks (250 mL) where 200 mL of 2,4-D solutions with initial concentrations of 50-300 mg/L were placed in these flasks. Equal amount of 0.3 g of activated carbon was added to each flask and kept in an isothermal (30°C) shaker at 120 rpm to reach equilibrium. All samples were filtered prior to the analysis in order to minimize the interference of carbon fines present in solution. The concentrations of 2,4-D in the supernatant solution before and after adsorption were determined using a double beam UV-visible spectrophotometer (Shimadzu 1700, Japan) at 284 nm. Each experiment was duplicated under identical conditions. The amount of adsorption at equilibrium by:

$$q_e = \frac{(C_o - C_e)V}{W} \quad (1)$$

where C_o and C_e (mg/L) are the liquid phase concentrations of 2,4-D at the initial and equilibrium conditions, respectively. V (L) is the volume of the solution and W (g) is the mass of CAC.

Adsorption Isotherm

Three isotherm models (Langmuir, Freundlich and Timken) were used to test the fitting of the experimental data. The Langmuir isotherm equation [14] is given as:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (2)$$

where C_e (mg/L) is the equilibrium concentration of the adsorbate, q_e (mg/g) is the amount of adsorbate adsorbed per unit mass of adsorbent, q_m (mg/g) is a monolayer adsorption capacity, and b (L/mg) is the equilibrium adsorption constant. The linear form of Freundlich [15] isotherm is given by the following equation:

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$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \quad (3)$$

where C_e (mg/L) is the equilibrium concentration of the adsorbate, q_e (mg/g) is the amount of adsorbate adsorbed per unit mass of adsorbent, K_F (mg/g(l/mg)^{1/n}) and n are Freundlich constants. In the case of, Timken isotherm [16], it is used in the form given below.

$$q_e = B \ln A_T + B \ln C_e \quad (4)$$

where $B = RT/b$ and b (J/mol) is the Temkin constant related to heat of sorption; A (L/g) is the Temkin isotherm constant, R (8.314 J/mol K) the gas constant and T (K) the absolute temperature.

Batch kinetic studies

The procedures of kinetic experiments were basically identical to those of equilibrium tests. The aqueous samples were taken at preset time intervals, and the concentrations of 2,4-D were similarly measured. The amount of adsorption at time t , q_t (mg/g), was calculated by:

$$q_t = \frac{(C_o - C_t)V}{W} \quad (5)$$

where C_o and C_t (mg/L) are the liquid-phase concentrations of 2,4-D at initial and any time t , respectively. V is the volume of the solution (L), and W is the mass of dry adsorbent used (g).

The pseudo-first-order equation given by Lagergren and Svenska [17] as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (6)$$

where q_e and q_t are the amounts of pesticide adsorbed (mg/g) at equilibrium and at time

t (h), respectively and k_1 is the rate constant adsorption (1/h).

The pseudo-second-order equation [18] is expressed as:

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (7)$$

Where k_2 (g/mg h) is the rate constant of pseudo-second-order adsorption.

RESULTS AND DISCUSSION

Effect of 2,4-D initial concentration and agitation time on adsorption uptake

The effects of agitation time and 2,4-D initial concentration on the adsorption uptake using CAC at 30 °C are shown in Fig. 1. The plots showed that the adsorption of 2,4-D increase with time till it reached a

constant value beyond which no more 2,4-D was further removed from the solution. The results revealed that the 2,4-D adsorption was fast at the initial stages of the contact period, and slowed down near equilibrium. 2,4-D adsorption was fast due to high affinity of the interacting groups on the surface of the activated carbon. The high adsorption rate at the beginning of adsorption was due to the adsorption of 2,4-D by the exterior surface of the adsorbent. When saturation was reached at the exterior surface, the pesticide molecules entered the pores of activated carbon and were adsorbed by the interior surface of the particles [19]. Fig. 1 shows that the contact time needed for 2,4-D solution with initial concentration of 50–100 mg/L will attain equilibrium in less than 4 h, while more than 10 h will be needed for 150–300 mg/L to reach the equilibrium.

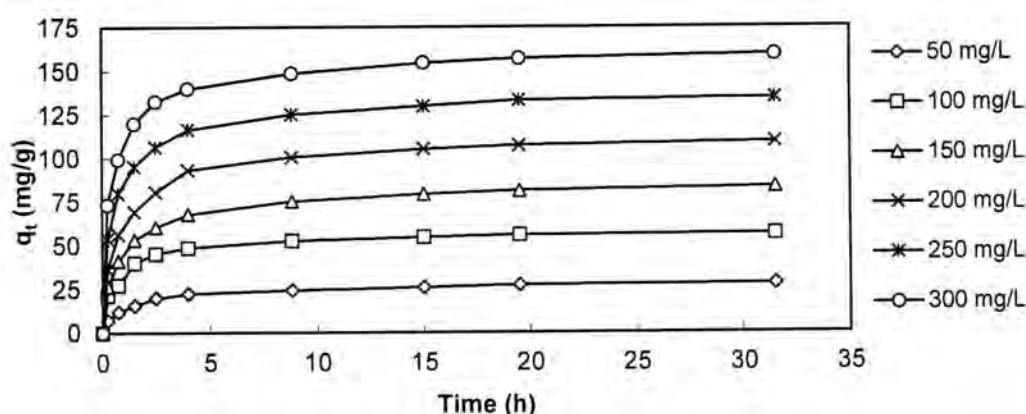


Figure 1: Effect of 2,4-D initial concentration and agitation time on 2,4-D adsorption uptake (30 °C and agitation = 120 rpm)

Adsorption isotherm

Adsorption isotherm was carried out using three isotherm models: the Langmuir, Freundlich and Temkin isotherm models. Table 2 summarizes the monolayer adsorption capacity according to the Langmuir model and the constants of the three isotherms together with their correlation coefficients at 30 °C. It was observed that the Langmuir model yielded the best fit since the R^2 value was relatively high and the Freundlich coefficient $1/n$ value below one.

Table 2: Isotherm models results

Langmuir isotherm model		Qm (mg/g)	b (L/mg)	R^2
		476.2	0.0042	0.932
Freundlich	isotherm	n	K_F	$[(mg R^2$

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model	/g)(L./mg) ^{1/n}]		
	1.19	5.3	0.93
Temkin isotherm model	A (L/g)	B (J/mol)	R ²
	5.84	63.5	0.92

Adsorption kinetics

The adsorption kinetics were studied using pseudo-first-order and pseudo-second-order models as given in Eqs. (6) and (7), respectively. Fig. 2 is plot for the pseudo-second-order kinetic for 2,4-D. The calculated R^2 and predicted equilibrium uptakes for pseudo second-order kinetic model are listed in Table 3. The values of the equilibrium uptake, q_e calculated are closer to the experimental, hence the pseudo-second-order kinetic model describes the adsorption of 2,4-D onto CAC better than the pseudo first-order kinetic model.

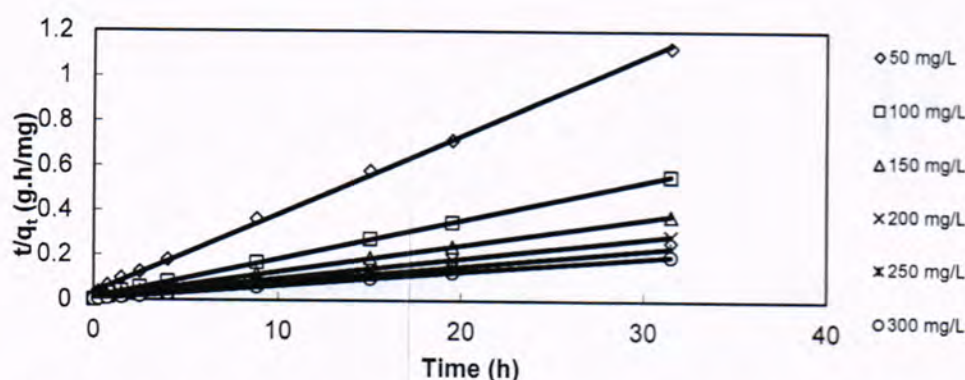


Figure 2: Pseudo-second-order kinetic for adsorption of 2,4-D onto CAC

Table 3: Pseudo-second-order results obtained at different initial 2,4-D concentrations

Initial conc. mg/L	$q_{e,exp}$ mg/g	k_2 (g/mg.h)	$q_{e,cal}$ (mg/g)	R^2
50	28.5	0.037	28.0	0.998
100	57.0	0.030	56.7	0.999
150	84.7	0.015	83.5	0.999
200	110.0	0.013	109.4	0.999
250	136.0	0.014	134.9	0.999
300	161.0	0.015	159.4	0.999

CONCLUSION

The present investigation showed that CAC was a promising adsorbent for the removal of 2,4-D from aqueous solutions over a wide range of concentrations. Equilibrium data were fitted to Langmuir, Freundlich and Temkin isotherms and the equilibrium data were best described by the Langmuir isotherm model, with maximum monolayer adsorption capacity of 476.2 mg/g. The adsorption kinetics was found to follow closely the pseudo-second-order kinetic model.

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Batch Adsorption Study of Methylene Blue Dye onto Date Stone Activated Carbon

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الخلاصة

تم في هذا العمل دراسة تأثير تغير التراكيز الابتدائية لمحاليل صبغة الميثيل الأزرق على عملية الامتصاص لهذه المحاليل في الكربون المنشط لنوى التمر. تم تحليل النتائج المستحصلة من التجارب العملية لهذا العمل باستخدام ثلاثة موديلات اتزان هي موديل لنكمر وموديل فريندليج وموديل تيمكن. نتائج الاتزان أشارت إلى نظام الامتصاص لهذا العمل مع موديل لنكمر حيث أعطى قدرة امتصاص 340 ملغم/غم عند درجة حرارة 30 °م ولمدى تراكيز ابتدائية لمحاليل صبغة الميثيل الأزرق من 50 إلى 300 ملغم/لتر. لقد بينت الدراسة فعالية الكربون المنشط لنوى التمر في إزالة وامتصاص صبغة الميثيل الأزرق من المحاليل السائلة وظروف العمل المثبتة.

ABSTRACT

In this work, the adsorption of methylene blue (MB) onto date stones activated carbon (DSAC) was studied with respect to initial MB concentration. The experimental data were analyzed by the Langmuir isotherm, the Freundlich isotherm and the Temkin isotherm. Equilibrium data fitted well with the Langmuir model with maximum adsorption capacity of 340 mg/g at 30 °C for MB concentration range of 50-300 mg/L. The results indicated that the DSAC is very effective for the adsorption of MB from aqueous solutions.

INTRODUCTION

The presence of dyes in effluents is a major concern due to their adverse effect to many forms of life. The discharge of dyes in the environment is worrying for both toxicological and esthetical reasons as dyes impede light

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penetration, damage the quality of the receiving streams and are toxic to food chain organisms (1). Industries such as textile, leather, paper, plastics, etc., are some of the sources for dye effluents (2). Methylene blue (MB), a cationic dye, is the most commonly used substance for coloring among all other dyes of its category. MB can cause eye burns, and if swallowed, it causes irritation to the gastrointestinal tract with symptoms of nausea, vomiting and diarrhea. It may also cause methemoglobinemia, cyanosis, convulsions and dyspnea if inhaled (3). Hence, the treatment of effluents containing such dye is of interest due to its harmful impacts on receiving waters.

Adsorption onto activated carbon has been found to be superior for wastewater treatment compared to other physical and chemical techniques, such as flocculation, coagulation, precipitation and ozonation as they possess inherent limitations such as high cost, formation of hazardous by-products and intensive energy requirements (1). However, commercially available activated carbons are still considered expensive (4). This is due to the use of non-renewable and relatively expensive starting material such as coal, which is unjustified in pollution control applications (5). Therefore, in recent years, this has prompted a growing research interest in the production of activated carbons from renewable and cheaper precursors which are mainly industrial and agricultural by-products, such as olives pits [6], silk cotton hull and maize (7), jute fiber (3), groundnut shell (8), corncob (9), bamboo (10), rattan sawdust (11) and date stones. Date stones (*Phoenix dactylifera*) are also a low-cost, abundantly available and renewable precursor for production of activated carbon as adsorbent for the removal different pollutants (dyes, pesticides, heavy metals etc) from aqueous solutions. The world production of dates is about 16,696.56 million tons yearly. Iraq has long been a major producer of dates (12).

The purpose of this work was to evaluate the adsorption potential of date stones activated carbon for methylene blue dye. The isotherm models data of the adsorption process were studied to understand which isotherm model describe the adsorption of methylene blue molecules onto DSAC.

MATERIALS AND METHODS

Methylene blue dye

Methylene blue (MB) supplied by Sigma-Aldrich was used as an adsorbate and was not purified prior to use. MB was chosen for this study because of its known strong adsorption onto solids. Deionized water was used to prepare all the solutions and reagents. Some properties of the MB dye, together with its chemical structure, are listed in Table 1.

Table 1: Some properties of the MB used

Properties	
Chemical formula	$C_{16}H_{18}ClN_3S \cdot 3H_2O$
Molecular weight	373.9 g/mol
Type	Basic dye
Solubility	Soluble in water
Solution pH	6.5
Wave length	668 nm

Batch equilibrium studies

Adsorption tests were performed in a set of Erlenmeyer flasks (250 mL) where 100 mL of MB solutions with initial concentrations of 50–300 mg/L were placed in these flasks. Equal mass of 0.3 g of date stone activated carbon with the particle size of 1–1.5 mm was added to each flask and kept in an isothermal shaker of 120 rpm at 30°C to reach equilibrium. The pH of the solutions was natural. Aqueous samples were taken from the solution and the concentrations were analyzed. All samples were filtered prior to the analysis in order to minimize the interference of the carbon fines with the analysis. The concentrations of MB in the supernatant solution before and after adsorption were determined using a double beam UV-visible spectrophotometer (Shimadzu-1700, Japan) at 668 nm. The calibration curves were obtained by plotting the MB absorbance, A_i versus the MB solutions concentrations, C (mg/L). Each experiment was duplicated under identical conditions. The amount of adsorption at equilibrium, q_e (mg/g), was calculated by:

$$q_e = (C_o - C_e)V / W \quad (1)$$

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where C_0 and C_e (mg/L) are the liquid phase concentrations of dye at the initial and equilibrium conditions, respectively. V is the volume of the solution (L) and W is the mass of dry adsorbent used (g).

Langmuir isotherm

Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies of adsorption with no transmigration of adsorbate in the plane of surface (13). The linear form of Langmuir isotherm equation is given as:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (2)$$

where C_e (mg/L) is the equilibrium concentration of the adsorbate, q_e (mg/g) is the amount of adsorbate adsorbed per unit mass of adsorbent q_m (mg/g) and b (L/mg) are the rate of adsorption and Langmuir constants related to adsorption capacity, respectively.

Freundlich isotherm

Freundlich isotherm on the other hand assumes heterogeneous surface energies, in which the energy term in Langmuir equation varies as a function of the surface coverage (14). The well-known logarithmic form of the Freundlich isotherm is given by the following equation:

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \quad (3)$$

where C_e (mg/L) is the equilibrium concentration of the adsorbate, q_e (mg/g) is the amount of adsorbate adsorbed at equilibrium per unit mass of adsorbent, K_F and n are Freundlich constants.

Temkin isotherm

Temkin and Pyzhev considered the effects of indirect adsorbate/adsorbate interactions on adsorption isotherms. The heat of adsorption of all the molecules in the layer would decrease linearly with

coverage due to adsorbate/adsorbate interactions (15). The Temkin isotherm has been used in the form as follows:

$$q_e = B \ln A_T + B \ln C_e \quad (4)$$

where $B = \frac{RT}{b}$ is the Temkin constant related to heat of sorption, A_T (L/g) is the Temkin isotherm constant, R is the gas constant (8.314 J/mol K), T (K) is the absolute temperature.

RESULTS AND DISCUSSION

Effect of contact time and initial dye concentration on adsorption equilibrium

Adsorption isotherms are usually determined under equilibrium conditions. Figure 1 show the adsorption capacity versus the adsorption time at various initial MB concentrations at 30 °C. It indicated that the contact time needed for MB solutions with initial concentrations of 50 –150 mg/L to reach equilibrium ranged between 4 and 6 h. For MB solutions with initial concentrations of 200 –300 mg/L, equilibrium time of 8 to 10 h were required. However, the experimental data were measured at 15 h to make sure that full equilibrium was attained.

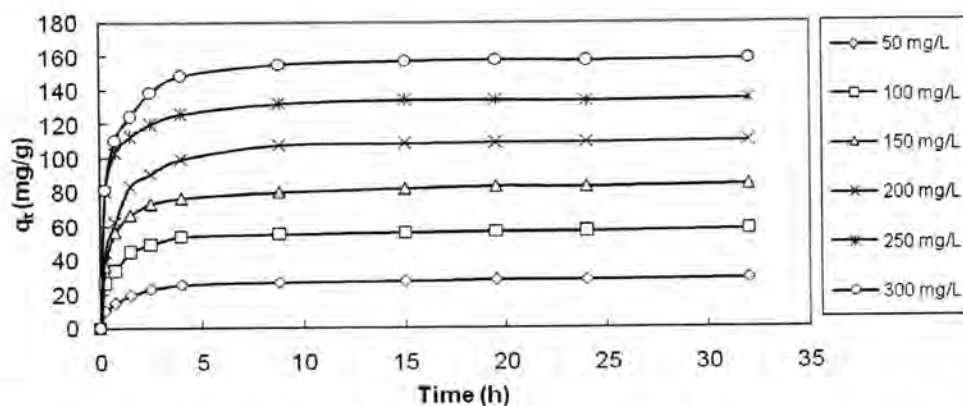


Figure 3: The adsorption capacity variation with contact time at various initial MB concentrations at 30 °C

Adsorption isotherms

The adsorption isotherm indicates how the adsorbed molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purposes (16). Adsorption isotherm is basically important to describe how solutes interact with adsorbents, and is critical in optimizing the use of adsorbents. Adsorption isotherm study was carried out on three isotherm models: the Langmuir, Freundlich and Temkin isotherm models. The applicability of the isotherm models to the adsorption study done as compared by judging the correlation coefficients, R^2 values. Table 2, listed the results of these three isotherm models, the Langmuir isotherm model yielded the best fit with the highest R^2 value compared to the other two models with maximum monolayer adsorption capacity of MB onto DSAC of 340 mg/g.

Table 2: Isotherm models results

Langmuir isotherm model	
q_m (mg/g)	340
b (l/mg)	0.0145
R^2	0.977
Freundlich isotherm model	
n	1.316
K_F [(mg /g)(l./mg) $^{1/n}$]	7.24
R^2	0.960
Temkin isotherm model	
A (l/g)	4.74
B (J/mol)	57.9
R^2	0.980

Table 3 List the maximum monolayer adsorption capacity of MB onto DSAC prepared in this work compared to some data obtained from the literature

Table 3: Comparison of the maximum monolayer adsorption of MB onto various adsorbents

Adsorbents	Maximum adsorption capacity (mg/g)	monolayer References
DSAC	340.0	This study
Commercial activated carbon F300	240.0	17
Jute fiber-based activated carbon	225.6	18
Mango seed kernel powder	142.9	19
Jute processing waste	22.5	20
Bamboo dust-based activated carbon	143.2	21
Coconut shell-based activated carbon	277.9	21
Groundnut shell-based activated carbon	164.9	21
Palm fiber-based activated carbon	277.8	22

CONCLUSIONS

Methylene blue was found to adsorb strongly onto the surface of the date stones -based activated carbon (DSAC). Equilibrium data were fitted to Langmuir, Freundlich and Temkin isotherms and the equilibrium data were best described by Langmuir isotherm model, with maximum monolayer adsorption capacity of 340 mg/g at 30 °C. The adsorption potential of the DSAC was comparable to commercial activated carbon and some other adsorbents reported in other studies.

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Study of Vitamin E, Homocysteine, C-RP, and Oxidative Stress in Coronary Heart Disease Patients with and without (Diabetes Mellitus or Hypertension)

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الخلاصة

أمراض الشرايين التاجية هو سبب اعتلال القلب والوفيات في العالم المتقدم. شملت الدراسة 90 مريضاً مصاباً بأمراض القلب التاجية كانوا يعالجون في مستشفى الصدر في محافظة ميسان (أمراض القلب التاجية = 30 مريضاً، وأمراض القلب التاجية مع مرض السكر النوع الثاني = 30 مريضاً وأمراض القلب التاجية مع ارتفاع ضغط الدم = 30 مريضاً) إضافة إلى 30 متطوع من الأشخاص السويين الذين يمثلون مجموعة السيطرة، للفترة من تشرين الأول 2009 ولغاية أيار 2010 وهذه أول دراسة من نوعها أجريت على سكان المناطق الريفية في محافظة ميسان في العراق.

تم قياس مستوى فيتامين E وكذلك عامل الخطر tHcy باستخدام جهاز كروماتوغرافيا السائل ذو الضغط العالي. وتم قياس المألون ثنائي اللدهيد MDA والكوليسترول ومستوى السكر الصائم و بروتين سي التفاعلي في المجاميع المستخدمة في هذه الدراسة. وأظهرت النتائج أن هناك انخفاض معنوي في مستوى فيتامين E ونسبة فيتامين E إلى الكوليسترول في كل من CHD و CHDD و CHDH مقارنة مع مجموعة السيطرة. وبالإضافة إلى ذلك لوحظ وجود زيادة معنوية في مستوى عامل الخطر tHcy وبروتين سي التفاعلي و المألون ثنائي اللدهيد MDA في مجاميع امراض القلب التاجية مقارنة مع مجموعة السيطرة.

أشارت نتائج الارتباط بين المتغيرات المستخدمة في هذه الدراسة مع المألون ثنائي اللدهيد MDA إلى دور الشد التأكسدي الذي قد يكون مهماً لمتابعة مستويات الفيتامينات المضادة للأكسدة مثل فيتامين E ونسبة فيتامين E إلى الكوليسترول لتحسين حالة مضادات الأكسدة لدى الأشخاص المصابين بأمراض القلب التاجية. استنتجنا من هذه الدراسة أن مستوى فيتامين E ونسبة فيتامين E إلى الكوليسترول ممكن أن تستعمل كدالة حيوية لتوقع الإصابة بأمراض القلب التاجية إلى سكان المناطق الريفية في محافظة ميسان - العراق. ويعد عامل الخطورة الجديد tHcy أفضل من CRP كعامل تنبؤ بالمرض.

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ABSTRACT

Coronary heart disease CHD is a cause of cardiac morbidity and mortality in the developed world. This study include 90 patients treated in AL – Sadder hospital (CHD = 30, coronary heart disease with diabetes mellitus (CHDD) = 30, and coronary heart disease with hypertension (CHDH) = 30) which aged was between (35 – 65) years. In addition 30 healthy volunteers represented the control cases, aged was between (25 – 45) years. The study period was from October 2009 to June 2010. This is the first study done in Missan district among inhabitants living in a rural area of Iraq. The concentrations of vitamin E, and novel risk factor total homocysteine (tHcy), were measured in sera of all groups by HPLC. Malondialdehyde (MDA), cholesterol, fasting blood glucose, and CRP were also determined in sera of all subjects, which included in this study. Results showed that there was a significant decrease in vitamin E levels and vit. E/cholesterol ratio in CHD, CHDD, and CHDH when compared to control group. In addition, a significant increase in tHcy, C-reactive protein (CRP), and MDA levels was observed in all groups of CHD patients when compared to control group. The results of correlation between the parameters, which used in this study and MDA reveal to the role of oxidative stress, which may be an importance of monitoring the level of antioxidant vitamins like vitamin E and the ratio of Vitamin E/cholesterol to improvement of antioxidant status in CHD patients. The conclusion of this study indicates that serum levels of vitamin E and the ratio of vitamin E/cholesterol may be using as biomarkers for predicting coronary heart disease mortality among inhabitants living in a rural area of Iraq. The novel risk factor tHcy is the best predictor of CHD risk than CRP.

INTRODUCTION

Coronary heart disease CHD is a cause of cardiac morbidity and mortality in the developed world. In many industrialized countries, death rates due to CHD have been falling for both men and women especially in the higher socio – economic groups who have undertaken lifestyle changes including cessation of smoking. This contrasts with a rising death rate in developing countries [1].

Coronary atherosclerosis disease or CHD is an inflammatory disease in which fatty substances, cholesterol, platelets, cellular waste products, and calcium accumulate on the inner lining (endothelium) of arteries. These plaques grow in size and may occlude the artery causing diminished blood flow and oxygen transport or may rupture and induce heart attacks or strokes[2].

Free radicals (FRs) are highly reactive molecules that react with and damage cells throughout the body, which are suspected of causing CHD [3].

Antioxidants are molecules such as lipid – soluble antioxidants (vitamin A, vitamin E, and beta- carotene), which can safely interact with FRs and terminate the chain reaction before vital molecules are damaged, and protect cell membranes from lipid peroxidation [4]. Vitamin E, blocks the chain reaction of lipid peroxidation by scavenging intermediate peroxy radicals. The α - tocopherol radical is much less reactive in attacking adjacent acid side chain and can be converted to α -tocopherol by vitamin C [5].

Identified common risk factors and their relationship with CHD are advancing age, gender difference, serum lipids, lipoproteins, hypertension, diabetes mellitus, smoking, homocysteine, CRP, and positive family history [6]. Total homocysteine (tHcy) and CRP are new risk factors that called novel risk factors for CHD. Homocysteine is a toxic, nonproteinogenic, highly reactive amino acid that is synthesized during protein catabolism. During the past few years, elevated blood levels of tHcy have been linked to increased risk of premature CHD [7]. C-reactive protein is one of the acute phase proteins that increase during systemic inflammation. A growing number of studies have examined whether CRP can predict recurrent CHD. High levels of CRP consistently predict recurrent coronary events in patients with unstable angina and acute MI. Higher CRP levels also are associated with lower survival rates in these patients. Many studies have suggested that after adjusting for other prognostic factors, CRP is useful as a risk predictor [8].

Cholesterol is a waxy steroid metabolite found in the cell membranes and transported in the blood plasma of all animals [9]. A high level of serum cholesterol is an indicator for diseases such as heart disease. High cholesterol can be caused by a high level of Low-density lipoprotein (LDL), LDL cholesterol is most likely to narrow arteries. A low level of High – density lipoprotein (HDL), also can promote atherosclerosis [10]. However, a high level of HDL cholesterol, which helps the body, clean up excess cholesterol, is desirable and lowers the risk of heart attack [11]. The aim of this study was to determine the oxidative stress, novel risk factors and vitamin E as antioxidant in coronary heart disease patients with and without diabetes mellitus or hypertension in Missan district among inhabitants living in a rural area of Iraq, and then finding the correlation between MDA with different parameters used in this study.

MATERIALS AND METHODS

Chemicals

All chemicals were used in this study and there sources are as follows: The concentrations of serum glucose, cholesterol, were measured

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by enzymatic colorimetric assay using kit supplied by Biomeriux– France. The concentration of vitamin E and homocysteine in the collected serum samples was determined using High – performance liquid chromatography assay according to Zhao *et al* [12] and method by Robert *et al*. [13] respectively. C – reactive protein was measured by rapid test for the qualitative and semi quantitative determination of CRP in serum by agglutination of latex particles on slide using a kit supplied by linear chemicals – Spain. The concentration of MDA in serum was determined according to Buege and Aust method enzymology [14].

Samples Collection

Ninety sera patients which included CHD = 30, CHDD = 30, and CHDH = 30 were recruited from the AL – Sadder hospital, Missan district, with age ranged (35 – 65) years. Healthy control group consisted of 30 individuals with age ranged (25 – 45) years. All individuals in this study were none had taken vitamin supplements or any drugs which effects on this study.

Preparation of Blood Samples

Ten milliliters of blood samples were taken from patients and normal controls in the morning after 12 hours fasting .Blood sample were left for 20 minutes at room temperature, after blood coagulation, the sera were separated by centrifugation at 3000 rpm for 15 minutes. Hemolysed samples were discarded. The sera were stored and frozen at -20°C until analysis [15].

Statistical analysis

The data was analyzed on the computer statistical program SPSS version 13. The mean \pm SD was also computed for the comparison of results. The comparison of mean between each group and control group was tested by Student's t–test. Results were considered statistically significant if P value is less than 0.05.

RESULTS AND DISCUSSION

Table (1) shows the distribution of patients groups and control according to the risk factors:

Table 1: Risk factors distribution of CHD patients in three groups and control group.

Variable		Control (mean \pm SD)	CHD (mean \pm SD)	CHDD (mean \pm SD)	CHDH (mean \pm SD)
Number (%)		30(100)	30(33.33)	30(33.33)	30(33.33)
Gender	Male	15	20	15	12
	Female	15	10	15	18
Age (years \pm SD)		34.00 \pm 8.40	51.43 \pm 10.72 (d)	55.29 \pm 5.19 (d)	57.05 \pm 6.35 (d)
Smokers (%)	Never	20	17	18	21
	Current	10	13	12	9
Weight (kg)		77 \pm 12.247	83.23 \pm 15.19	84.71 \pm 12.67	82.3 \pm 12.217
Height (m)		1.643 \pm 0.498	1.627 \pm 0.466	1.603 \pm 0.427	1.597 \pm 0.397
Body mass index (kg/m ²)		28.59 \pm 4.62	31.43 \pm 5.0	33 \pm 5.02	31.6 \pm 3.87 (a)
Hypertension (mmHg)	Systolic	119.57 \pm 0.786	118.66 \pm 16.76	116.43 \pm 16.51	153 \pm 34.81 (b)
	Diastolic	79.285 \pm 1.25	75.83 \pm 12.32	75 \pm 9.57	90.5 \pm 19.86
FBG (mmol/L)		3.8 \pm 0.276	6.9 \pm 3.99	13.7 \pm 8.45 (d)	6.76 \pm 4.04
Cholesterol(mg/dL)		128.21 \pm 13.66	190.56 \pm 28.33 (d)	176.62 \pm 12.35 (c)	185.25 \pm 30 (d)

a: The mean difference is significant at the 0.05 level,

b: The mean difference is significant at the 0.01 level,

c: The mean difference is significant at the 0.001 level,

d: The mean difference is significant at the 0.0001 level, FBG= Fasting blood glucose.

The data showed no significant differences in mean age and sex in three groups of patients (CHD, CHDD, and CHDH) compared with control group. The number current smoking patients in this study were less than never smoking in all groups, therefore the role of this risk factor is not clear in this study. It's found only significant differences in mean BMI ($p < 0.05$) in CHDH patients when compared to control group, while there was no significant differences in CHD and CHDD as compared to control group. Losing weight reduce the risk of disorders [16]. The results show there is no significant differences in mean fasting blood glucose in patients with and without hypertension (CHDH and CHD) compared with control group. Fasting blood glucose was increased significantly ($p < 0.0001$) in serum CHDD patients when compared to control group. The prevalence of

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hypertension (systolic blood pressure) was found only significant differences ($p < 0.01$) in CHDH patients when compared to control group, while there was no significant differences in systolic blood pressure in CHD and CHDD as compared to control group. In addition, there was non-significant increase in diastolic blood pressure in all groups as compared to control group. The results of cholesterol show highly significant differences in CHD patients ($p < 0.0001$), CHDD ($p < 0.001$), and CHDH ($p < 0.0001$) as compared to control group.

Table (2) shows high significant decrease in the level of vitamin E and vit. E/cholesterol ratio in CHD, CHDD, and CHDH patients as compared to control group.

Table 2: Serum levels of total homocysteine, vitamin E, vitamin E/cholesterol ratio, CRP, and malondialdehyde (MDA) in different groups of CHD.

Group type	Component	Mean	SD	P
CHD	Homocysteine (mg/dL)	0.1709	0.0544	0.042
CHDD		0.1776	0.0025	0.016
CHDH		0.1705	0.0075	0.050
Control		0.1592	0.0176	-----
CHD	Vitamin E (mg/dL)	0.1066	0.0067	0.016
CHDD		0.0992	0.0029	0.0001
CHDH		0.1049	0.0559	0.006
Control		0.1143	0.0035	-----
CHD	Vitamin E/cholesterol ratio	5.7755	1.0115	0.0001
CHDD		5.6876	0.4086	0.0001
CHDH		5.9410	0.4172	0.0001
Control		9.4123	1.0128	-----
CHD	CRP (mg/L)	110.666	63.8648	-----
CHDD		144.000	55.4256	0.320
CHDH		117.600	60.7656	0.702
Control		-----	-----	-----
CHD	MDA ($\mu\text{mol/L}$)	3.5732	2.8490	0.003
CHDD		4.3685	0.9402	0.003
CHDH		3.5000	1.5719	0.006
Control		0.8017	0.2582	-----

Vitamin E is an important antioxidant vitamin, playing an essential protective role against FRs damage [17]. The nutritional requirement for vitamin E (10 mg/day) varies with the dietary intake of Polyunsaturated fatty acid. For this reason, vitamin E is the main antagonist of lipid peroxidation. its protection of membranes is important for proper functioning of the vascular endothelial barrier, for reduction of proliferation stimuli for myocytes of the tunica media, and for decrease in chemo tactic factors for monocytes [18]. Vitamin E supplementation was based on the reduction of cardiovascular events seen in the Cambridge Heart Antioxidant Study [19].

There is evidence that vitamin E/cholesterol ratio is a more reliable criterion for vitamin E status than plasma vitamin E alone [20]. Thus, vitamin E status should be observed and compared again with this ratio. Nevertheless, the similar result obtained from the investigation of plasma vitamin E ratio that only CHD patient's group had significantly decreased in the vitamin E ratio comparing to the normal subjects. There are several reports that were considered with the effect of low vitamin E level of sensitivity of red blood cells to oxidative damage. The depletion of vitamin E on the hematopoietic system of several species has shown the changes in red cell mass, size and increase in peroxidation of cell membrane [21-22]. The lower levels of vitamin E status and high levels of plasma MDA in CHD complicated T2DM patients may be supported by these evidences.

Rimm *et al.* [23], observed that increase intake of vitamin E is associated with a reduced risk of CHD. This finding is also consistent with geographic correlation between serum vitamin E, coronary mortality rates, and reduced serum vitamin E in patients with CHD.

Our results were agreement with Peerapatdit *et al.* [24], who found that the vitamin E level in normal group was significantly higher ($p < 0.0001$) than in T2DM complicated with CHD. Galley *et al.* [25], used vitamin E in combination with zinc, vitamin C, and β -carotene showed a modest, significant reduction in BP over eight weeks of therapy. Pezeshkian *et al.* [26], found in their study in contrast of CHD with control group ($p < 0.001$) the ratio of vitamin E/cholesterol of patients showed a meaningful reduction, so the increase of mean levels of the anthropometric parameters, serum levels of lipids and lipoproteins, on the coronary the reduction of vitamins are the indictors of aggravation of atherosclerosis, and produce vascular stenosis. At the end, these changes lead to the rise of serum MAD levels. Some researchers believe that the ratio of vit. E/cholesterol is a clear index of vitamin E for showing the CHD in control and patients groups [27]. The results show a significant increase in the levels tHcy and CRP in all groups of CHD patients. A similar trend of significance was noticed in the serum level of MDA in different groups.

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Detection of an independent effect of tHcy on the risk of CHD in clinical studies remains difficult due to the many factors that can affect tHcy level. Aging and lifestyle behaviors can contribute to mild elevations in tHcy without associated hyperhomocysteinemia. We found that tHcy levels did not differ between males and females, patient with cholesterol levels less than 200 mg/dL had significantly higher tHcy levels as compared to their respective controls, this results was agreement with Mashal *et al* [28], they found a significant increase in the mean fasting tHcy was (14.2 ± 7.39) when compared to control group (10.0 ± 3.8). Our results are agreement with Bandarian *et al* [29], Clarke *et al* [30], Christen *et al* [31], they found high serum levels of tHcy, may be the risk factor of CHD in an Iranian urban population than in control group [29-31]. According to the results in study of Nygard *et al* [32], Omland *et al* [33], it has been suggested that tHcy is an independent predictor of mortality in stable and acute CHD. Joubran *et al* [34], has been conducted to hyperhomocysteinemia as a risk factor for CHD in an Arab population. Several studies suggest that elevated tHcy level has both atherogenic and thrombogenic effects. Hyperhomocysteinemia causes endothelial dysfunction by increasing oxidant stress [35-36] and decreases the release of NO, impairing vasodilation [37]. Excess of tHcy stimulates smooth – muscle cell proliferation and collagen synthesis promoting intima – media thickening [38]. Hyperhomocysteinemia is also considered to have thrombogenic activity by increasing platelet aggregation and causing abnormalities in the coagulation system [39]. High tHcy level is also shown to be associated with increased lipid peroxidation [40]. Soinio *et al* [41], found elevated plasma homocysteine level is an independent predictor of CHD events in patients with T2DM. Some reports describe a significant relationship between tHcy and BP levels, Boushey *et al*. [42], examined 27 reports of studies on the relationship between tHcy and CHD. Overall, the population data indicate that plasma tHcy higher than the 90th percentile were associated with an increased risk of fatal and nonfatal atherosclerotic disease in the coronary, cerebral, and peripheral circulation. Fakhrzadeh *et al* [43], found a significant association between hypertension and high serum tHcy concentration. Other studies reported a graded, positive association between tHcy and the risk for CHD [44].

Recent finding suggest that laboratory testing for tHcy levels can improve the assessment of risk. It may be particularly useful in patients with a personal or family history of CHD, but in whom the well – established risk factors (smoking, high blood cholesterol, high BP) do not exist [45].

Moreover, the increase of serum CRP concentration was found more frequently in the CHD patients with T2DM. Our data points to the inflammation in the progression of CHD. This finding are agreement with Rudzite *et al.* [46], who found that the examination of both neopterin and CRP Indexes is necessary to find the presence of inflammation, infection or trauma and so prognosticate, the course of CHD. Buckley *et al.* [47], found that CRP is strong evidence associated with CHD events and suggests that adding CRP to risk prediction models among initially intermediate-risk persons improves risk stratification.

Type 2 diabetes mellitus is associated with oxidative stress and increase free radical formation [48]. Oxidative stress causes reduction of the antioxidant status of the body [49]. The prolonged exposure to hyperglycemia also leads to the increased oxidative stress [50]. Therefore, our study also attempted to estimate the levels of MAD, a marker of lipid peroxidation and found that the levels of MDA were higher in diabetics compared to controls. Uzel *et al.* [51], Gallow *et al.* [52], Ayden *et al.* [53], and Seghrouchni *et al.* [54] reported similar results in T2DM patients.

Our results show continues increase of MAD concentration in CHD with or without T2DM or hypertension. This increase is in a good agreement with Tosukhowong *et al.* [55], who found patients with CHD had higher MAD level than control group, which represent the oxidative damage products of lipid and proteins. Some investigators have found a correlation between prooxidant – antioxidant imbalance of the severity of coronary lesions [56]. Oxidative stress – related studies in patients with CHD have been usually done by measuring lipid peroxidation and/or antioxidant power in plasma [57]. Our results are in agreement with Panah Mogadam *et al.* [58], who found the higher total cholesterol and MAD levels compared to healthy control, suggest an enhanced oxidative stress situation in CHD patients, so they used serum MAD as a diagnostics biomarker in CHD.

Table (3) shows ANOVA analysis and the results of correlation between oxidative stress index (represented by MDA level) and concentration of other parameters in CHD, CHDD, and CHDH groups. The results in Table (3) show significant negative correlation between vitamin E and MDA ($r=-0.557$, $P<0.001$) in CHD, significant negative correlation ($r=-0.502$, $P<0.005$) in CHDD, and significant negative correlation ($r=-0.372$, $P<0.043$) in CHDH. In Table (3), the significant levels (represented by P values) show highest negative significant correlation between MDA and the ratio of vitamin E/cholesterol in CHD patients ($r=-0.678$, $P<0.0001$), in CHDD patients ($r=-0.462$, $P<0.018$), and CHDH patients ($r=-0.681$, $P<0.0001$) as compared to vitamin E alone. This gives a preliminary confirmation for the direct effect of MDA on vitamin E levels when compared with other micronutrients. Vitamin E may be the most potent inhibitor of lipid oxidation because it is fat – soluble and constitutes

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part of the LDL molecule. David *et al* [27] showed a meaningful relation between vitamin E and MDA in myocardial cells of hypertension rats. Pezeshkian and co – workers [26] suggest that decrease of antioxidant vitamin E and C, the ratio of Vit. E/cholesterol and increase MDA serum levels play important roles in the pathogenesis of coronary artery disease patients [26].

The non – significant increase of inflammatory markers including CRP in all groups indicates that CRP is portend a poor prognosis in patients with established CHD. Our finding results are agreement with study of Eric *et al* [59].

Results in Table (3) show positively significant correlation between MDA levels and tHcy in CHD, CHDD, and CHDH patients groups. The highly significant elevated in tHcy versus MDA indicates that tHcy induced oxidative stress and ROS or lipid peroxidation production and decrease NO· availability[60].

There is evidence that Homocysteine exerts its effect by promoting oxidative damage [61]. The accumulations of tHcy also produce reactive oxygen species including superoxide, which initiate lipid peroxidation and support the oxidation of LDL, this tHcy – induced disturbance in oxidative metabolites also leads to overproduction of oxidative radicals that induce internal injury, activate elastase, and increased calcium deposition [62]. Ventura *et al.*[63], found a significant positive correlation ($r = 0.47$, $P < 0.05$) between tHcy and MDA in human plasma [63]. Valiūnienė *et al.* [64], found a weak positive correlation between blood serum level of tHcy and MDA as a marker of lipid peroxidation in patients with CHD throughout the acute phase of acute coronary syndromes such as stable angina patients ($r = 0.13$).

The conclusion of this study indicates that serum levels of vitamin E and the ratio of vitamin E/cholesterol may be particularly promising as biomarkers for predicting coronary heart disease mortality among inhabitants living in a rural area of Iraq. The novel risk factor tHcy is the best predictor of CHD risk than CRP and the levels of tHcy are increasing significantly with oxidative stress.

Table 3: Correlation coefficients and the significance levels of different serum chemical components in all groups of patients with CHD

Component Vs. MDA (mg/dL)	CHD				CHDD				CHDH			
	R ²	r	P	Slope	R ²	r	P	Slope	R ²	r	P	Slope
Vitamin E (mg/dL)	0.310	-0.557**	0.001	-174.4	0.252	-0.502**	0.005	-106.1	0.1384	-0.372*	0.043	-85.54
Vit. E/cholesterol ratio	0.459	-0.678**	0.0001	-16730	0.430	-0.462*	0.018	-24008	0.4643	-0.681**	0.0001	-24637
tHcy (mg/dL)	0.426	0.653**	0.0001	279.69	0.248	0.498*	0.005	137.11	0.1879	0.433*	0.017	144.72
CRP (mg/L)	0.0216	0.147	0.439	0.015	0.0009	-0.031	0.873	0.0099	0.0073	0.086	0.651	0.0008

* Correlation is significant at the 0.05 level.

** Correlation is significant at the 0.01 level.

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التأثير الحيوي للزنك والكوبلت على جنس *Cypridopsis* من المستهلكات الاولية في النظام البيئي المائي.

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ABSTRACT

The present study deals with problem of Biological impact of elements Zn & Co as a $ZnCl_2$ & $CoCl_2$ on Ostracoda crustacean which live in freshwater. This was done by examining its effecting on Biological characters of individuals of *Cypridopsis*. Both element used at allowed concentration which recommended by FAO (2mg/l & 0.5 mg/l) and dupuled the concentration to (5, 10, 15, 20). The concentrations of both elements used in experiment were (2, 10,20,30,40 and 0,5, 2.5 ,5 ,7.5,10 mg/l). Tests were performed to assess the survival period, mortality percentage rate and body structure.

The result showed that there are serious effects for all levels of concentrations used in this study. It is started from 2 & 0.5 mg/l through marked effect on individuals of *Cypridopsais* during 6 - 12 hours with Zn & 12- 24 hours with Co respectively, and When the mortality rate measured the results showed that Individuals of *Cypridopsais* recorded 100% percentage at less than 6 - 12 hour, with Zn and 12- 48 hour with Co respectively. After administration also the results prepared that the elements had possibility to change the pH of water from 7.6 to 5.5 .That which lead to toxics effect lest on the body structure no also on the level of basic food of these crustacean and inhibited its role as bioclaner and important organisms in equilibrium of Hydroecosystem.

الخلاصة

تناولت الدراسة الحالية تأثير تراكيز مختلفة من عنصري الزنك والكوبالت بشكل $ZnCl_2$ ، $CoCl_2$ على الخصائص الحيوية لإفراد جنس *Cypridopsis* من القشريات الدرعية ، أستخدمت التراكيز المسموحة بيئيا في المياه من قبل منظمة FAO وهي (2 ملغم /لتر و 0.5 ملغم/لتر) لكلا العنصرين وأخرى مضاعفة بمقدار 5،10،15،20 مرة،وبذلك تصبح التراكيز المستخدمة 2،10،20،30،40 ملغم/لتر لعنصر Zn، و 0.5، 2.5، 5، 7.5 ، 10ملغم/لتر لعنصر Co. تم متابعة مستوى التأثير على فترة البقاء، نسبة الموت وتركيب الاغلفة الجسمية.

التأثير الحيوي للزنك والكوبلت على جنس *Cypridopsis* من المستهلكات الأولية في النظام البيئي المائي إبراهيم وثائر ومنتهى

أظهرت النتائج وجود تأثيرات جوهريّة على فترة البقاء بالمعاملة مع جميع التراكيز المستخدمة حتى على مستوى التراكيز المسموح بها (2 و 0.5 ملجم /لتر) حيث بدأ Zn في الدراسة، Co التأثير الحيوي بعد مرور 6 ساعات لغاية 12 ساعة مع الزنك و بين 12 - 24 ساعة مع بالتعاقب. وعند حساب نسبة الموت بين افراد القشري نجد انها سجلت نفوق تام 100% مع الزنك في أقل من 6-12 ساعة ، ومع الكوبلت 12-48 ساعة وحسب التراكيز المستخدمة. كذلك بينت النتائج أن كلا العنصرين كان لهما القابلية على تغيير الاس الهيدروجيني من 8 - 6.5 الامر الذي قاد الى تأثير شامل على اغلفة الجسم ولواحقه وكذلك على القاعدة الغذائية لهذه القشريات الامر الذي عطل دورها البيئي كمنظفات حيوية وكائنات مهمة في عملية التوازن داخل النظام المائي.

المقدمة

لكي تستمر الحياة بشكل طبيعي لا بد أن يكون هناك إتزان في الأنظمة البيئية، وحتى نقرب من إدراك وفهم طبيعة العلاقة التي تربط بين مكونات البيئة المحيطة بنا يمكننا تصور النظام البيئي على انه معادلة كيميائية إنعكاسية متزنة الطرفين اركانها المصادر الطبيعية للوسط وكتلة الاحياء التي تشغل هذا الوسط، ولذلك فأن تكامله يتميز بأن تكون له القدرة على إستيعاب التغير الطارئ عليه للحفاظ على كائناته ثم العودة إلى الوضع الطبيعي تدريجيا عند تغير الظروف المؤثرة عن طريق خاصية المرونة الذاتية التي يمتلكها. لكن التلوث من المشكلات الهامة التي تواجه مختلف النظم البيئية وتهدد توازنها من خلال احداث الخلل في ديناميكية العلاقات الحيوية وسلاسل الطاقة والغذاء التي تمثل محور بناء المادة العضوية ومسار نقل الطاقة البيئية بين مكونات الغلاف الحيوي، لأن التلوث في جوهرة عبارة عن تغير كمي ونوعي في مكونات البيئة الحية بحيث يؤدي هذا التغير إلى أختلال في توازن البيئة الطبيعي (1، 2)، ومن أكثر النظم تعرضاً لمعظم هذه الملوثات هو الوسط المائي، لكون الماء عامل مشترك بين كل أنشطة الانسان والاغلفة الحيوية الأخرى ولهذا يعتبر متلقي لنواتج كل هذه العمليات (3)، (4). ومن بين المجاميع الحيوية المهمة التي تتعرض لهذا التلوث القشريات الصدفية أو الدرعية Ostracoda ، اللاقريات الواسعة الانتشار في البيئات البحرية والمياه العذبة، والتي تمتاز أفرادها بوجود درقة أو قشرة تغطي أجسامها ذات مصراعين وهي بذلك تشبة المحارات الدقيقة، والجذع غير واضح التعقيل وتكون زوائد الرأس مسئولة بشكل أساسي عن الحركة والتغذية، كما ينتهي الجذع في هذه الحيوانات بشعبتين ذيليتين ومنها ما ليس له جهاز تنفسي خاص ولكنها تعمل على تبادل الغازات في الوسط الذي تعيش فيه، كما تختلف فيما بينها من حيث التركيب

واللون وطريقة المعيشة وعادات التغذية، فمنها ذات أغذاء ترشيحي أو بلعمي أو مفترسة، وهي كمعظم القشريات حرة المعيشة وتحتل أهمية بيئية متميزة كما يشير الباحثون (7، 6، 5، 8) لعدة أسباب منها:

- 1- تعتبر ركن اساسي في السلاسل الغذائية المائية لأنها تحتل المستوى الثانير كمفترسات للطحالب والبكتريا ومرشحات للمواد العضوية
- 2- تعتبر مصدر هام للبروتينات حيث تكون غذاء مفضل للأسماك التي بدورها تمتد الإنسان بالبروتينات.
- 3- تلعب دورا هاما في عملية تنقية المياه وخاصة من المخلفات العضوية ومختلف انواع البكتريا.
- 4- أهميتها في دراسة التطور وعلم الحفريات والتنقيب عن البترول والتغيرات المناخية وغيرها من الدراسات العملية التطبيقية.
- 5- تعتبر كواشف بيئية لدراسة التلوث بمختلف اشكاله لكونها عالية الحساسية لمعظم الملوثات.

المعادن الثقيلة ودورها في البيئة المائية:

تعرف المعادن الثقيلة على إنها عناصر يتعدى وزنها الذري 100 و تتعدى كثافتها 5غم/سم³، وترجع خطورتها إلى كونها عناصر إنتقالية، ومعنى هذا إن لها القدرة على تكوين مركبات ثابتة مع مجموعة كبيرة من المركبات العضوية وغير العضوية الموجودة في أجسام الكائنات الحية. ولذلك يعتبر التعرض لها مشكلة خطيرة وحادة لميل هذه المركبات للتجمع والتراكم داخل الأنظمة البيئية الحية المختلفة (9). كما أن طبيعة الأضرار وحجمها يعتمد بدرجة كبيرة على ما يمكن تسميته بالدور الكيميائي- الحيوي لأي من هذه العناصر في العمليات الحيوية، بمعنى أن الصفات الكيميائية- الحيوية للعناصر النادرة تلعب دور مهم في تحديد طبيعة الأضرار الناتجة عنها، لأن ذلك يرتبط أساسياً بالعلاقة الوثيقة بين خصائص العنصر وسلوكه في الوسط البيئي أودخوله الاجسام الحيوية كعنصر بديل لبعض العناصر الضرورية للنمو وبناء الخلايا والتراكيب الجسمية (1، 10) وبالطبع فإن الضرر الناتج من هذه العناصر يزداد بزيادة تركيزها في الجسم وتظهر تأثيراتها على الكائن الحي تبعاً لنوع لكائن وطبيعة العنصر ونسبة الزيادة في الوسط، كما أن استخدام هذه المعادن كأملح أو مواد سامة يؤدي إلى مشاكل لا حصر لها، وعندما تنتشر في البيئة فأنها في العادة لا تزاح أو تتلف بسرعة كما أنها لاتفقد سميتها نتيجة نشاطات الأيض، وبناء على هذا لابد من العناية والمراقبة عند تدفق هذه المواد إلى البيئة .

التأثير الحيوي للزنك والكوبلت على جنس *Cypridopsis* من المستهلكات الأولية في النظام البيئي المائي إبراهيم وثائر ومنتهى

ونتيجة لزيادة نشاطات الإنسان المختلفة أدى ذلك الى زيادة تلوث البيئة المائية بكثير من المعادن الثقيلة السامة، سواء كانت مياه جوفية أو سطحية كالأنهار والبحيرات والبحار والمحيطات، أي أن جميع أشكال المياه على سطح الأرض قد نالها جزء من هذا التلوث بطريقة أو بأخرى. والتلوث هنا يحدث إما مباشرة بإلقاء النفايات في مصادر المياه أو بالإرتشاح من التربة المجاورة لمصدرها، وتتوزع المعادن الثقيلة بعدة مستويات في النظام المائي اما في المناطق السطحية أو القاعية أو تبقى عالقة بين طبقاته، وتلعب الأحياء الدقيقة دوراً هاماً في تحديد الشكل التي توجد عليه المعادن الثقيلة في المحتوى المائي، فبعضها يترسب بواسطة النشاط البيولوجي لبعض أنواع البكتيريا التي تنتج منتجات كيميائية تتفاعل مع المعادن الذائبة في الماء أو الموجودة على هيئة رواسب معدنية غير ذائبة ويتم ذلك عن طريق تكوين كبريتيد الهيدروجين، ومن المعادن القابلة للترسيب على هيئة كبريتيد هي النحاس والزنك والرصاص والحديد. كما تعمل الكثير من الأحياء المائية كعامل مساعد في أتمام بعض التفاعلات المتعلقة بالمعادن أو في أستخلاص المعادن التي لها قيمة إقتصادية، وتشمل تفاعلات الأكسدة والأختزال والأكلية (11،12).

العناصر المدروسة:

الزنك (Zn): يوجد الزنك في الوسط بنسبة 0.02 % من القشرة الأرضية كما يوجد في خامات مختلفة بالإضافة إلى وجوده في التربة والنبات والحيوان وفي الفحم المستخرج من الأرض، حيث انه من خلال الأكسدة والأنحلال في الماء يتحول وينتقل في المياه السطحية والباطنية بكميات كبيرة ليترسب في طمي الأنهار على شكل كبريتيد أو أكسيد أو كربونات الزنك . وللزنك تأثيرات سامة على جسم الإنسان والحيوان والنبات تعتمد على الفترة الزمنية التي يتعرض فيها الكائن الحي لتراكيزه وأمتصاصه في الجسم، و يعتمد ذلك على عدة عوامل منها حاجة الجسم له، وجود العناصر المسببة للتداخل معه مثل Cu و Cd . ويمكن للزنك أن يلوث الماء والهواء والتربة والأغذية، فزيادة تركيزه في أجسام الكائنات عن النسبة الطبيعية تؤدي إلى التسمم، وتتعلق حدة التسمم بطبيعة الجسم وعمر الكائن المعرض (13، 14).

الكوبالت (Co): يوجد الكوبالت في الطبيعة بنسبة قليلة في التربة من 1- 40 ppm كما يمكن أن يوجد بكميات أكبر ،هذا إضافة إلى وجوده في النباتات والحيوانات والمياه، فقد وجد على سبيل المثال بان 37 % من مجموع العينات الـ (727) المأخوذة من الأنهار والبحيرات في الولايات المتحدة الأمريكية، تحتوي بشكل متوسط على 1 ppm ، أما في الهواء فقد وجد بأن تركيزه يقدر بحوالي 0.006 ug/m^3 ، يستخدم الكوبالت في عديد من الصناعات، كما في

صناعة الفولاذ و السبائك مع Mo- W- Be- Al- V- Ni- Cr- Cu التي تستخدم في صناعة السكاكين وقطع الطائرات والدهانات وغيرها. يحدث تلوث الوسط به ويتحقق التسمم بالكوبالت أثناء أستخراجه وانتشاره بكمية كبيرة على شكل جزيئات قابلة للأنحلال. (1، 15).

الجنس المدروس: *Cypridopsis*

حيوان قشري صغير يعيش في المياه العذبة كالبرك والمستنقعات، جسمه مغطى بدرقة ذات مصراعين ويتم فصل هذان المصراعان بمفصل ظهري وعضلة مقربة، والدرع بيضوي في المنظرين السطحي والبطني ويبلغ حوالي 0.62 ملم وذو أربع مناطق داكنة، المصراع الايسر اطول قليلا من الايمن ومتراكب عليه بطنيا وفي بعض الاحيان على العكس، أهلاب الاستشعار للامس الاول نامية بشكل جيد ومختزلة في بعض الانواع، القطعة الطرفية لملمس الفكوك المساعدة اسطوانية أو متطاولة، الصفيحة الاهتزازية للقدم الصدري الاول تحمل (1-5) خيوط، القدم الصدري الثاني ذو 5 قطع، جذع القدم الذنبى مثلث الشكل. يضم هذا الجنس ثلاثة انواع سجلت لأول مرة للعلم في العراق وهي *C. reticulates*, *C. euphraticus*, *C. iraqensis* تم التعرف عليها في عدة مواقع في منطقة الفرات الاوسط وجنوب بغداد (5).

المواد وطرائق العمل

جمع العينات وتحضير المزارع الدائمة:

جمعت العينات التي تم دراستها من بعض المسطحات المائية حول مدينة بابل وسط العراق بواسطة الشباك الكاشطة من الطبقة السطحية للقاع وتحت البقايا النباتية المتحللة التي تمثل اماكن وفرة هذه القشريات كما ذكرت (5)، وضعت العينات في حاويات بلاستيكية ونقلت مباشرة إلى المختبر وهناك وزعت إلى مزارع دائمة في أحواض زجاجية حجم 30x30x60 سم³ بصورة مستقلة، وتركت العينات لمدة اسبوعين في المختبر داخل وسط محضر لغرض تأقلم الكائنات مع الظروف المخبرية والتخلص التدريجي من المواد الملوثة كطريقة للحجر الصحي حيث تم استبدال الماء كل ثلاثة ايام وكما ذكر (9). تم عزل الجيل الاول من القشريات والثاني والثالث، وأخذت القشريات التي أخضعت للتجربة من الجيل الرابع. ووزعت في كؤوس زجاجية نظيفة ومعقمة بحجم 1 لتر تحتوي تربة وماء ومواد عضوية و كما في الخطوات التالية: وضع تربة بعمق من 5 سم (غسلت بالماء المقطر عدة مرات)، وماء لغاية 300 سم (ماء الشرب) مسحوب الايونات بأجهزة تنقية المياه نوع (Reverse Osmosis System, T33) كمية من المغذيات المختلفة مثل الطحالب وحيدة الخلية من نوع *Chlorella*، عوامل منشطة للوسط تمثلت بالخميرة بتركيز 0.5 جم/لتر بمقدار 1 ملل أسبوعياً، سماد عضوي بتركيز 0.5 جم/لتر

التأثير الحيوي للزنك والكوبلت على جنس *Cypridopsis* من المستهلكات الأولية في النظام البيئي المائي
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جدول (2) فترة بقاء ونفوق أفراد جنس *Cypridopsis* تحت تأثير كلوريد الكوبلت $CoCl_2$

التركيز ملغم /لتر	قبل المعاملة	بعد 3 ساعة	بعد 6 ساعة	بعد 12 ساعة	بعد 24 ساعة	بعد 2 يوم	بعد 4 يوم	بعد 6 يوم	بعد 8 يوم	بعد 10 يوم	بعد 12 يوم	بعد 14 يوم	بعد 16 يوم	بعد 18 يوم	بعد 20 يوم
الشاهد	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
0.5	✓	✓	✓	✓	✓	×	×	×	×	×	×	×	×	×	×
2.5	✓	✓	✓	✓	×	×	×	×	×	×	×	×	×	×	×
5	✓	✓	✓	✓	✓	×	×	×	×	×	×	×	×	×	×
7.5	✓	✓	✓	✓	×	×	×	×	×	×	×	×	×	×	×
10	✓	✓	✓	✓	✓	×	×	×	×	×	×	×	×	×	×

✓ بقاء ، × نفوق

ثانياً : نسبة هلاك الأفراد (النفوق) تحت تأثير المعادن المستخدمة:

عند متابعة الجدول (3) الذي يبين نسبة النفوق تحت تأثير عنصر الزنك نجد ما يلي: عند التركيز 2 ملغم/لتر لم يسجل أي هلاك خلال 3 ساعات الأولى بينما هلك حوالي 80 % من الحيوانات بعد مرور 6 ساعات ، وسجلت نسبة 100% بعد مرور 12 ساعة، وعند التركيز 10 ملغم/لتر سجلت النسبة 40 % بعد مرور 3 ساعات والنسبة 100 % بعد 6 ساعات ، أما التركيز 20 ملغم/لتر سجل النفوق بنسبة 60% بعد مرور 3 ساعات و 100% بعد 6 ساعات. وعند التراكيز العالية (30،40) ملغم/لتر حصل النفوق بعد مرور 3 ساعات بنسبة 60 % و 100% بعد 6 ساعات عند تركيز 30 ملغم/لتر، أما التركيز 40 ملغم/لتر فكانت نسبة النفوق بعد 3 ساعات 20%، و 60 % و 100% بعد مرور 6، 12 ساعة على التوالي.

جدول (3) نسبة نفوق أفراد جنس *Cypridopsis* تحت تأثير كلوريد الزنك $ZnCl_2$

التركيز/ملغم/ لتر	3 ساعة	6 ساعة	12 ساعة	24 ساعة
2	0	80 %	100 %	-
10	40 %	100 %	-	-
20	60 %	100 %	-	-
30	60 %	100 %	-	-
40	60 %	20 %	100 %	-

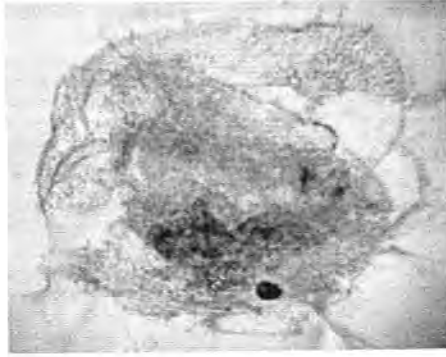
وعند المقارنة مع نتائج الجدول (4) والذي تبين نسبة نفوق الأفراد تحت تأثير عنصر الكوبالت Co نجد أن النتائج كانت كما يلي : عند التركيز 0.5 ملغم/لتر لم يسجل أي نفوق خلال 3 ساعات الأولى بينما نفق حوالي 40% من الحيوانات خلال 6، 12 ساعة اللاحقة، ونسبة 100% بعد 24 ساعة، وعند التركيز 2.5 ملغم/لتر سجلت نسبة النفوق (40%، 100%) بعد 12، 24 ساعة على التوالي ، وعند زيادة التركيز إلى 5 ملغم/لتر كان نفوق القشريات بعد 12، 24، 48 ساعة ونسبة (40%، 20%، 100%) على التوالي، وفي حالة التراكيز العالية 7.5، 10 ملغم/لتر سجل النفوق بعد 6، 12 ساعة بنسبة (60%، 100%) بالنسبة للتركيز 10 ملغم/لتر. أما التركيز 15 ملغم/لتر كانت نسبة النفوق بعد 6 ساعات 40%، وبعد مرور 12، 48 ساعة أصبحت (60%، 100%) على التوالي، وعند تحليل هذه النتائج بناءً على نتائج الجدولين 3، 4 نجد أن التراكيز المختلفة رغم تحقيقها لنسبة هلاك 100% لجميع الأفراد من البالغات والصغار لكنها اختلفت في توزيع هذه النسبة خلال الفترة من بداية التجربة اليوم الثاني الذي يمثل الحد الأعلى للبقاء وهذا يتفق مع التفسير الذي ذكرناه عند دراسة فترة البقاء حيث كان تأثيرها متفاوت أيضا وربما يعود ذلك الى الاختلاف في كفاءة الافراد ودرجة مقاومتها لوجود العنصر ونشاطها في التغذية والحركة داخل الوسط وكذلك مقدار التغير في قيم الاس الهيدروجيني الذي سجل انحرافا نحو الحامضية من 8.5 في الوسط الشاهد الى حوالي 6.5 بعد اليوم الثاني من المعاملة بالمعادن المستخدمة في الدراسة وهذا يقود الى التسريع في شدة تأثير المعادن على الاحياء المائية، وهذه الاستنتاجات تتفق مع ماذكره الباحثون (9)، (10، 20).

جدول (4) نسبة نفوق أفراد جنس *Cypridopsis* تحت تأثير كلوريد الكوبالت $CoCl_2$.

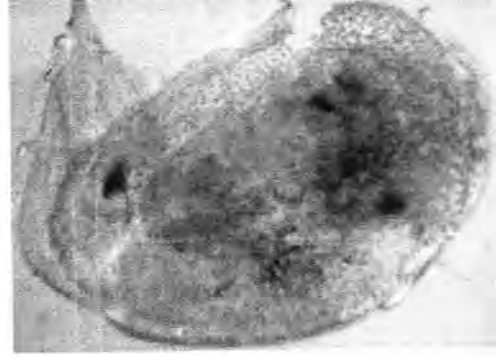
التركيز ملغم/لتر	بعد 3 ساعة	بعد 6 ساعة	بعد 12 ساعة	بعد 24 ساعة	بعد 2 يوم	بعد 4 يوم	بعد 6 يوم
0.5	0	40 %	40 %	100 %	-	-	-
2.5	0	0	40 %	100 %	-	-	-
5	0	0	40 %	20 %	100 %	-	-
7.5	0	60 %	100 %	-	-	-	-
10	0	40 %	60 %	60 %	100 %	-	-

التأثير الحيوي للزنك والكوبلت على جنس *Cypridopsis* من المستهلكات الأولية في النظام البيئي المائي إبراهيم وثائر ومنتهى

ثالثاً: متابعة تغيرات شكل الجسم ولواحقه وتحطم الأغلفة اثر التعرض لعناصر Zn , Co من خلال استعراض الصور من (1-5) التي تم أخذها لكل مرحلة من مراحل تأثير التراكيز (2،10،20،30 و 40 ملغم/لتر) من عنصر الزنك على أفراد القشري نجد النتائج التالية: في الصورة (1) بداية انفصال الصدفتين من الناحية البطنية وتحلل المحتويات وهذا التأثير للتركيز 2 ملغم/لتر خلال اقل من 12 ساعة. أما في الصورة (2) يظهر التأثير أشد حيث نلاحظ تكسر الصدفة التي تحيط بالجسم وتحطم اللواحق وتلاشي منطقة إرتباط السيتوبلازم وهذا التأثير للتركيز 10 ملغم/لتر خلال اقل من 6 ساعات.

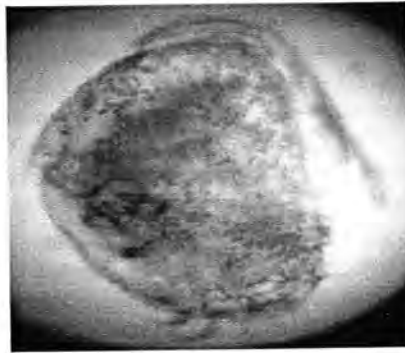


الصورة (2)

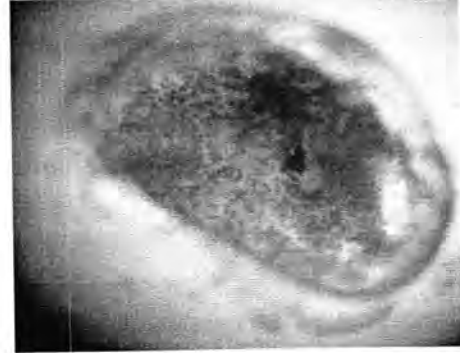


الصورة (1)

من الصورة (3) يظهر تأثير التركيز 20 ملغم/لتر كان أسرع وذلك خلال أقل من 6 ساعات، حيث يتبين تكور الجسم وسحب اللواحق مع بداية تصدع للصدفة من الجهة البطنية وظهور بقع شفافة للدلالة على تأثر المادة الكلسية. أما الصورة (4) للتركيز 30 ملغم/لتر فيظهر فيها انفصال للصدفة من الجهة البطنية في النصف الأول من الجسم مع بداية تحلل واضحة وهذا التأثير خلال اقل من 6 ساعات.



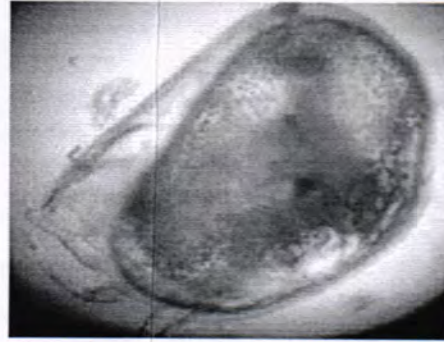
الصورة (4)



الصورة (3)

في الصورة (5) يتضح تأثير التركيز 40 ملغم/لتر خلال اقل من 6 ساعات بانفصال تام للصدفة من الجهة البطنية الخلفية أكثر من الأمامية وبداية لتغير اللون، وتأثر واضح لمنطقة

الارتباط السيتوبلازمي، وظهور بقع بيضاء شفافة مما يبين أن التأثير على المادة الكلسية أكبر من التراكيز السابقة.

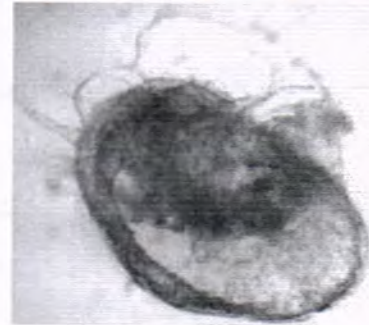


الصورة (5)

وعند متابعة تأثير عنصر الكوبلت بتراكيز (10,7.5,5.2.5,0.5) على القشري المدروس في مراحل زمنية مختلفة من المعاملة، نجد أن التأثيرات كانت متباينة بينه وبين عنصر الزنك وكما مبين في الصور من 6-10 حيث كانت التأثيرات كمايلي: الصورة (6) بدأ تأثير التركيز 0.5 ملغم/لتر خلال أقل من 24 ساعة حيث يظهر تغير اللون وتحلل المحتويات الداخلية وخروجها من الناحية البطنية وإنحسار الأحشاء في أحد جوانب الصدفة. وعند التركيز 2.5 ملغم/لتر وكما في الصورة (7) نلاحظ أن التشوهات قد بدأت خلال أقل من 12 ساعة حيث يظهر انفصال الصدفة من الأعلى، وشحوب اللون، وتحلل المحتويات الداخلية.



الصورة (7)



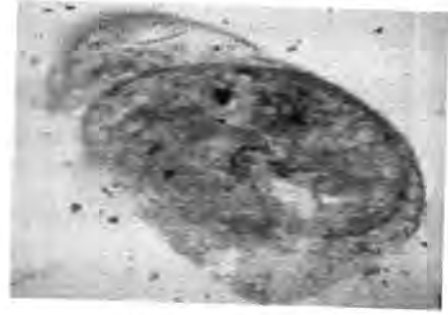
الصورة (6)

وفي الصورة (8) يتضح تأثير التركيز 5 ملغم/لتر خلال فترة أقل من 12 ساعة بظهور انفصال للصدفة في الثلث الأمامي للجسم، وتحلل للمحتويات الداخلية. أما في الصورة (9) الت توضح تأثير التركيز 7.5 ملغم/لتر خلال أقل من 24 ساعة حيث يظهر انفصال للصدفة من الناحية الظهرية وأندفاع التراكيب الداخلية (الأحشاء) لأحد الأطراف وبداية لتحلل المحتويات الداخلية.

التأثير الحيوي للزنك والكوبلت على جنس *Cypridopsis* من المستهلكات الأولية في النظام البيئي المائي إبراهيم وثائر ومنتهى

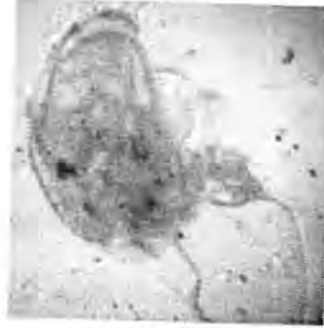


الصورة (9)



الصورة (8)

في الصورة (10) يتضح تأثير التركيز 10 ملغم/لتر خلال فترة أقل من 6 ساعات حيث يظهر انفصال مبدئي للصدفة من الناحية البطنية الأمامية، وبداية لتغير اللون، وظهور البقع الشفافة نتيجة لتأثر المادة الكلسية للصدفة بشكل أكبر من التراكيز السابقة.



الصورة (10)

ومن تحليل النتائج المبينة في الجداول 1، 2، 3، 4 والصور التوضيحية نجد أن هنالك تذبذب في شدة التأثير بين التراكيز المختلفة سواء على فترة البقاء أو تركيب أغلفة الجسم حيث ظهر على عكس ما هو متوقع، حيث كان التأثير على البالغات أسرع منه على الصغار وربما يعود ذلك لكون عنصر الزنك من العناصر الضرورية للحياة وقد يشترك في عدد كبير من الفعاليات الجسمية، وربما تم سحبه مع الكالسيوم لبناء قشرة الجسم وهذا ما جعل تأثيره على الصغار أقل وربما البالغات لا تحتاج لسحب الكالسيوم حيث تم فيها إكمال بناء القشرة مما يدفع بالزنك للدخول إلى الجسم بشكل أكبر نتيجة للسلوك المعروف لهذا العنصر بتكوين مركبات مشتركة مع العناصر الأخرى الموجودة في الوسط المائي وهذا يتفق مع آراء الباحثين (7، 9). أما بما يخص عنصر الكوبلت لربما يعود التأثير الشديد لكون جزيئات العنصر قابلة للانحلال كلما كانت كميته كبيرة في الوسط. وعند المقارنة بين تأثير كلاً من العنصرين *Zn*, *Co* نجد من النتائج المرفقة بالجدول أن للزنك تأثير أكبر على أفراد القشري *Cypridopsis* ويعود ذلك لخواص الزنك حيث أنه له أهمية غذائية ومستواه في الوسط يزيد من كمية امتصاصه من قبل الأحياء المائية المختلفة وخاصة الطحالب والدايتومات. وهذا يتفق مع دراسات الباحثين

(13، 16) عند تفسير نتائج تأثير الزنك على مختلف الاحياء المائية. كذلك تبين نتائج الجداول 5، 6 أن التراكيز المختلفة رغم تحقيقها لنسبة هلاك 100% لجميع الأفراد لكنها اختلفت في توزيع هذه النسبة خلال الفترة من بداية التجربة حتى اليوم السادس الذي يمثل الحد الأعلى للبقاء. ومن خلال إلقاء نظرة على النتائج نجد كذلك أن نسبة الهلاك مختلفة بين الافراد تحت تأثير التراكيز المختلفة، وهذا يتفق مع التفسير الذي ذكرناه عند دراسة فترة البقاء حيث كان تأثيرها بما يتعلق بعنصر الزنك وهذا يتفق مع ماذهب اليه الباحثون (14) الذين اشاروا الى أن تأثير وسمية الزنك يرتبط بعمر الكائن الحي وتركيز العنصر ونوعية الوسط، كذلك يتفق مع أراء الباحثين (15، 17، 18) الذين اكدوا على أن وجود المعادن الثقيلة في الوسط المائي يعمل على تغير سلوك الكائن الحي من حيث النشاط العام ونوعية التغذية من خلال التأثير على طبيعة الاس الهيدروجيني بالاتجاه الحامضي كما أن سلوك العنصر هو الاخر يتأثر بتغير نوع الوسط البيئي وبذلك تتأثر عملية النفاذ المباشر أو التأثير على الاغلفة الجسمية وهذا التفسير يتفق مع ماذكره الباحثون (3، 7، 14، 20، 21) من خلال دراساتهم على مستويات غذائية مائية مختلفة تمثلت بالهائمات النباتية والحيوانية و الطحالب المختلفة والقشريات المختلفة.

كما يمكن تفسير تغير نسب التأثير في الوسط البيئي وعلى القشري المدروس الى دور الأحياء الدقيقة الموجودة في وسط التغذية والتي تلعب دوراً هاماً في تحديد الشكل التي توجد عليه المعادن الثقيلة في المحتوى المائي، فبعض المعادن تترسب بواسطة النشاط البيولوجي لبعض أنواع البكتيريا التي تنتج منتجات كيميائية تتفاعل مع المعادن الذائبة في الماء أو الموجودة على هيئة رواسب معدنية غير ذائبة، ويتم ذلك عن طريق تكوين كبريتيد الهيدروجين. ومن المعادن القابلة للترسيب على هيئة كبريتيد هي معادن النحاس والزنك والرصاص والحديد. كما تعمل الكثير من الأحياء المائية كعامل مساعد في أتمام بعض التفاعلات المتعلقة بالمعادن أو في استخلاص المعادن التي لها قيمة إقتصادية، وتشمل تفاعلات الأكسدة والأختزال والألكلة ، وهذا يتفق مع ماذكره الباحثون (3، 11، 22) .

أما نسبة الهلاك عند المعاملة بكلوريد الزنك للتركيز 2 ملغم/لتر فكانت 80%، 100% عند أقل من 12 ساعة، وللتركيز 10 ملجم/ لتر %، 100% عند أقل من 6 ساعات، وللتركيزين 20، 30 ملغم/ لتر 60%، 100% عند أقل من 6 ساعات، وللتركيز 40 ملغم/لتر و 20 %، 100% عند أقل من 12 ساعة. وعند المعاملة بكلوريد الكوبالت كانت نسبة الهلاك للتركيزين 0.5، 2.5 ملغم/لتر هي 40%، 100% عند أقل من 24 ساعة، وللتركيز 5 ملجم/لتر 20%، 40%، 100% عند أقل من 48 ساعة، وللتركيز 7.5 ملغم/لتر كانت النسب 60%، 100% عند أقل من 12 ساعة، وللتركيز 10 ملغم/لتر كانت النسب 40%، 60%، 100% عند أقل من 48 ساعة.

التأثير الحيوي للزنك والكوبلت على جنس *Cypridopsis* من المستهلكات الأولية في النظام البيئي المائي إبراهيم وثائر ومنتهى

وعند استعراض هذه النتائج نراها متناسقة مع طبيعة التأثير السابق على فترة البقاء الذي يعتمد على مقدار التركيز وعمر الكائن الحي ونشاطه في معظمها ولكن لوحظ أن النسبة قد تغيرت بعض الشيء عند المقارنة بين التراكيز الواطئة والمرتفعة لنفس العنصر، وربما يعود ذلك الى كمية التركيز التي تدخل الجسم ودرجة تحسس الحيوان لوجود العنصر في الوسط عندما يكون بدرجة قليلة أو مرتفعة وماهي آلية التعامل معه، وهذا يتفق مع ماذهب اليه الباحث (9، 13) حيث وجد أن هنالك اختلاف في تأثير كلا من الامونيوم واللكروميوم على انواع مختلفة من القشريات ومنها القشريات الدرعية وهذا الاختلاف استند الى تباين التراكيز القليلة والمتوسطة والعالية من حيث شدة التأثير وزمنه ونوعية التأثير وخاصة في نسبة الموت والتأثير على الاغلفة الجسمية.

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تأثير إضافة أوراق نبات الزعتر (*Thymus vulgaris*) المطحونة إلى العليقة في بعض الصفات الدموية لفروج اللحم

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ABSTRACT

This study was conducted to investigate the influence of adding (*Thymus vulgaris*) leaves powder to the diet on certain blood traits of broiler chickens during a period from 15-12-2009 to 10-2-2010. A total of 300 broiler chicks, one day old were used and randomly allocated to four treatment groups (3 replicates per group; 25 chicks each). (*Thymus vulgaris*) leaves powder was supplemented to the diet of broiler chickens at the levels of 0 (control group, T₁), 500 mg/Kg of diet (T₂), 750 mg/Kg of diet (T₃) and 1000 mg/Kg of diet (T₄). These treatments were applied during the entire period of experiment (8 weeks). Blood traits included in this study were red and white blood cell counts, hematocrit, hemoglobin concentration, differential leucocyte count. Results revealed that supplementation to the diet of broiler chickens with (*Thymus vulgaris*) leaves powder (T₂, T₃ and T₄) resulted in significant ($p < 0.01$) increase in red and white blood cell counts, hematocrit and hemoglobin concentration and significant decrease in heterophil to lymphocyte ratio. Furthermore, the improvement in blood characteristics included in the president study was associated with the increasing of concentration of (*Thymus vulgaris*) leaves powder to the diet since the best means of studied blood traits were recorded for the high concentration of (*Thymus vulgaris*) leaves powder to the diet (T₄) in comparison with the other two treatments of (*Thymus vulgaris*) leaves powder to the diet (T₂ and T₃).

الخلاصة

تم إجراء هذا البحث لدراسة تأثير إضافة أوراق نبات الزعتر المطحونة إلى العليقة في بعض الصفات الدموية لفروج اللحم خلال الفترة من 15-12-2009 و لغاية 10-2-2010. تم استخدام 300 فرخ فروج لحم بعمر يوم واحد وزعت عشوائياً على أربع معاملات (بواقع 3 مكررات لكل معاملة، 25 فرخ لكل مكرر). وكانت المعاملات كالاتي: المعاملة الأولى: تمثل مجموعة السيطرة (T₁)، والمعاملات الثانية (T₂) والثالثة (T₃) والرابعة (T₄): تمثل إضافة أوراق نبات الزعتر المطحونة إلى العليقة بمستوى 500، 750 و 1000 ملغم / كغم علف على التوالي. طبقت المعاملات المذكورة أعلاه طول فترة التربية (8 أسابيع) وتمت دراسة تأثير المعاملات على

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نهاد

عدد كريات الدم الحمر والبيض ومكداس الدم وتركيز الهيموغلوبين والعدد التفريقي لكريات الدم البيض. أشارت نتائج الدراسة إلى إن المعاملة بأوراق نبات الزعتر المطحونة (T2 و T3 و T4) أدت إلى زيادة عالية المعنوية ($p < 0.01$) في عدد كريات الدم الحمر والبيض وتركيز الهيموكلوبين ومكداس الدم وانخفاض عالي المعنوية ($p < 0.01$) في نسبة الخلايا المتغايرة إلى الخلايا اللمفية. إضافة لذلك فإن التحسن في صفات الدم التي شملتها الدراسة الحالية كان مترافقاً مع زيادة تركيز أوراق نبات الزعتر المطحونة في العليقة، إذ أن التركيز 1000 ملغم من أوراق نبات الزعتر المطحونة في العليقة (T4) قد سجل أفضل المعدلات للصفات المدروسة مقارنةً بالتركيزين 500 و 750 ملغم من أوراق نبات الزعتر المطحونة في العليقة (T2 و T3).

المقدمة

نبات الزعتر أو السعتر ويسمى أيضاً الصعتر هو نبات مشهور من الفصيلة الشفوية وتكثر زراعته بصفة عامة في دول حوض الأبيض المتوسط ويطلق عليه صفة مفرح الجبال لأنه يعطر الجبال برائحته الذكية وله رائحة عطرية قوية و طعمه حار مر قليلاً (1) ، وتنتشر زراعة نبات الزعتر في الأردن وسوريا وشمال العراق ويعد الزعتر *Thymus vulgaris* احد النباتات الطبية المهمة وهو من الأعشاب التي تتميز بكونها مصدراً طبيعياً للمواد المضادة للأكسدة (2) إذ يحتوي على مواد أساسية مضادة للأكسدة وهي الفينولات والفلافونيدات (3) وان عملية الأكسدة الذاتية Autooxidation يمكن أن توقف أو تثبط بإضافة مواد مضادة للأكسدة ويعتبر الزعتر احد النباتات العطرية والطبية الذي يتم استخدامه في الأغذية لمنع حدوث الأكسدة الذاتية (4) والجزء الفعال والمستخدم طبياً في نبات الزعتر هو الأوراق والقمم النامية الزهرية حيث تحتوي الأوراق على زيوت طيارة volatile oils بنسبة (5 - 25 %) ويحتوي هذا الزيت على حوالي 55% من المواد الفينولية واهما الثايمول Thymol والكارفكرول Carvacrol اللذان تعزى لهما الفوائد الطبية لنبات الزعتر (5) وكذلك على مواد صمغية راتنجية Resins وتانين Tanin وحامض اللينوليك Linoleic acid (6) ويحتوي نبات الزعتر على المواد الفعالة التالية : Thymol بنوعيه phenols وهو المهم طبياً و Borneol, menthone, carvacrol و pinene, cymene, linalool . ومن أهم استخدامات أوراق نبات الزعتر الطبية أشار (7) إلى إن أوراق الزعتر المطحونة تستخدم بوصفها مادة لها خواص حافظة من التلف حيث تستخدم في حفظ المستحضرات الطبية والتجميلية وإضافة رائحة عطرية للمستحضر الطبي إضافة إلى دورها في حماية الجلد من منع نمو الجراثيم والفطريات حيث تعمل على تثبيط نمو الجراثيم الموجبة والسالبة (8) عندما يكون تركيز الثايمول 38,60% أما من جانب تأثيرات أوراق نبات الزعتر

على الكلوكوز فلا بد من الإشارة إلى دراسة (9) حيث أدى إلى انخفاض تركيز الكلوكوز في مصل دم فروج اللحم عند المعاملة بأوراق نبات الزعتر ومن جهة أخرى فقد أشارت (10) إلى أن استخدام أوراق نبات الزعتر أدى إلى حصول زيادة معنوية في أوزان الجسم للجردان المصابة بداء السكري مع انخفاض في مستوى الكلوكوز والكوليسترول والكليسيريدات الثلاثية ومستوى الشحوم الواطنة الكثافة أما (11) فقد بين إلى إمكانية استخدام نبات الزعتر كمسكن للمغص المعوي ولمعالجة التهاب المعدة والأمعاء وقرحة المعدة فهو منظم لوظائف الجهاز الهضمي كما يستخدم الثايمول داخلياً كطارد للديدان فضلاً عن استخدامه في تعقيم الفم والأسنان والجلد وهو يعتبر مضاداً للتهابات (12). كما ثبت فعالية نبات الزعتر في علاج الصداع والشقيقة وحالات التهاب الشعب المعدي (13). إن أعشاب الزعتر أو موادها الأولية آمنة الاستعمال بصورة عامة ولم يظهر لحد الآن تأثيرات سلبية أثناء استخدام الزعتر، لذا يهدف البحث الحالي إلى دراسة اثر إضافة أوراق نبات الزعتر المطحونة إلى العليقة في بعض الصفات الدموية لفروج اللحم .

المواد وطرائق العمل

أجريت هذه الدراسة للمدة من 2009-12-15 و لغاية 2010-10-2 وذلك في حقل دواجن أهلي تابع إلى القطاع الخاص في محافظة بابل-الهاشمية. واستخدم فيها 300 فرخ فروج اللحم ، تم تربية الأفراخ وفق نظام التربية الأرضية في قاعة تحتوي على أربعة حظائر ، حيث قسمت كل حظيرة بحواجز سلكية مشبكه إلى ثلاثة أقسام كل قسم بعده 2 X 2 م ، إذ تم توزيع الأفراخ عشوائياً على 4 معاملات يتكون كل منها من 3 مكررات إذ احتوى كل مكرر على 25 فرخاً (75 فرخاً لكل معاملة) . تم تقديم العلف للطيور بشكل حر ، إذ قدمت عليقتان ، عليقة البادئ من عمر 1 - 4 أسابيع وعليقة النمو من عمر 4 - 8 أسبوع (الجدول 1). تم إضافة أوراق نبات الزعتر المطحونة و التي تم شرائها من الأسواق المحلية في بغداد-الشورجة إلى عليقة الأفراخ اعتباراً من عمر يوم واحد وبتراكيز 0 (مجموعة المقارنة ; T1) ، 500 ملغم / كغم علف (T2) ، 750 ملغم / كغم علف (T3) و 1000 ملغم / كغم علف (T4). تم جمع الدم في الأسبوعين 6 و 8 من 15 طير من كل معاملة (5 طيور من كل مكرر) بصورة عشوائية إذ تم جمع الدم من الوريد العضدي حيث تم استخدام أنابيب حاوية على مانع تخثر Potassium EDTA لمنع تخثر الدم ، تم حساب مكداس الدم باستخدام أنابيب شعيرية خاصة حاوية على مانع تخثر حسب الطريقة التي أشار إليها (14). وتم تقدير تركيز الهيموغلوبين عن طريق تحويله إلى مركب معقد Cyanomethemoglobin باستعمال كاشف دراينكنز Drabkins reagent وحسب الطريقة التي أشار إليها (15). و قدر عدد خلايا الدم الحمر والبيض وفقاً للطريقة التي أشار إليها (16) . تم تقدير نسبة الخلايا المتغايرة / الخلايا اللمفية (Heterophil / lymphocyte ratio)

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نهج

باستخدام شرائح زجاجية حيث يتم وضع قطرة من الدم على الشريحة الزجاجية ويتم نشرها بعناية فائقة بشريحة زجاجية أخرى توضع فوق قطرة الدم وتسحب فوق الشريحة الأولى بزاوية 45 درجة دون الضغط عليها بقوة وتترك لتجف بمعدل 10 دقائق بعد ذلك يتم تصبيغ الشرائح بمزيج من صبغتي Wright Gimsa وفقاً لطريقة (17). يتم إجراء العد باستخدام المجهر الضوئي تحت قوة تكبير (1000) بوضع قطرة زيت على الشريحة وفقاً لطريقة (18) بعد ذلك يتم حساب نسبة الخلايا المتغايرة إلى الخلايا اللمفية.

جدول 1: نسب المواد العلفية الداخلة في تكوين العلائق المستخدمة في التجربة مع التركيب الكيمياوي المحسوب

المواد العلفية	العليقة البادنة	العليقة النهائية
ذرة صفراء	62.0	64.0
شعير	-	5.0
كسبة فول الصويا	34.0	27.0
بريمكس *	3.0	3.0
حجر الكلس	0.7	0.7
ملح	0.3	0.3
المجموع	100	100
التحليل الكيمياوي المحسوب **		
البروتين	20.35	17.99
الطاقة الممتلئة (كيلو سعرة/كغم علف)	2851.7	2894.6
الكالسيوم	0.86	0.84
الفسفور	0.44	0.43
ميثايونين	1.13	1.10
ميثايونين+سيستين	1.48	1.42
لايسين	1.08	0.91

* كل كغم من البريمكس يتكون من: 4% بروتين خام، 550 كيلو سعرة طاقة ممثلة، 16% كالسيوم، 10.6% فسفور، 4.0% صوديوم، 2750 ملغم منغنيز، 1670 ملغم حديد، 2670 ملغم زنك، 335 ملغم نحاس، 8.35 ملغم كوبالت، 50 ملغم يود، 6.7 ملغم سيلينيوم، 27 ملغم ميثايونين، 27.6 ميثايونين + سيستين، 1.350 ملغم نياسين، 400000 وحدة دولية فيتامين A، 85000 ملغم فيتامين D₃، 1400 ملغم فيتامين E، 100 ملغم فيتامين K₃، 85 ملغم فيتامين B₁، 200 ملغم فيتامين B₂، 400 ملغم فيتامين B₆ و 0.680 ملغم فيتامين B₁₂.

** تم حساب التركيب الكيميائي تبعاً لتحاليل المواد العلفية الواردة في (19).

استعمل التصميم العشوائي الكامل (CRD) Completely Randomized Design لدراسة تأثير المعاملات المختلفة في الصفات المدروسة، وقورنت الفروق المعنوية بين المتوسطات باختبار (20) متعدد الحدود واستعمل البرنامج الجاهز (21) في التحليل الإحصائي.

النتائج والمناقشة

يتضح من الجدول (2) أن استخدام أوراق نبات الزعتر المطحونة في العليقة لفروج اللحم أدى إلى زيادة عدد كريات الدم الحمر وبمعنوية عالية ($P < 0.01$). وان طبيعة هذه الزيادة كانت متزامنة مع الزيادة الحاصلة في تركيز أوراق نبات الزعتر المطحونة في العليقة وذلك في الأسبوعين السادس والثامن حيث سجلت المعاملة T4 أعلى مستوى حيث بلغت 2.37 مليون خلية/ ملم³ دم في الأسبوع السادس و 2.41 مليون خلية / ملم³ دم في الأسبوع الثامن ثم تلتها المعاملة T3 وبعدها أعقبها المعاملة T2 وجاءت معاملة السيطرة T1 أخيراً حيث سجلت أدنى مستوى لعدد كريات الدم الحمر حيث بلغت 2.08 مليون خلية/ ملم³ دم في الأسبوع السادس و 2.18 مليون خلية / ملم³ دم في الأسبوع الثامن. وقد تعزى هذه الزيادة في عدد كريات الدم الحمر نتيجة لحاجة الجسم لتلبية المتطلبات الجديدة لنقل المواد الغذائية والأوكسجين إلى الخلايا بسبب زيادة معدل الايض للطيور التي تناولت أوراق نبات الزعتر المطحونة في العليقة . وقد يكون السبب في ارتفاع عدد كريات الدم الحمر في معاملات أوراق نبات الزعتر المطحونة هو احتواءها على بعض المركبات الفينولية والتي تساعد على حماية خلايا الدم من الأضرار التي قد تحدث لها نتيجة الأكسدة (22) .

جدول 2: تأثير إضافة مستويات مختلفة من أوراق نبات الزعتر المطحونة في العليقة في عدد كريات الدم الحمر + الخطأ القياسي لفروج اللحم

المعاملات	عدد كريات الدم الحمر (مليون/ ملم ³)	
	الأسابيع	
	8	6
T1	d 2.18± 0.01	d 2.08± 0.012
T2	c 2.25± 0.05	c 2.21± 0.04
T3	b 2.32± 0.03	b 2.28± 0.03

تأثير إضافة أوراق نبات الزعتر (*Thymus vulgaris*) المطحونة إلى العليقة في بعض الصفات الدموية لفروج اللحم

نهاد

a	a	T4
2.41± 0.06	2.37± 0.04	
**	**	مستوى المعنوية

T1: مجموعة السيطرة و T2، T3 و T4: إضافة أوراق نبات الزعتر المطحونة إلى عليقة الطيور بالتركيز 500، 750 و 1000 ملغم / كغم علف، بالتتابع. المتوسطات التي تحمل حروفا مختلفة ضمن العمود الواحد تختلف معنويا * عند مستوى $P < 0.05$ ، ** عند مستوى معنوية $(P < 0.01)$.

حيث أشار (22) إلى أن المركبات الفلافونية الموجودة في أوراق نبات الزعتر المطحونة تعتبر من مضادات الأكسدة شديدة الفعالية من خلال حماية العديد من المواد التمثيلية المهمة مثل البروتين الدهني واطى الكثافة Low density lipoprotein وكريات الدم الحمر ضد مختلف عوامل الإجهاد المؤكسدة من خلال ميكانيكية التخلص من الجذور الحرة وتثبيط تأكسد دهون أغشية الخلايا.

يتضح من الجدول (3) أن قيم مكداس الدم أخذت منحى مطابق تقريبا للتغيرات الحاصلة في إعداد خلايا الدم الحمر في الأسبوع الثامن مع وجود فارق بسيط وهو عدم وجود فرق معنوي بين المعاملتين T2 و T3 في الأسبوع السادس من العمر. ويرتبط مقياس مكداس الدم بعدد خلايا الدم الحمر حيث كلما ازداد عدد كريات الدم الحمر يؤدي إلى زيادة في مقياس مكداس الدم (23). ولقد كان لتركيز أوراق نبات الزعتر المطحونة الأثر الكبير في مقياس مكداس الدم حيث نلاحظ من الجدول (3) انه كلما ازداد تركيز أوراق نبات الزعتر المطحونة في العلف ازدادت قيم مكداس الدم (PCV)، وقد سجلت المعاملة T4 (1000ملغم/كغم علف) أعلى مستوى لمقياس مكداس الدم حيث بلغت 30.90% في الأسبوع السادس و 31.75% في الأسبوع الثامن وبفارق معنوي عالي ($P < 0.01$) مقارنة بجميع معاملات التجربة، ثم تلتها المعاملة T3 (750 ملغم/ كغم علف) وسجلت 27.04 في الأسبوع السادس و 27.22 في الأسبوع الثامن وقد تفوقت بمعنوية عالية ($P < 0.01$) على المعاملتين T1 و T2. أما المعاملة T2 (500 ملغم/ كغم علف) فلم تسجل فرقا معنويا في مكداس الدم بينها وبين المعاملة T3 في الأسبوع السادس بينما انخفضت وبمعنوية عالية ($P < 0.01$) عن المعاملتين T3 و T4 الأسبوع الثامن، إلا أنها رغم ذلك فقد تفوقت بفارق معنوي عالي ($P < 0.01$) على معاملة السيطرة T1 في الأسبوعين السادس والثامن حيث بلغت 26.10 و 26.35% على التوالي وقد جاءت معاملة السيطرة في المرتبة الأخيرة حيث انخفضت بفارق معنوي عالي ($P < 0.01$) عن جميع معاملات تراكيز أوراق نبات الزعتر المطحونة وبلغت

23.05 و 23.30 في الأسبوعين السادس والثامن على التوالي، وفي هذه الدراسة قد تبين أن زيادة التراكيز أدت إلى زيادة عالية المعنوية ($P < 0.01$) في قيم مكداس الدم، وإن هذه الزيادة كانت مرتبطة بزيادة تركيز أوراق نبات الزعتر المطحونة في العليقة .

يتضح من الجدول (3) أن الزيادة الحاصلة في تركيز الهيموغلوبين تشابه تلك التي حصلت لإعداد خلايا الدم الحمر حيث أن تركيز الهيموغلوبين يرتبط ارتباطاً مباشراً بعدد خلايا الدم الحمر (24). لذلك فإن طبيعة هذه الزيادة في تركيز الهيموغلوبين كانت مرتبطة ارتباطات قوية بتركيز أوراق نبات الزعتر المطحونة في العليقة وذلك في الأسبوعين السادس والثامن من العمر حيث تفوقت المعاملة T4 إذ سجلت 8.52 و 8.5 على التوالي متفوقة وبمعنوية عالية ($P < 0.01$) على جميع معاملات التجربة، أما المعاملة T3 فقد تفوقت بفرق معنوي عالي أيضاً على كل من المعاملة T1 و T2، أما المعاملة T2 فقد تفوقت وبمعنوية عالية أيضاً على معاملة السيطرة. من هنا تبين أن للتركيز دور مهم في زيادة تركيز الهيموغلوبين، وقد تبين في دراستنا هذه إن زيادة تركيز أوراق نبات الزعتر المطحونة إلى (1000 ملغم/ كغم علف) قد أدت إلى زيادة في الفارق المعنوي ($P < 0.01$) مقارنة بمعاملة السيطرة.

جدول 3: تأثير إضافة مستويات مختلفة من أوراق نبات الزعتر المطحونة في العليقة في مكداس الدم وتركيز الهيموغلوبين \pm الخطأ القياسي لفروج اللحم

المعاملات	مكداس الدم (PCV) %		تركيز الهيموغلوبين (غم/100مل)	
	الأسابيع		الأسابيع	
	6	8	6	8
T1	c 23.05 \pm 0.25	d 7.99 \pm 0.44	d 23.30 \pm 0.26	d 8.04 \pm 0.40
T2	b 26.10 \pm 0.36	c 8.18 \pm 0.37	c 26.35 \pm 0.38	c 8.22 \pm 0.39
T3	b 27.04 \pm 0.36	b 8.33 \pm 0.37	b 27.22 \pm 0.13	b 8.35 \pm 0.36
T4	a 30.90 \pm 0.44	a 8.52 \pm 0.39	a 31.75 \pm 0.14	a 8.56 \pm 0.35
مستوى المعنوية	**	**	**	**

T1: مجموعة السيطرة و T2، T3 و T4: إضافة أوراق نبات الزعتر المطحونة إلى العليقة الطيور بالتراكيز 500، 750 و 1000 ملغم / كغم علف ، بالتتابع. المتوسطات التي تحمل حروف مختلفة ضمن العمود الواحد تختلف معنوياً، ** عند مستوى معنوية ($P < 0.01$) .

تأثير إضافة أوراق نبات الزعتر (*Thymus vulgaris*) المطحونة إلى العليقة في بعض الصفات الدموية لفروج اللحم

نهاد

يتضح من الجدول (4) وفيما يتعلق بإعداد كريات الدم البيض، فإن المعاملة بأوراق نبات الزعتر المطحونة أدت إلى زيادة عالية المعنوية في إعداد خلايا الدم البيض مع زيادة تركيز أوراق نبات الزعتر المطحونة في العليقة عند الأسبوعين السادس والثامن وقد تبين أنه كلما ازداد تركيز أوراق نبات الزعتر المطحونة ازدادت معه عدد كريات الدم البيض وأن هناك فروقات عالية المعنوية ($P<0.01$) بين المعاملات T1 و T2 و T3 و T4. حيث سجل أعلى عدد لها في المعاملة T4 حيث بلغت 29.95 و 30.28 ألف خلية/ملم³ ثم تلتها T3 حيث سجلت 27.60 و 27.96 ألف خلية/ملم³ دم ثم أعقبها T2 وبلغت 26.62 و 26.78 ألف خلية/ملم³ دم ثم جاءت بالمرحلة الأخيرة معاملة السيطرة حيث بلغت 22.74 ألف خلية/ملم³ دم و 23.07 ألف خلية/ملم³ دم في الأسبوعين السادس والثامن على التوالي. أي حصل ارتفاع معنوي عالي ($p<0.01$) بعد زيادة تركيز أوراق نبات الزعتر المطحونة إلى مستويات أعلى أي 500 ملغم/كغم علف، 750 ملغم/كغم علف و 1000 ملغم/كغم علف وكان التفوق في جميع معاملات تركيز أوراق نبات الزعتر المطحونة في الأسبوعين السادس والثامن.

وذكر (25) بأن أوراق نبات الزعتر المطحونة تمتلك قابلية كبيرة على تعزيز وظيفة الجهاز المناعي في الجسم. كما أشار (26) إلى أن أوراق نبات الزعتر المطحونة تعتبر مضاد بكتيري وبالتالي قد يؤدي إلى زيادة في أعداد خلايا الدم البيض.

يتضح من الجدول (4) حصول انخفاض عالي المعنوية ($P<0.01$) في نسبة الخلايا المتغايرة إلى الخلايا اللمفية مع زيادة تركيز أوراق نبات الزعتر المطحونة في الأسبوعين السادس والثامن وسجلت أدنى مستوى لهذه النسبة المعاملة T4 (1000 ملغم/كغم علف) وبلغت 0.23 لكلا الأسبوعين السادس والثامن. ثم ارتفعت هذه النسبة في المعاملة T3 (750 ملغم/كغم علف) وبمعنوية عالية ($P<0.01$) عن سابقتها T4. وقد استمرت بالارتفاع هذه النسبة في المعاملة T2 (500 ملغم/كغم علف) وبمعنوية عالية أيضا ($P<0.01$). ثم بعد ذلك وصلت مستوى نسبة الخلايا المتغايرة إلى الخلايا اللمفية إلى أعلى مستوى لها في معاملة السيطرة حيث سجلت 0.27 في الأسبوع السادس و 0.28 في الأسبوع الثامن وبفارق معنوي عالي ($P<0.01$) مقارنة بمعاملات أوراق نبات الزعتر المطحونة.

جدول 4: تأثير إضافة مستويات مختلفة من أوراق نبات الزعتر المطحونة في العليقة في أعداد كريات الدم البيض ونسبة الخلايا المتغايرة/ الخلايا اللمفاوية \pm الخطأ القياسي لفروج اللحم.

المعاملات	أعداد كريات الدم البيض (ألف/مل ³)		نسبة الخلايا المتغايرة/ الخلايا اللمفاوية (H / L)	
	الأسابيع		الأسابيع	
	6	8	6	8
T1	d 22.74 \pm 0.27	d 23.07 \pm 0.09	a 0.27 \pm 0.003	a 0.28 \pm 0.003
T2	c 26.62 \pm 0.11	c 26.87 \pm 0.17	b 0.26 \pm 0.03	b 0.25 \pm 0.03
T3	b 27.60 \pm 0.29	b 27.96 \pm 0.29	c 0.25 \pm 0.002	c 0.24 \pm 0.002
T4	a 29.95 \pm 0.09	a 30.28 \pm 0.12	d 0.23 \pm 0.002	d 0.23 \pm 0.002
تأثير المعنوية	**	**	**	**

T1: مجموعة السيطرة و T2، T3 و T4: إضافة أوراق نبات الزعتر المطحونة

إلى عليقة الطيور بالتراكيز 500، 750 و 1000 ملغم / كغم علف ، بالتتابع.

المتوسطات التي تحمل حروف مختلفة ضمن العمود الواحد تختلف معنوياً، ** عند مستوى معنوية (P<0.01) .

إن انخفاض نسبة خلايا الهيتروفيل إلى الخلايا اللمفية تعطي انطباعاً جيداً عن صحة الطير فقد ذكر (27) بأن نسبة الخلايا الهيتروفيل/ الخلايا اللمفية هي أفضل مقياس للكشف عن حالة الطيور العامة ومستوى الإجهاد الذي تتعرض له وإن ارتفاع هذه النسبة عن المعدل العام يدل على تعرض الطيور لإجهاد شديد. وقد يعود السبب في انخفاضها إلى المعاملة بأوراق نبات الزعتر المطحونة الذي يحوي المركبات الفلافونية والتي تؤدي أدواراً بايولوجية مهمة فهي تقوي الصحة وتقلل من خطر الإصابة بالأمراض وتعمل كمعامل مضادة للالتهاب.

يستنتج من هذه الدراسة إلى إمكانية استخدام أوراق نبات الزعتر المطحونة كإحدى الإضافات الغذائية المهمة في علائق فروج اللحم حيث كان لها تأثيراً إيجابياً في تحسين صفات الدم لذكور فروج اللحم .

نوصي بإضافة أوراق نبات الزعتر المطحونة لتحسين صفات الدم لفروج اللحم ابتداءً من الأسبوع الأول . يفضل إضافة 1000 ملغم / كغم علف من أوراق نبات الزعتر المطحونة للحصول على أفضل صفات للدم لذكور فروج اللحم .

تأثير إضافة أوراق نبات الزعتر (*Thymus vulgaris*) المطحونة إلى العليقة في بعض الصفات الدموية
لفروج اللحم

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تأثير إضافة أوراق نبات الزعتر (*Thymus vulgaris*) المطحونة إلى العليقة في بعض الصفات الدموية لفروج اللحم

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تلوث مياه نهري ديالى ودجلة جنوب بغداد وتأثيرهما على تواجد الفطريات المائية

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ABSTRACT

In this research five stations, three on Diyala and two on Tigris rivers southern Baghdad, were chosen to study physical, chemical and biological characteristics of the water. The samples were taken from station's through different periods from February to December 2009. The ecological studying showed that temperature variability was between 10.5 - 29.5 ° C , hydrogen concentrations were ranged between pH 6.8 – 8. Electrical conductivity and salinity were ranged between 985 – 4920 μsem . and 0.61 – 3.08 g / l respectively. Biological Oxygen Demand and Chemical Oxygen Demand were ranged between 3.2 – 18.2 mg / l and 2.2 – 7.3 mg / l respectively. The hardness was ranged between 210 - 1617 mg / l. The turbidity values were ranged between 14 . 4 – 42 NTU and it was higher in Diyala than in Tigris river. Fourteen species were isolated belong to six genera : *Achlya klebsiana* , *A . amricana* , *A . prolifroides* , *Achlya .sp.* , *Saprolegnia* , *ferax* , *S . anisospora* , *S . diclina* , *Saprolegnia.sp.*, *Dictyuchus sterile*, *D. carpophorus*, *D. polysporus* , *Pythium ultimum* , *Pythiopsis cymosa* , *Leptomitius lacteus*. The genus *Saprolegnia* was the most prevalent and the genus *Pythiopsis* was the least prevalent. Also, result showed that *S . anisospora*, *S . ferax* , *A . prolifriodes* , *S . diclina* , *D . carpophorus* , *Leptomitius lacteus* can consider as indictors of water pollution. The *D . polysporus* and *Pythopsis cymosa* were a first record in Iraq .

الخلاصة

تم في هذا البحث اختيار خمس محطات ، ثلاث منها على نهر ديالى أما المحطتان الأخريان فهما على نهر دجلة جنوب بغداد. أخذت النماذج من محطات الدراسة على فترات زمنية مختلفة لمدة سنة كاملة ابتداء من شهر شباط ولغاية كانون الأول 2009 . أظهرت نتائج الدراسة البيئية بأن درجة حرارة المياه تراوحت بين 10.5 - 29.5 °م خلال مدة الدراسة ، كما تراوحت قيم الأس الهيدروجيني في محطات الدراسة بين 6.8 – 8.3 ، وقيم التوصيلية والملوحة تراوحت بين 985 – 4920 مايكروسمنز/ سم و 0.61 - 3.08 غم/ لتر على التوالي ، أما قيم المتطلب الكيميائي والحيوي للأوكسجين تراوحت بين 3.2 – 18.2 ملغم/ لتر و 2.2 – 7.3 ملغم/ لتر على

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التوالي ، أما العكرة فتراوحت بين 14.4 – 42 TUN وكانت معدلاتها في نهر ديالى أعلى من نهر دجلة ، وتراوحت قيم العسرة بين 210 – 1617 ملغم/ لتر، حيث سجلت أعلى المعدلات في محطة رقم 3 . وتم عزل وتشخيص 14 نوعاً تعود إلى ستة أجناس من الفطريات البيضية Oomycetes وهي:

Achlya klebsiana , *A . americana*, *A.. prolifroides* , *Achlya sp.*,
Saprolegnia. ferax, *S. anisospora*, *S . diclina* , *Saprolegnia sp.* ,
Dictyuchus sterile , *D. carpophorus* , *D. polysporus* , *Pythium ultimum*
Pythiopsis cymosa , *Leptomit. lacteus*. أظهرت النتائج أن أعلى عدد للعزلات هو 46 عزلة كانت في محطة رقم 5 على نهر دجلة ، أما أقل عدد فهو 16 عزلة في المحطة رقم 3 قرب مصبات الرستمية ، وكان الجنس *Saprolegnia* أكثر الأجناس تواجداً وأقل الأجناس وجوداً هو الجنس *Pythiopsis* . وبينت النتائج إنه يمكن اعتبار الأنواع التالية كأدلة حياتية على تلوث مياه الأنهار *A . prolifroides*, *D . carpophorus*, *D. polysporus* , *Leptomit. lacteus*, *Pythopsis cymosa* , *S . ferax* , *S. anisospora*, *S. diclina* ، علماً بأنه تم لأول مرة عزل لكل من الفطر *D. polysporus* والفطر *P. cymosa* من مياه نهر دجلة حيث لم تسجل سابقاً في مياه الأنهار العراقية، ويعد أول تسجيل لها في المياه العراقية.

المقدمة

تستمد مدينة بغداد مياهها من نهر دجلة الذي يقسمها إلى شطرين إثناء مروره فيها، وتعد من أكثر المدن التي تضيف مستويات عالية من التلوث إلى النهر بسبب حجم السكان وعدد المصانع والمنشآت المقامة على ضفتي النهر(1).. يتعرض هذا النهر إلى عمليات تلوث غير مسيطر عليها في معظم الأحيان (2)، وهذا يستدعي إجراء مراقبة ودراسات مستمرة لمياه النهر جنوب بغداد بسبب الأثر الذي يلعبه انخفاض منسوب المياه فيه من جهة وتأثير مياه نهر ديالى عليه من جهة أخرى، لأن نهر ديالى يستلم كمية لا يمكن تجاهلها من مياه الصرف الصحي القادمة من مناطق الخالص وبعقوبة وبغداد عند نقطة التقائه بنهر دجلة قرب منطقة سلمان باك وبذلك تعد منطقة جنوب بغداد من أهم المناطق التي تسبب تلوث مياه نهر دجلة . لقد أخذ نهر ديالى مجالاً واسعاً في دراسة مصادر التلوث بسبب محطة الرستمية حيث تعد أحد أهم أسباب تلوث ماء دجلة جنوب بغداد، فقد أشار (3) إلى أن مياه النهرين عسرة جداً مع ارتفاع واضح في تلوث مياه نهر ديالى مقارنة بنهر دجلة ، لذا ارتفع معدل التلوث في نهر دجلة بعد المصب، وقام الربيعي (4) بدراسة التأثيرات البيئية لنهر ديالى على نهر دجلة. كذلك قام الحسني

(5) بدراسة المؤشرات البيئية للمياه المترشحة من منطقة الدورة وتأثيرها في نوعية مياه نهر دجلة. تتعرض مياه نهر دجلة في مدينة بغداد إلى التلوث بسبب تزايد عدد سكانها وتفاقم مشكلة إنشاء المصانع والمنشآت الصناعية والمزارع على ضفاف النهر علاوة على انخفاض منسوب المياه في النهر بشكل ملحوظ في السنوات الأخيرة إضافة إلى عدم وجود ضوابط صارمة للحد منها على الأقل (6)، أما الشمر (7) فقد بينت أن نسبة تلوث المياه في نهر دجلة كانت أقل قبل التقاء بنهر ديالى. تعد الفطريات المائية من الكائنات التي لها أهمية بيئية وتحتل ضمن السلسلة الغذائية في النظام البيئي موقع الكائنات المحللة حيث أن لها القدرة على إفراز الإنزيمات التي تساعدها في التطفل والترمم وفي تحليل الأحياء الميتة والبقايا النباتية والحيوانية. حيث أكد (8) على إمكانية 123 نوع فطري من الفطريات المائية التطفل على 31 نوع من الحيوانات المائية وتسبب لها أمراض مختلفة. ففي العراق توجد عدة دراسات تناولت عزل الفطريات المائية من مياه الأنهار وعلاقتها بالأحياء المائية (9، 10، 11). الهدف من البحث الحالي هو دراسة تلوث مياه نهر ديالى ونهر دجلة جنوب بغداد من الناحية الفيزيائية والكيميائية والحيوية.

المواد وطرائق العمل

مواقع الدراسة :

تم اختيار خمس مواقع (محطات نهريّة) ، ثلاث منها على نهر ديالى هي: 2 و 3 و 4 ، الأولى قبل محطة الرسمية والثانية قرب مصبات الرسمية أما المحطة الثالثة فكانت بالقرب من نقطة التقاء نهر ديالى بنهر دجلة ، أما المحطتان الأخريان فهما 1 و 5 ويقعان على نهر دجلة جنوب بغداد ، الأولى تقع على نهر دجلة قبل التقائه برافده ديالى والأخرى بعد التقائه بنهر ديالى.

الفحص الفيزيائي والكيميائي:

لقد جمعت عينات الماء من جميع المحطات الخاصة بدراسة الخصائص الفيزيائية والكيميائية بقناني بلاستيكية نظيفة ومعقمة سعة 1 - 2 لتر ، أما العينات الخاصة بالفحوصات الحيوية وعزل الفطريات المائية فجمعت في قناني زجاجية معقمة ومعقمة سعة 250 مل، فتحت تحت سطح الماء عمق 10 - 30 سم لتفادي التلوث بالفطريات غير المائية من فطريات الهواء والترية وأغلقت القناني بأحكام وهي تحت الماء ، ونقلت العينات مباشرة إلى المختبر في ، مدة لا تتجاوز 2 - 3 ساعات وفي ظروف مبردة باستخدام صندوق مبرد في الأيام الحارة في فصل الصيف لأجراء الفحوصات المختبرية اللازمة.

تم قياس وتسجيل درجة الحرارة للمياه مباشرة في محطات الدراسة عند أخذ العينات بوضع محرار زئبقي مدرج 0 - 100 م في الماء لمدة 15 دقيقة . وتم قياس الأس الهيدروجيني باستخدام جهاز pH - meter بعد جلب العينات الى المختبر مع استخدام مجموعة من المحاليل

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الدارثة Buffer solutions . كما تم قياس الملوحة اعتماداً على قيم التوصيلة الكهربائية بواسطة استخدام جهاز قياس التوصيلية Conductivity meter .

استخدمت طرق التحليل القياسية في تقدير الفوسفات والكبريتات والكلوريد. وقدر الكالسيوم والمغنسيوم والعسرة الكلية بإتباع الطرق التي اعتمدت في (12)، حيث استخدم الكاشف المخلي Ethylene diamine tetra acetic acid disodium salt (EDTA – Na₂) لتقدير العسرة الكلية وتركيز العنصرين من خلال تسحيحه مع عينات الماء ، وتم قياس المتطلب الحيوي للأوكسجين BOD بحضن قنيتين من قناني ونكلر 250 مل فيها ماء من كل محطة من محطات الدراسة لمدة خمسة أيام داخل الحاضنة بدرجة 20 م° بعد أن تم قياس مقدار الأوكسجين الذائب قبل الحضن ثم قيس مقدار الأوكسجين الذائب بعد الحضن وتم تحديد قيمة BOD من حساب الفرق بين الأوكسجين الذائب في العينة قبل حضن العينات وبعد الحضن ، وقيس المتطلب الكيميائي للأوكسجين COD باستخدام طريقة الداكرومات حيث أخذ 50 مل من النموذج ومزج مع 75 مل من حامض الكبريتيك المركز وكبريتات الزئبق كعامل مساعد للأكسدة وتم غليانه مع التحريك المستمر وبعد تبريده أضيف إليه 25 مل من داكرومات البوتاسيوم (نورمالية 0.25) ثم سحج مع كبريتات الأمونيوم الحديدية و حسبت قيمة COD وعبر عن النتائج ب ملغم / لتر ، ولتقدير العناصر النزرة التي شملت الكاديوم والكروم والزنك والحديد والرصاص والنحاس باستخدام جهاز طيف الامتصاص اللهب .

الفحص الحيوي :

جمعت العينات الخاصة بعزل الفطريات المائية في قناني زجاجية معتمدة نظيفة ومعقمة سعة 250 مل ، فتحت تحت سطح الماء بعمق 10 – 30 سم لتفادي التلوث بالفطريات غير المائية من فطريات الجو والترية ، وأغلقت القناني بأحكام وهي تحت الماء ، أما عينات الماء الخاصة بدراسة الخصائص الفيزيائية والكيميائية فجمعت بقناني بلاستيكية نظيفة ومعقمة سعة 1 – 2 لتر ، ونقلت العينات مباشرة الى المختبر في مدة لا تتجاوز 2 – 3 ساعات وفي ظروف مبردة باستخدام صندوق مبرد في الأيام الحارة من فصل الصيف لأجراء الفحوصات المختبرية اللازمة.

نفذ الفحص الحيوي لتقدير أعداد الأجناس وأنواع الفطريات المائية المتواجدة في مياه نهري ديالى ودجلة، اعتمدت طريقة الطعوم والمصائد (13)، استخدمت بذور السمسم *Sesamum indicum* والدخن *Oenonisetum spicatum* وأنصاف بذور الذرة الصفراء *Zea mays* . أخذت بذور نظيفة وعقمت بالموصدة لمدة 10 دقائق ، رجت عينات الماء من كل محطة مع المكررات بلطف ثم سكبت في أطباق بتري زجاجية قطر 9 سم معقمة وأضيف لها 2 – 3 مل من محلول الكلورامفينيكول chloramphenicol بتركيز 1000 ملغم/لتر (250 ملغم من المضاد / 250 مل

من الماء المقطر (للتخلص من التلوث البكتيري) ثم وضعت البذور المعقمة في الأطباق وحضنت عند درجة حرارة 20 ± 2 °م لمدة 48 ساعة ثم نقلت البذور بعد غسلها عدة مرات بماء مقطر معقم ومحلول الكلورامفينيكول إلى أطباق بتري معقمة حاوية على 10 مل ماء مقطر خالي من الأيونات و 2 - 3 مل من محلول الكلورامفينيكول وثلاث بذور جديدة معقمة ثم حضنت بدرجة الحرارة نفسها وتمت مراقبة النمو الفطري على البذور يومياً باستخدام المجهر المركب الضوئي وعند ظهور الخيوط الفطرية غير المقسمة تركت عدة أيام عند نفس الدرجة الحرارية حتى تستطيل الخيوط الفطرية بحيث يمكن فصلها وعمل المزارع النقية منها ، أما الأطباق التي لم يظهر فيها نمو فقد أهملت بعد مرور شهر .

عزل وتشخيص الفطريات المائية :

عزلت الفطريات المائية على وسط زرعي صلب هو أكار مسحوق الذرة (Corn Meal Agar (CMA، المدعم بمحلول المضاد الحيوي كلورامفينيكول chloramphenicol، بعد استطالة الخيوط الفطرية وتركت الأطباق لمدة يوم كامل في الحاضنة للتأكد من خلوها من التلوث على أن لا تترك أكثر من يومان لحين استعمالها وإنما تحفظ بدرجة 4°م. وبعد اكتمال استطالة الخيوط الفطرية حضرت منها مزارع نقية وذلك بقطع خيط فطري واحد أو أكثر ونقلها في ظل ظروف معقمة إلى الوسط ألزري المحضر بعد التأكد من خلوه من التلوث المايكروبي وتم الزرع داخل حلقات راير Raper's Rings وهي عبارة عن حلقة زجاجية قطرها 2 سم استخدمت لتحديد انتشار النمو البكتيري ، وحضنت بدرجة 20 ± 2 °م ، وبعد فترة 2 - 5 يوم لوحظ تكون مستعمرات نقية واضحة ذات خيوط فطرية بيضاء اللون.

ولتشخيص الفطريات المعزولة فقد تم الاعتماد على طبيعة الخيوط الفطرية ، طريقة انطلاق الابواغ الحافظة السابحة من الحواظ البوغية ، أشكال الحواظ البيضية والابواغ البيضية وأعدادها داخل الحواظ من خلال الاستعانة بالمصادر المتخصصة (14، 15).

التحليل الإحصائي :

تمت معاملة نتائج الفحوصات البيئية الفيزيائية والكيميائية و الحيوية بعلاقات رياضية وإحصائية لغرض الحصول على الاستنتاجات التي يتطلبها الهدف من الدراسة ومن أهم العلاقات الإحصائية المستخدمة هو تحليل التباين باتجاهين Analysis Of Variance (ANOVA) ، استخدمت هذه الطريقة لتحديد معنوية الفروق في الخصائص المدروسة والفروق الموقعية و الشهرية لغرض تحديد معنوية نتائج التجارب المختبرية.

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النتائج والمناقشة

الفحوصات الفيزيائية والكيميائية:

الأشكال 1 ، 2 ، 3 ، 4 و 5 تبين نتائج كل من درجات الحرارة ، الأس الهيدروجيني ، العكورة ، التوصيلية والملوحة على التوالي، ويتضح من النتائج أن أعلى معدل لدرجات الحرارة سجل في شهر آب وأقل معدل لدرجات الحرارة سجل في شهر كانون الأول. أما بالنسبة لدرجات الأس الهيدروجيني فكانت مرتفعة في جميع المحطات وسجلت محطات نهر دجلة مستويات أعلى مما هو عليه في نهر ديالى. أما العكورة والتوصيلية والملوحة فسجلت أعلى مستوياتها في المحطة 3 على نهر ديالى القريبة من محطة المعالجة في الرستمية، بينما سجلت أقل مستوياتها في المحطة 1 على نهر دجلة قبل التقاءه بنهر ديالى مما يؤكد دور نهر ديالى في زيادة معدلات التلوث في نهر دجلة. وعلى ضوء هذه المعطيات تم اختيار نتائج شهر آب عن الأشهر الحارة ونتائج شهر كانون الأول عن الأشهر الباردة للتعرف على نوع العلاقة بين الظروف الجوية وخصوصا الحرارة والخصائص قيد الدراسة.

جدول 1 و 2 يوضحان نتائج فحوصات المياه للمحطات المدروسة على نهري ديالى ودجلة جنوب بغداد حيث. فقد تراوحت درجة الحرارة ما بين 10.5 م° في شهر كانون الأول عند المحطة 5 على نهر دجلة إلى 29.5 م° في شهر آب عند المحطتين 2 و 4 على نهر ديالى، وكانت درجة الحرارة نوعاً ما في نهر ديالى أعلى من نهر دجلة بسبب انخفاض منسوب المياه في نهر ديالى وتعد درجة الحرارة من الخصائص البيئية المهمة التي تؤثر على العمليات الحيوية المختلفة لتأثيرها المباشر في العمليات الانزيمية وذوبان الغازات والأملاح في المياه. وإن ارتفاع درجة الحرارة في فصل الصيف قد أثر تأثيراً سلبياً على أعداد الفطريات المائية المعزولة وهذا عائد إلى تأثير عملية إنتاج وانتشار الأبواغ السابحة لهذه الفطريات بالتغيرات التي تحصل على درجة الحرارة (16).

أما قيم الأس الهيدروجيني فقد تراوحت ما بين 6.8 pH في شهر كانون الأول عند المحطة 2 على نهر ديالى و 8.3 pH في شهر آب عند المحطة 5 على نهر دجلة ، وإن درجة الأس الهيدروجيني تميل إلى القاعدية الخفيفة بسبب وفرة أيوني الكربونات والبيكربونات ، وتبين أيضاً إن معدلاتها تقل في فصل الشتاء وتزداد خلال فصل الصيف بسبب نشاط الهائمات المائية، مع العلم إن درجات الأس الهيدروجيني مرتفعة نسبياً في نهر دجلة منه في نهر ديالى ويعود ذلك إلى ما يضاف من مواد عضوية إلى نهر ديالى والتي تكون غازات ثنائي أوكسيد الكاربون وكبريتيد الهيدروجين التي لها تأثير في تغيير مدى الأس الهيدروجيني، هذا ما يجعل هذا العامل ينحرف عن قيمته المثلى لنمو الفطريات المائية مما يجعل هذا العامل لا يؤثر بشكل كبير في تواجد هذه الفطريات ويتفق هذا مع ما توصل إليه (17).

وبخصوص العكورة فقد اختلفت القراءات بين محطات الدراسة وكذلك ضمن أشهر السنة ويلاحظ ارتفاع قيم الكدرة في النصف الثاني من عام 2009 في كل محطات الدراسة وذلك للارتفاع القليل في منسوب مياه نهر دجلة الذي سجل في أشهر الخريف والشتاء حيث نتج عنه زيادة في كمية المواد المنجرفة مثل الطين والغرين ، وهذا يتفق مع ما أشارت إليه (18)، ولوحظ إن قيم العكورة في محطات نهر ديارى هي أعلى من محطة رقم 1 لنهر دجلة نتيجة حجم الإضافات التي تدخل هذا النهر من محطات التصفية من محطة الرستمية ، وكانت تتراوح ما بين 14.5 – 28.3 NTU في شهر آب و 28.7 – 42.0 NTU في شهر كانون الأول ، وهذا ما يساعد على زيادة نشاط وظهور الفطريات المائية. علما" إن العكورة العالية تقلل من اختراق الضوء وبالتالي تؤثر على عملية البناء الضوئي وينتج عن ذلك انخفاض كمية المواد العضوية التي تترمم عليها الفطريات المائية فتقل أعدادها.

وأعطت نتائج تحاليل التوصيلية أعلى القيم خلال شهر كانون الأول لكل المحطات قيد الدراسة وأن أعلى القيم كانت في المحطة رقم 3 حيث وصلت إلى 4920 مايكروسمنز/ سم والتي من خلالها يمكن أن يلاحظ حجم ومستوى التلوث في مياه هذا النهر، وقد كانت نتائج فحص الملوحة مماثلة للتوصيلية فكانت أعلى القيم خلال شهر كانون الأول لكل المحطات وأن أعلى القيم هي في المحطة رقم 3 حيث وصلت إلى 3.08 غم / لتر ، حيث تزداد في نهر ديارى عنه في نهر دجلة وذلك بسبب الإضافات الكبيرة من مياه المبال في المنطقة إضافة كميات المواد المضافة من محطة الرستمية . ومن المعروف أن لبعض الفطريات المائية القدرة على تحمل الملوحة ، حيث إن تراكيبها الخضرية أكثر تحملاً للملوحة من تراكيبها التكاثرية الجنسية واللاجنسية عند وجودها في الأنظمة المائية متغايرة الملوحة ، وقد تكون الملوحة هي أحد الأسباب التي تسببت في اختزال الأنواع في نهر ديارى مقارنة مع نهر دجلة .

وأظهرت نتائج تحاليل الـ BOD_5 أن أغلب القيم المرتفعة كانت خلال فصلي الربيع والصيف وذلك بسبب حدوث ظاهرة الإثراء الغذائي في هذين الفصلين مما يؤدي إلى نمو الهائمات النباتية وبعد موتها وتحللها تحتاج إلى نسب عالية من الأوكسجين مما يؤدي إلى رفع قيم الـ BOD والتي هي غالباً ما تكون عالية في نهر ديارى وذلك بسبب ضخ المياه من محطة الرستمية. حيث سجلت أعلى القيم 5.1 و 16.9 و 6.7 ملغم / لتر في محطات النهر الثلاث (2 و 3 و 4) على التوالي. وتبين أيضاً" إن قيم الـ COD سجلت أعلى القيم في نهر ديارى وبالأخص عند محطة رقم 3 بالقرب من مصبات الرستمية فبلغت 7.3 ملغم/ لتر. إن زيادة التلوث العضوي وارتفاع قيمة COD أدى إلى خفض نشاط الفطريات المائية ومنع تكوين الحوافظ البوغية وبالتالي قلة الأبواغ

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السابحة ، علما" أن الارتفاع الكبير في نسبة المواد العضوية يؤثر سلباً على تواجد معظم الفطريات المائية (19).

أما بخصوص العسرة الكلية فقد يبين إنها مرتفعة جداً في مياه نهر ديالى مقارنة بمياه نهر دجلة ويلاحظ من هذه الدراسة إن قيم العسرة قلت تدريجياً في النصف الثاني من العام فتراوحت قيمها ما بين 340 – 1114 ملغم/لتر في جميع المحطات (جدول 2) نتيجة الاختلاف في منسوب المياه خلال فصل الشتاء وهذا يتفق مع دراسة (20).

وقد سجلت الدراسة الحالية زيادة أيون الكالسيوم على أيون المغنيسيوم في جميع المحطات مع ملاحظة إن تركيز الأيونين في نهر ديالى كان أعلى من نهر دجلة وخصوصاً في مياه المحطة 4 حيث سجلت 370.00 ملغم/لتر للكالسيوم و 84.25 ملغم/لتر للمغنيسيوم (جدول 2) ، وقد يعود بسبب ذلك إلى تردي كفاءة معالجة مياه الصرف الصحي وكذلك إلى الانخفاض الكبير في منسوب مياه نهر ديالى (4).

وبينت نتائج تحليل الصوديوم والبوتاسيوم إن تراكيزهما غير منتظمة ولم تأخذ نمطاً معيناً خلال أشهر السنة ويعود ذلك إلى إن الأنهار خلال مسيرها تتعرض إلى تغيرات في العمق ومعدل الجريان وجيولوجية المناطق المحاذية وطبيعة القاع ، فقد كانت مرتفعة في مياه نهر ديالى مقارنة بنهر دجلة ويرجع مصدر هذه الزيادة لغسل مياه الأنهر للتربة العلوية والحقول الزراعية، فسجل الصوديوم أعلى تركيز له عند المحطة 3 فيبلغ 780 ملغم / لتر أما البوتاسيوم فسجل هو الآخر أعلى تركيز له في المحطة ذاتها هو 18.12 ملغم/لتر (جدول 2) ، وكان هو أقل الأيونات الموجبة تركيزاً وهذا يتفق مع (7).

لقد كانت تراكيز الفوسفات عالية في محطات نهر ديالى مقارنة بمحطات نهر دجلة (جدول 1 و2)، وأعطت المحطة 3 في شهر آب أعلى تركيز هو 3.1 ملغم / لتر ، وهذا الارتفاع يشجع ظاهرة الإثراء الغذائي، ومن أهم مصادر الفوسفات هي فضلات المصانع والأسمدة ومياه البزل ومياه الصرف الصحي والمنظفات (21).

وسجلت الكلوريدات نتائج مماثلة للفوسفات فكانت التراكيز عالية في نهر ديالى وأعلىها في محطة (3) وهو 312.7 ملغم / لتر (جدول 1) ، ومن الملاحظ إن التراكيز كانت عالية في أشهر الصيف ثم بدأت تقل نسبياً في النصف الثاني من السنة بسبب اختلاف منسوب المياه، وتمثل مياه المبازل ومياه سقي الأراضي الزراعية علاوة على المخلفات الصناعية السائلة من أهم مصادر تلوث المياه بالكلوريدات (22).

وأظهرت نتائج تحاليل العناصر الثقيلة ، التي شملت العناصر: Fe , Pb, Cu, Cr, Cd , Zn ، بأن مياه نهر ديالى أكثر تلوثاً بهذه العناصر من مياه نهر دجلة حيث فاقت الحدود المسموح بها

لتصنيف تلوث المياه ، وأن أشهر الصيف سجلت أعلى التراكيز (جدول 1) نتيجة لتبخر المياه وقلة عامل التخفيف (23) ، حيث بلغت تراكيز العناصر 0.010 , 0.075 , 1.600 , 0.900 1.300 , 0.100 ملغم/ لتر على التوالي ، وكان الزنك أكثر العناصر تواجداً في كل المحطات والكروم أقلها تركيزاً ، والأخير لم يسجل له تواجد في مياه نهر دجلة وهذه النتيجة لا تتفق مع (24) الذي سجل تواجد للكروم في نهر دجلة. كما أظهرت نتائج التحليل ان تواجد كل من الكاديوم والرصاص كان مرتفعاً في نهر ديالى وينسب أعلى من النسب المسموح بها، أما في نهر دجلة فكان معدل الكاديوم ضمن الحدود المسموح بها في محطة 1 ولم يظهر في محطة رقم 5 ، أما تركيز الرصاص فكان مرتفعاً في المحطة 1 لقربها من مجموعة من المصانع التي تلقي مخلفاتها إلى النهر مباشرة دون معاملة مثل معامل المشروبات الغازية والإسمنت ومعامل الجلود لذلك ظهر بنسبة أكبر من محطة رقم 5 على النهر. أما النحاس الذي يعد من العناصر الثقيلة الأساسية لم يسجل له أي وجود في نهر دجلة.

الفحوصات الحيوية:

تم اختيار الفطريات المائية لغرض دراسة تأثير الواقع الفيزيائي والكيميائي لمياه نهري ديالى ودجلة على تواجد وانتشار الفطريات المائية. يوضح جدول 3 أجناس وأعداد الفطريات المائية المعزولة خلال مدة الدراسة حيث تم عزل و تشخيص ستة أجناس من الفطريات المائية في 5 محطات من مياه نهري ديالى ودجلة جنوب بغداد تعود الى صنف الفطريات البيضية Oomycetes أربعة منها عائدة لرتبة Saprolegniales وهي *Achlya* , *Dictyuchus* , *Pythiopsis* و *Saprolegnia* وجنس واحد عائد لرتبة Peronosporales هو الجنس *Pythium* وجنس واحد آخر عائد لرتبة Leptomitales هو الجنس *Leptomitius* . وتظهر النتائج إن الجنس *Saprolegnia* كان أكثر الأجناس انتشاراً إذ تم عزل 57 عزلة من ضمن 141 عزلة من محطات الدراسة حيث سجل أعلى نسبة تردد 40.43 % مقارنة بالأجناس الأخرى مما يؤكد بأنه الفطر الأكثر شيوعاً ، وكان تواجده مرتفعاً في الفترات التي تكون فيها درجات الحرارة منخفضة وهذا يتفق مع ما أشار إليه كل من (25) و (11).

يليه الجنس *Achlya* الذي عزلت منه 43 عزلة من مجموع 141 عزلة الذي سجل نسبة تردد بلغت 30.49 % . أما الجنس *Dictyuchus* فقد تواجد في جميع مواقع الدراسة وبنسبة تردد 10.63 % ، حيث عزلت له 15 عزلة. وظهر الجنس *Pythium* في الأشهر الباردة فقط وبنسبة تردد 3.55 % وكان عدد العزلات 5 فقط من مجموع 141. ولم يظهر الجنس *Pythopsis* في مياه نهر ديالى وظهر في مياه نهر دجلة فقط وبواقع 4 عزلات ونسبة تردد 2.84 % . والجنس الأخير هو *Leptomitius* حيث عزل من جميع المحطات ماعدا محطة رقم 1 وتواجد على مدار السنة ماعدا تشرين الأول، حيث ظهرت له 17 عزلة وشكل نسبة تردد 12.06 %.

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وأظهرت النتائج أن 37 عزلة من بين 141 عزلة تعود للمحطة رقم 1 في منطقة الدورة جنوب بغداد و 20 عزلة للمحطة رقم 2 على نهر ديالى قبل محطة الرستمية و 16 عزلة من المحطة رقم 3 قرب مصبات الرستمية و 22 عزلة من المحطة رقم 4 بعد محطة الرستمية على نهر ديالى قرب الزعفرانية و 46 عزلة من المحطة رقم 5 على نهر دجلة في منطقة سلمان باك. حيث أظهرت النتائج إن أعلى عدد من العزلات ظهرت في محطة رقم 5 بعد التقاء نهر دجلة برفاده ديالى جنوب بغداد في منطقة سلمان باك يليها المحطة رقم 1 ثم محطات نهر ديالى 4 و 3 و 2 حيث كانت الأعداد متقاربة ومحدودة فيها مقارنة بنهر دجلة قبل الرافد وبعد الرافد.

وبين جدول 4 أعداد وتردد أنواع الفطريات التي تعود للأجناس أعلاه ، وكان النوع *S. anisospra* أكثر أنواع هذا الجنس تردداً حيث تواجد بنسبة 11.4 % ، أما الأنواع الأخرى التي تم تشخيصها وهي *S. diclina* و *S. ferax* فأعطت نسب تردد أقل 9.3 % و 4.2 % على التوالي ، إضافة إلى نوع آخر لم يتم تشخيصه *Saprolegnia* sp. إن وجود هذه الأنواع في المياه يشير إلى تلوث المياه العضوي في وهذا يتفق مع (26). أما الجنس *Achlya* الذي عزلت منه 43 عزلة من مجموع 141 عزلة وكان النوع *A. proliferoides* أكثر الأنواع المشخصة تردداً وينسبة 7.8 % يليه الأنواع *A. klebsiana* و *A. amricana* وينسب 5.7 % ، 1.4 % على التوالي ، إضافة إلى نوع آخر لم يتم تشخيصه *Achlya* sp. سجل نسبة 15.6 % ، وقد لوحظ في هذه الدراسة أن النوع *A. proliferoides* قدر في كل محطات الدراسة وفي جميع الأشهر المدروسة ما عدا شهر آب وظهر حتى في المحطة رقم 3 بنسبة 6.25 % . وهذا يتفق مع ما ذكره (27) من أن أنواع هذا الجنس تتواجد في مياه المناطق التي تتصف بكثرة التلوث العضوي.

أما الجنس *Dictyuchus* فقد ظهرت له 15 عزلة ، وظهر النوع *D. Sterile* . في جميع المحطات المدروسة وشكل النسبة الأكثر 7.8 % في حين ظهر النوع *D. Carpophoruas* في المحطات 3 و 4 مما يدل على تحمله العالي للتلوث وهذا يتفق مع ما ذكره (17). أما الجنس *Pythium* فظهرت له 5 عزلات من مجموع 141 عزلة وظهر في شهري تشرين الأول وكانون الأول أي أنه يعد من الفطريات التي تفضل درجات الحرارة المعتدلة ، وهذا ما أشار إليه كل من (27 و 16) حيث عزل له نوع واحد فقط هو *P. ultimum* في المحطات 1 و 2 و 5 ولم يسجل له حضور ضمن محطة 3 و 4 . هذه النتيجة تبين بأنه يفضل المواقع التي تتصف بكثرة المواد العضوية.

وأما الجنس *Pythopsis* فقد ظهرت منه 4 عزلات في محطتين هما 1 و 5 على نهر دجلة فقط ولم يسجل في نهر ديالى ، وهذا النوع لم يسجل سابقاً في العراق حسب ما متوفر من مصادر

عراقية والظاهر من النتائج ان الفطر حساس للتلوث ولم يتحمل مصادر التلوث العالية لذلك لم يظهر في نهر ديالى.

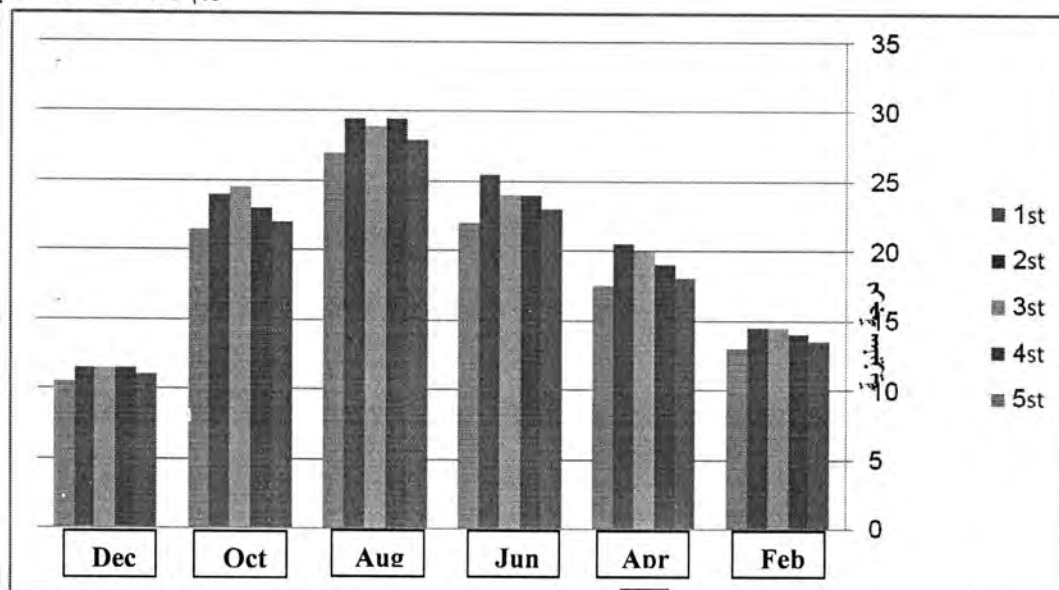
وهناك فطر آخر مهم جداً لأنه فطر الملوثات عزل في هذه الدراسة هو *Leptomitius. lacteus* حيث عزل من جميع المحطات ماعدا المحطة رقم 1، وتواجد على مدار السنة ماعدا تشرين الأول حيث ظهرت 17 عزلة 7 منها من محطة الرستمية حيث شكل 43.75 % من الفطريات المعزولة من المحطة رقم 3. علماً أن هذا الفطر هو من الفطريات الرمية التي تتواجد في المياه ذات التلوث العضوي ويستخدم لتنقية المياه الملوثة طبيعياً لأنه يستهلك المواد العضوية ويحولها الى عناصرها (27).

علماً بأنه تم ولأول مرة عزل الفطرين *D. polysporus* و *P. cymosa* من مياه نهر دجلة ، حيث لم يسجل لهما سابقاً أي تواجد في مياه الأنهار العراقية ، وبذلك يعد تواجدهما في مياه نهر دجلة تسجيل جديد في العراق.

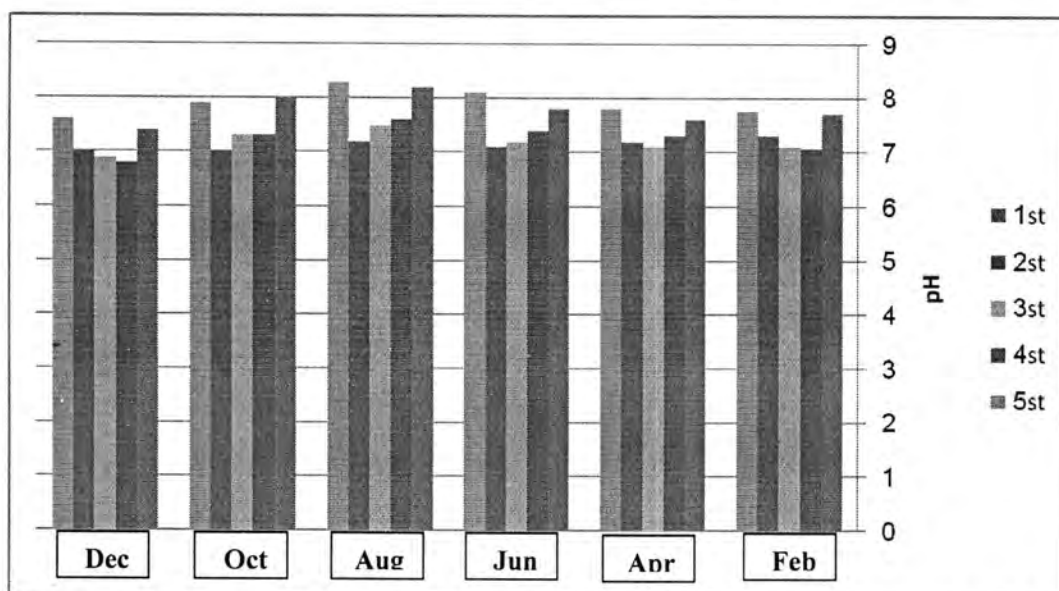
عند مقارنة نتائج الفحوصات الكيمياوية مع البيولوجية لنهر دجلة لوحظ أن تلوث النهر يزداد بعد التقائه برافده ديالى وهذا يتفق مع الدراسات السابقة (28 و 23) وينتج عن ذلك زيادة أنواع الفطريات لما يليق به هذا الرافد من مواد عضوية إلى نهر دجلة التي تعتبر مصدر التغذية للفطريات مع العلم أن الأنواع كانت محدودة في نهر ديالى لقلة التهوية وتركيز الأوكسجين الذائب ولوجود المنظفات التي تقلل من تنوع الأنواع.

نستنتج من هذه الدراسة أن مياه نهر ديالى تحتوي نسب عالية من الملوثات الكيمياوية خصوصاً بعد محطة المعالجة في الرستمية فتسببت بزيادة تلوث مياه نهر دجلة جنوب بغداد ، وكانت أعداد أجناس وأنواع الفطريات المائية أقل في مياه نهر ديالى مقارنة بمياه نهر دجلة ، كما أن معدلات تلوث المياه قلت نسبياً في مياه النهرين في النصف الثاني من السنة بسبب ارتفاع مناسيب المياه فيها.

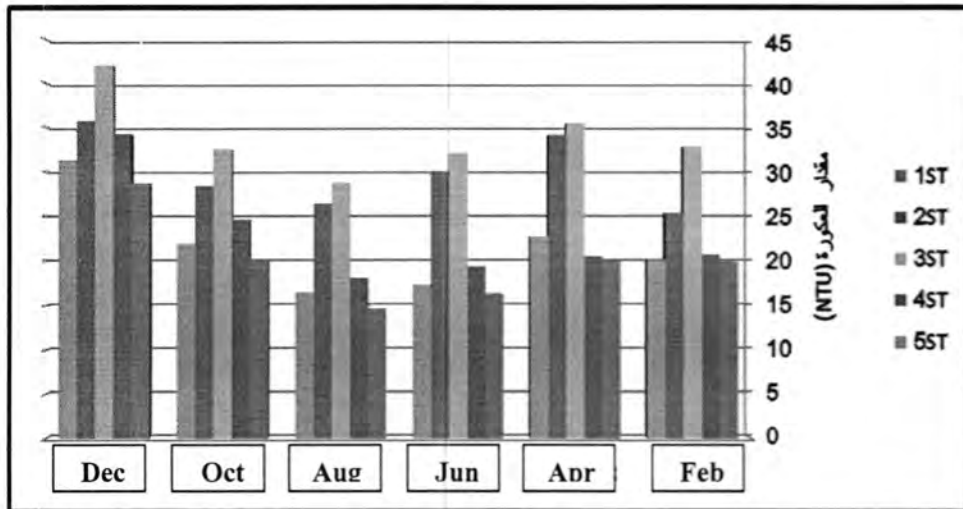
تلوث مياه نهري ديالى ودجلة جنوب بغداد وتأثيرهما على تواجد الفطريات المائية
ريم وعبدالرضا وحسوني



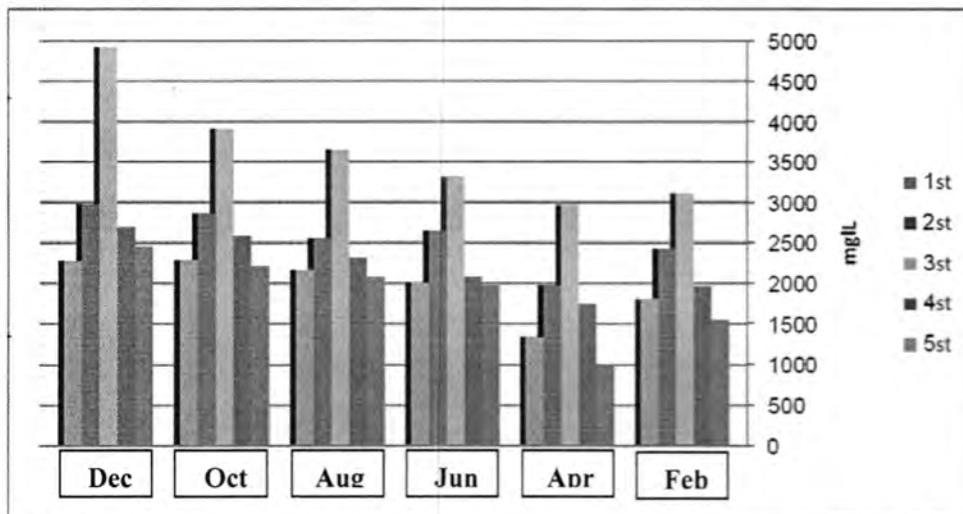
شكل - 1 : يوضح التغيرات الشهرية في درجة الحرارة لمياه المواقع قيد الدراسة



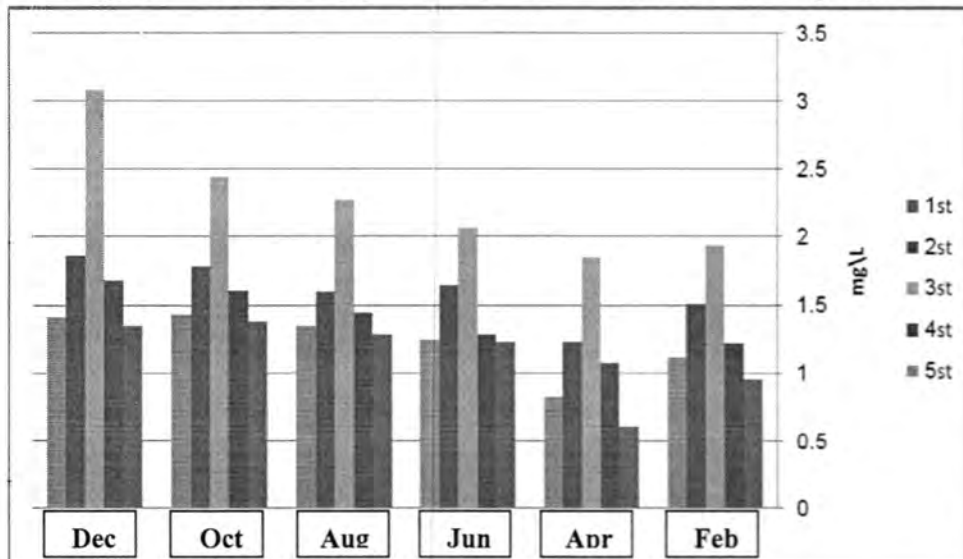
شكل - 2 : يوضح التغيرات الشهرية في درجة الأس الهيدروجيني لمياه المواقع قيد الدراسة



شكل - 3 : يوضح التغيرات الشهرية لدرجة العكورة في مياه المواقع قيد الدراسة



شكل - 4 : يوضح التغيرات الشهرية لمقدار التوصيلية الكهربائية في مياه المواقع قيد الدراسة



شكل - 5 : يوضح التغيرات الشهرية لدرجة الملوحة في مياه المواقع قيد الدراسة

تلوث مياه نهري ديالى ودجلة جنوب بغداد وتأثيرهما على تواجد الفطريات المائية

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جدول 1: الفحوصات الفيزيائية والكيميائية لمياه نهري ديالى ودجلة لشهر آب و قيمة P-value

P- value	محطات عينات المياه على نهري ديالى ودجلة جنوب بغداد					نوع الفحص
	(5)	(4)	(3)	(2)	(1)	
0.44NS	27.0	29.5	29.0	29.5	28.0	Temp.
0.53NS	8.300	7.200	7.500	7.600	8.200	PH
0.01**	16.300	26.400	00828.	18.000	14.500	Tur.(NTU)
0.04*	2170	2560	3650	2320	2080	EC(µcn/cm)
0.26NS	1.350	1.600	2.280	1.450	1.290	Salinity(g/l)
0.00**	4.700	5.600	11.300	4.000	3.700	BOD (mg/l)
0.00**	3.500	4.500	7.300	3.400	2.800	COD (mg/l)
0.02*	340.000	738.000	1114.00	951.000	467.00 0	Hard.(mg/l)
0.00**	97.670	295.000	137.110	122.000	77.840	Ca (mg/l)
0.00**	68.000	85.800	111.700	76.880	47.320	Mg (mg/l)
0.00**	63.000	583.000	596.000	143.000	65.000	Na (mg/l)
0.00**	8.100	16.800	9.900	9.700	3.500	K (mg/l)
0.03*	0.090	1.700	1.800	1.000	0.600	Zn (mg/l)
0.00**	0.000	0.010	0.010	0.000	0.000	Cd (mg/l)
0.00**	0.000	0.030	0.075	0.010	0.000	Cr (mg/l)
0.00**	0.000	0.085	0.100	0.050	0.000	Cu (mg/l)
0.01**	0.000	0.500	1.300	0.000	0.000	Pb (mg/l)
0.11NS	0.300	1.200	0.900	0.800	0.400	Fe (mg/l)
0.00**	0.900	1.500	3.100	1.900	0.100	PO4 (mg/l)
0.02*	28.330	287.400	312.70	222.300	54.550	Cl (mg/l)

*=Significant at 0.05 % , **=Significant at 0.01 % , NS=Not Significant

جدول 2: الفحوصات الفيزيائية والكيميائية لمياه نهري ديالى ودجلة لشهر كانون الأول وقيمة

P-value

P- value	محطات عينات المياه على نهري ديالى ودجلة جنوب بغداد					نوع الفحص
	(5)	(4)	(3)	(2)	(1)	
0.70NS	10.5	11.5	11.5	11	11.3	Temp.
0.84NS	7.300	7.000	6.900	6.800	7.400	PH
0.01**	31.300	35.700	42.000	34.200	28.70	Tur.(NTU)
0.14NS	2282	2980	4920	2695	2457	EC(µcn/cm)
0.41NS	1.420	1.870	3.080	1.680	1.530	Salinity(g/l)
0.00**	3.900	5.300	6.800	3.300	3.200	BOD (mg/l)
0.00**	3.900	4.700	7.100	3.400	2.700	COD (mg/l)
0.03*	231.000	287.000	336.000	210.000	168.000	Hard.(mg/l)
0.00**	92.490	370.000	134.230	84.080	67.270	Ca (mg/l)
0.00**	63.510	84.250	112.720	40.520	13.750	Mg (mg/l)
0.00**	69.000	670.000	780.000	160.000	72.000	Na (mg/l)
0.00**	7.000	18.120	10.200	10.00	2.700	K (mg/l)
0.04*	0.005	0.0750	0.450	0.080	0.000	Zn (mg/l)

0.01**	0.000	0.050	0.240	0.010	0.000	Cd (mg/l)
0.00**	0.000	0.050	0.090	0.000	0.000	Cr (mg/l)
0.00**	0.000	0.030	0.070	0.001	0.000	Cu (mg/l)
0.01**	0.000	0.900	1.000	0.400	0.000	Pb (mg/l)
0.18NS	0.000	0.100	0.200	0.500	0.600	Fe (mg/l)
0.00**	0.800	1.200	2.900	2.400	0.350	PO ₄ (mg/l)
0.02*	29.990	78.90	99.960	179.940	59.980	Cl (mg/l)

*=Significant at 0.05 %, **=Significant at 0.01 %, NS=Not Significant

جدول 3: يوضح أجناس الفطريات المعزولة من مياه المحطات المختارة على نهري ديالى ودجلة جنوب بغداد والنسب المئوية لتردد كل منها على مدار الأشهر المختلفة

محطات نهري ديالى ودجلة					التردد (%)	مجموع العزلات	أشهر السنة						أجناس الفطريات
5	4	3	2	1			1 ك	1 ت	أب	حزيران	نيسان	شباط	
19	8	6	7	17	40.43	57	14	11	-	3	15	14	<i>Saprolegnia</i>
16	7	1	7	12	30.49	43	9	14	1	5	11	3	<i>Achlya</i>
5	2	2	2	4	10.63	15	6	3	-	-	3	3	<i>Dictyuchus</i>
2	-	-	1	2	3.55	5	2	3	-	-	-	-	<i>Pythium</i>
2	-	-	-	2	2.84	4	1	3	-	-	-	-	<i>Pythiopsis</i>
2	5	7	3	-	12.06	17	-	1	5	6	3	2	<i>Leptomitius</i>
46	22	16	20	37	100.00	141	31	36	6	14	32	22	مجموع العزلات

جدول 4: يوضح أنواع الفطريات المعزولة من مياه المحطات المختارة على نهري ديالى ودجلة جنوب بغداد والنسب المئوية لتردد كل منها على مدار الأشهر المختلفة

محطات نهري ديالى ودجلة					التردد (%)	مجموع العزلات	أشهر السنة						أجناس الفطريات
5	4	3	2	1			1 ك	1 ت	أب	حزيران	نيسان	شباط	
8	2	2	3	7	15.60	22	5	4	0	2	6	5	<i>Saprolegnia sp.</i>
5	2	0	3	6	11.34	16	5	4	0	1	3	3	<i>S. anisospora</i>
4	3	2	1	3	9.22	13	3	2	0	0	4	4	<i>S. ferax,</i>
2	1	1	1	1	4.25	6	1	1	0	0	2	2	<i>S. diclina</i>
7	5	1	3	6	15.60	22	7	6	0	4	5	0	<i>Achlya sp.</i>
4	1	1	1	4	7.82	11	1	4	0	1	3	2	<i>A. prolifroides</i>
3	1	0	2	2	5.67	8	1	3	1	0	2	1	<i>A. klebsiana</i>
2	0	0	0	0	1.42	2	0	1	0	0	1	0	<i>A. americana</i>
4	1	0	2	4	7.82	11	4	4	0	0	1	2	<i>Dictyuchus sterile</i>
0	1	1	1	0	2.12	3	1	0	0	0	1	1	<i>D. carpophorus</i>
1	0	0	0	0	0.72	1	0	0	0	0	1	0	<i>D. polysporus</i>

تلوث مياه نهري ديالى ودجلة جنوب بغداد وتأثيرهما على تواجد الفطريات المائية

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2	0	0	1	2	3.54	5	2	3	0	0	0	0	<i>Pythium ultimum</i>
2	0	0	0	2	2.83	4	1	3	0	0	0	0	<i>Pythiopsis cymosa</i>
2	5	7	3	0	12.05	17	0	1	5	6	3	2	<i>Leptomitius lacteus</i>
46	22	16	20	37	100.00	141	31	36	6	14	32	22	المجموع الكلي للعلقات
13	10	7	11	10		51	11	12	2	5	12	9	المجموع الكلي للأنواع

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دراسة تأثير عديد السكريد الشحمي لبكتريا *Klebsiella oxytoca* في كلية

الفران البيضاء

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ABSTRACT

The effect of *K. oxytoca* purified LPS on kidney of mice was studied the results showed that transurethral injection of bacterial LPS in female mice induced histological changes in the kidney tissue which include hydropic degeneration of the kidney tissue, blood vessels congestion and lymphocytic infiltration.

الخلاصة

تم دراسة تأثير عديد السكريد الشحمي (LPS) المنقى من بكتريا *Klebsiella oxytoca* في كلية اناث الفران البيضاء السويسرية. أظهرت النتائج انه عند حقن الفران بمادة LPS عديد السكريد الشحمي عن طريق الاحليل تسبب في حدوث تغيرات نسيجية في الكلية شملت التغيرات بحدوث التكتس الاستسقائي لنسيج الكلية اذ حدث انكماش في الكبيبة، احتقان بالاعوية الدموية وارتشاح الخلايا اللمفية في نسيج الكلية.

المقدمة

تعتبر بكتريا *Klebsiella oxytoca* العائدة للعائلة المعوية Enterobacteraceae من احد مسببات التهاب المجاري البولية اذ تعد هذه البكتريا منتهزة للفرص (Opportunistic) وتعد من البكتريا المسببة للاصابات المتعلقة بالمستشفيات (Nosocomial infection) حيث تشكل *Klebsiella spp.* 8 % من البكتريا المسببة للاصابات المتعلقة بالمستشفيات (1,2) وتوجد هذه البكتريا بموطنين شائعين هما: البيئة وتتمثل بسطح الماء والمجاري والتربة وعلى النباتات، اما الموطن الاخر فهو سطح الطبقة المخاطية (Mucosa surface) للبائن ولاسيما الانسان، و الخيل، والخنزير اذ تستوطن فيها، و يعمل LPS على تحفيز الخلايا البلعمية لاطلاق الساييتوكينات، وعامل الورم التخريري Tumor necrosis factor (3) وينشط العامل المتمم بمسلكيه البديل والكلاسيكي (4) كما وجد ان LPS يسبب العديد من التغيرات النسيجية والوظيفية للكلية ونخر النبيبات الكلوية Renal tubular necrosis وتناقص في كمية البوتاسيوم في انسجة الكلية (5). لذلك اعدت هذه الدراسة لاستخلاص LPS من بكتريا *Klebsiella oxytoca* ودراسة تأثيره على كلى الفران البيضاء السويسرية.

المواد طرائق العمل

- تشخيص البكتريا: شخصت البكتريا باستخدام الاختبارات البايوكيميائية واستخدام شريط epi 20 الخاص بتشخيص البكتريا المعوية حسب ما جاء في (1,6,7,8).
 - الاستخلاص والتقية: تم استخلاص LPS بطريقة ويستفال (9) بوساطة الفينول الساخن ونقي باستخدام هلام Sepharose Cl-6B-200 كما جاء في (10)
 - دراسة التغيرات النسيجية للكلية في الفئران السويسرية البيضاء.
- تم استخدام اناث الفئران السويسرية البيضاء في الدراسة البالغة وتتراوح اوزانها بين 20 - 23 غرام اذ شملت الدراسة على خمس مجاميع من الفئران السويسرية بواقع اثنين لكل مجموعة اذ مثلت المجموعة الاولى مجموعة السيطرة (control) التي حقنت بدارئ الفوسفات الملحي 0.05 مل منه اما المجموعة الثانية حقنت بالبكتريا بتركيز 10^6 خلية لكل مل والمجموعة الثالثة بتركيز 200 مايكروغرام من عديد السكريد الشحمي لكل 0.05 مل من دارئ الفوسفات الملحي , المجموعة الرابعة كان التركيز 250 مايكروغرام لكل 0.05 مل من الدارئ اما المجموعة الخامسة فكان التركيز 300 مايكروغرام لكل 0.05 مل من الدارئ (11) اذ حقنت الفئران عن طريق الاحليل (Transurethally) اذ عقم الاحليل والمنطقة المحيطة به بالكحول الايثيلي بتركيز 70 % ومن ثم ادخل انبوب Polyethelene catheter قطره 0.6 ملليمتر , ثم ادخلت ابرة طبية عن طريق هذا الانبوب (ابرة انسولين) (12,13) .
- التثبيت والتقطيع : تم تشريح الفئران المحقونة بعديد السكريد الشحمي وبالبكتريا بعد خمسة ايام من الحقن وانتزعت منها الكلية واستخدمت طريقة هومسن (1972) لتحضير المقاطع النسيجية (14) .

النتائج والمناقشة

- تميزت التغيرات النسيجية بشكل عام في الكلية بحدوث حالة التنكس الاستسقائي (Hydropic degeneration) .
- فقد تميزت مجموعة الفئران المحقونة بالعالق البكتيري 1×10^6 خلية /مل بقياسها مع السيطرة شكل (1) , بحدوث الانكماش في الكبيبة (Shrinkage of glomerula) مما ادى الى اتساع الفراغ البيني للكبيبة (Capsular space) , شكل (2b,2d) .
- وكذلك ادى الى ارتشاح الخلايا الالتهابية (Infiltration of inflammatory cells) في خلايا النبيبات الجامعة (Collecting tubules) , وحدث الانسلاخ في خلايا النبيبات الكلوية شكل (2c) , وتميزت الاوعية الدموية بحدوث تنكس في خلايا البطانة (Endothelium) لخلايا الوعاء الدموي (blood vessel) مما سبب في حدوث الاحتقان الدموي (Congestion) في

خلايا النبيتات الكلوية ، مع ملاحظة كريات الدم الحمر (RBC)، وحدث تجمع في الخلايا اللمفية (Lymphocytes) شكل (2a) مما يدل على حدوث الالتهاب في خلايا النبيتات الكلوية ، ولوحظت الارومة الليفية التي كانت مصاحبة للخلايا اللمفية وخلايا كريات الدم الحمر (RBC)، كما تميزت النبيتات بحدوث الفجوات (Vaculation) شكل (2b) اذ ان تكون الفجوات هي من مراحل التتسكس الاستسقائي ، وتميز تجويف الكلى بتكوين الحصى (Crystal) الناتج من تأثير اليوريز الذي تنتجه البكتريا اذ يسبب الانزيم ترسب املاح الكالسيوم والمغنيسيوم على شكل حصى في تجويف الكلى شكل (2d) ، وكان تأثير العالق البكتيري اكثر من تأثير LPS على الرغم من تشابه التأثير .

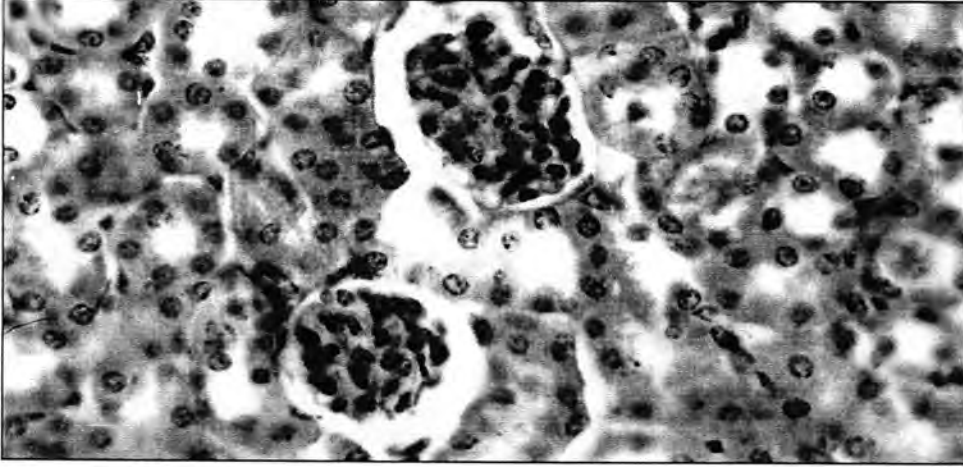
اما التغيرات النسيجية للفئران المحقونة بعديد السكريد الشحمي بتركيز 300 مايكروغرام /0.05 مل من عديد السكريد الشحمي فقد تميزت بحدوث الانكماش الحاصل في الكبيبة ، وتتكس خلايا الوسطية (Mesengeal cell) الواقعة على خلايا البطانة للكبيبة (Endothelial cells) شكل (3a) واحتقان الكبيبة، كما حدث التتسكس الاستسقائي لخلايا النبيتات الكلوية شكل (3a) واحتقان الاوعية الدموية ، وحدث النزف الدموي نتيجة تتكس خلايا البطانة للوعاء الدموي ، وتجمع السوائل الدموية داخل النسيج ، وتكون الوذمة (Edema) ، وحدث زيادة في انسجة الكلية (Hyperplasia) الذي هو عبارة عن تجمع في خلايا النسيج ، وانسلاخ الخلايا المبطنة للنبيتات الكلوية ، وكذلك حدوث الارتشاح الهائل في الخلايا اللمفية شكل (3b) .

اما التركيز 250 مايكروغرام /0.05 مل من عديد السكريد الشحمي فقد تميز بحدوث انكماش في محفظة بومان ، مما سبب اتساع الفراغ البيني للكبسولة (Capsular space) وتجمع الخلايا الوسطية (Mesengeal cells) في محفظة بومان التي تعمل بوصفها خلايا التهابية (Phagocytic cells) شكل (4a)

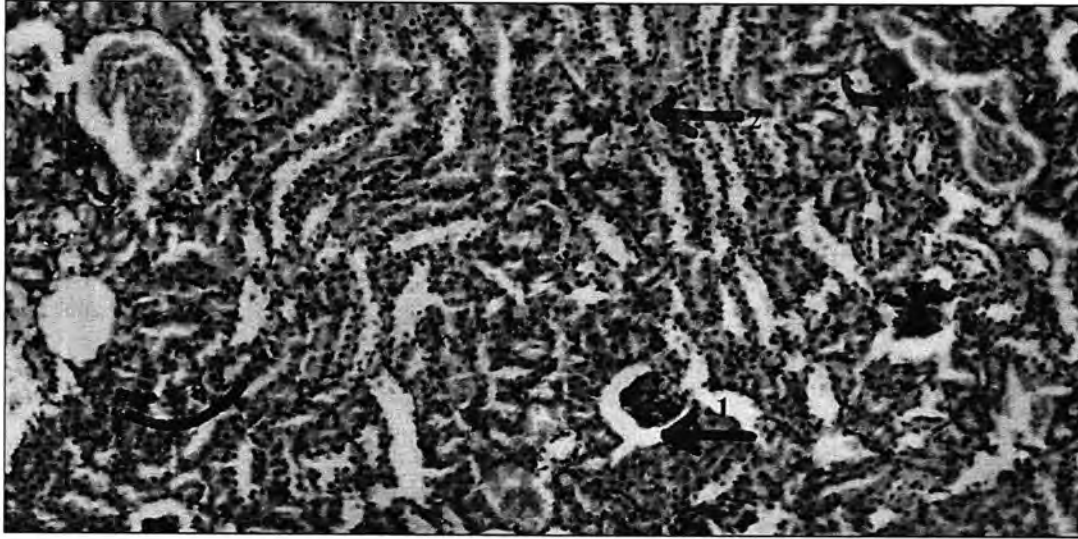
وكذلك تميزت بحدوث ارتشاح في الخلايا اللمفية وتكون مصاحبة للارومة الليفية (Fibroblast) شكل (4b) وحدث تتكس في خلايا البطانة للوعاء الدموي ، مما سبب بخروج RBCs الى النبيتات الكلوية وكذلك لوحظت التنسج في محفظة بومان .

اما تركيز 200 مايكروغرام /0.05 مل من عديد السكريد الشحمي في الفئران المحقونة ، فيشابه تأثير 250 و 300 مايكروغرام /0.05 مل ولكن بشدة اقل شكل (5a,5b) . اذن الـ LPS يسبب العديد من التغيرات النسيجية والوظيفية في الكلى وكذلك نخر النبيتات الكلوية Renal tubular necrosis حيث اتفقت هذه النتائج مع كل من الباحثين وهم Zhao وجماعته 2001 و Hewett و Roth 1993 و Hansen 2004 (6,5,14).

رغد ومي

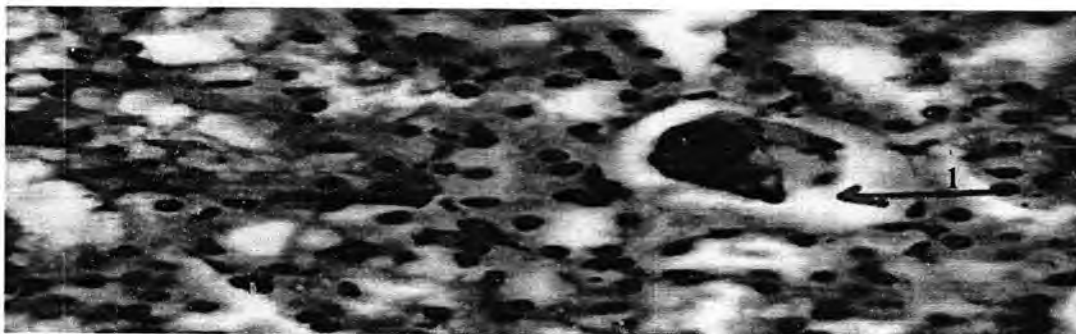


شكل-1: السيطرة لكلى الفئران المحقونة بدائى الفوسفات الملحي بقوة تكبير H and E X 40

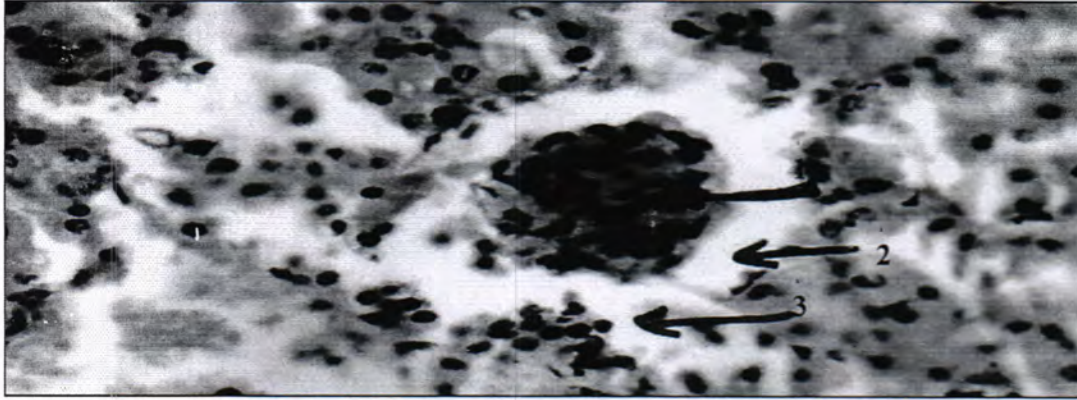


شكل-2a: كلية الفئران المحقونة بالعائق البكتيري 1X106 خلية/مل يوضح الانكماش الحاصل في الكبيبة (1)، ويوضح ارتشاح الخلايا اللمفاوية (2)، واحتقان الاوعية الدموية (Congestion) وكذلك تحطم الاوعية الدموية (3)، وحدوث النزف في خلايا النبيبات الكلوية (4)، تحت قوة تكبير

H and E , 10X



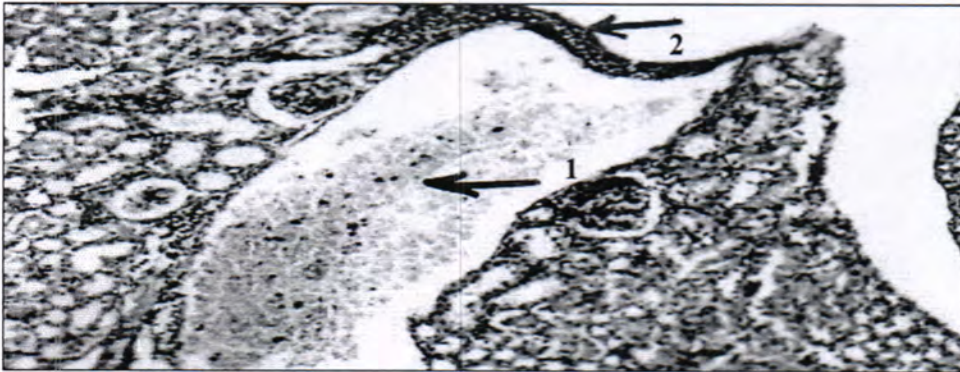
شكل (2b) كلية فئران محقونة بالعائق البكتيري 1X106 خلية / مل يوضح انكماش الكبيبة واتساع الفراغ البيني للكبسولة (1) تحت قوة تكبير H and E, 40 X



شكل-2c: كلية الفئران المحقونة بالعائق البكتيري 1×10^6 خلية / مل يوضح الانكماش الحاصل في الكببية وكذلك الاحتقان الدموي لها (1) وكبر الفراغ البيني للكبسولة (2)، وانسلاخ خلايا النيببات الكلوية (3) ، تحت قوة تكبير 40 X H and E

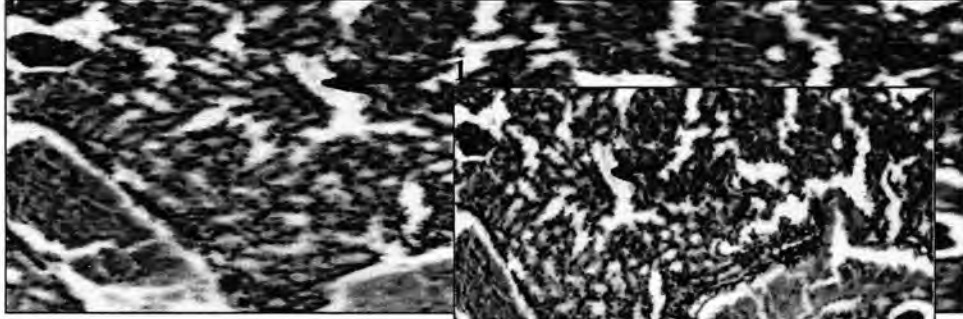


شكل-2d: كلية الفئران المحقونة بالعائق البكتيري 1×10^6 خلية / مل يوضح تكون الحصا Crystal في الفراغات البينية للكلية (1) ، تحت قوة تكبير 40 X H and E



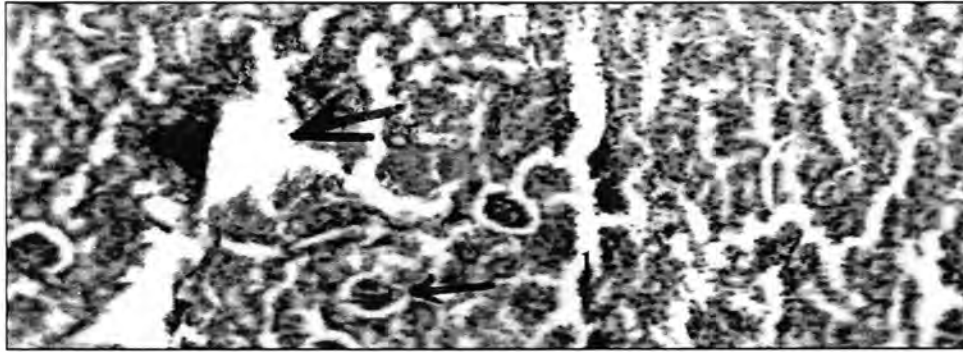
شكل-3a: كلية الفئران المحقونة بعديد السكريد الشحمي بتركيز 300 مايكروغرام / 0.05 مل يوضح الارتشاح في الخلايا اللمفية والارومة الليفية (2) واحتقان الوعاء الدموي (1) تحت قوة تكبير 10X H and E

رغد ومي



شكل-4b: حمى بتركيز 300 مايكروغرام / 0.05 مل

يوضح خرابات الكلى بين السليبات الحوية (1)، تحت قوة تكبير H and E , 10X



شكل-4a: كلية الفئران المحقونة بعديد السكريد الشحمي بتركيز 250 مايكروغرام / 0.05 مل

يوضح الانكماش بالكبيبة (1)، واحتقان الاوعية الدموية Congestion وتحطم الاوعية

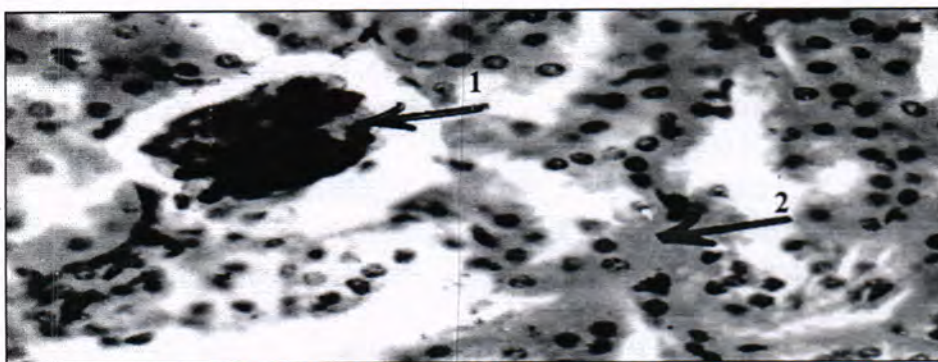
الدموية (2)، تحت قوة تكبير H and E , 10X



شكل-4b: كلية الفئران المحقونة بعديد السكريد الشحمي بتركيز 250 مايكروغرام / 0.05 مل

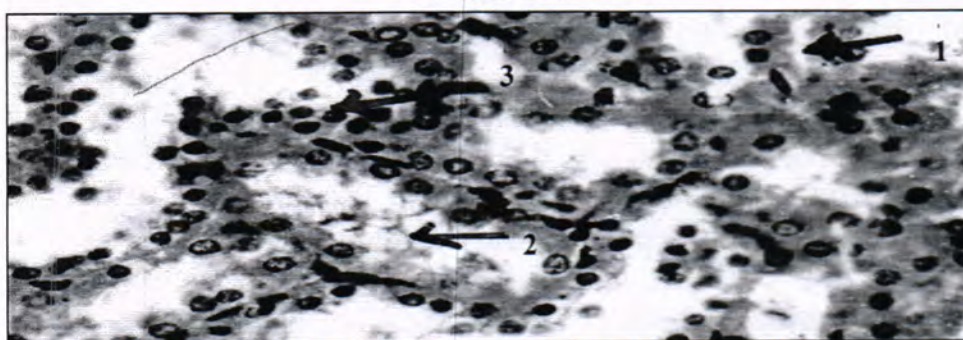
يوضح يوضح الارتشاح الحاصل في الخلايا اللمفية والارومة الليفية (1) تحت قوة تكبير

H and E , 10X



شكل-5a: كلية الفئران المحقونة بعديد السكريد الشحمي بتركيز 200 مايكروغرام / 0.05 مل يوضح انكماش الكبيبة (1)، والنزف الدموي الشديد لخلايا النيبب الكلوي (2) تحت قوة تكبير 40X

H and E ,



شكل-5b: كلية الفئران المحقونة بعديد السكريد الشحمي بتركيز 200 مايكروغرام / 0.05 مل يوضح النزف الدموي لخلايا النيبب الكلوي (1) , وتكون الفجوات (Vaculation) (2), والتتكس الاستسقائي (3) تحت قوة تكبير 40X H and E ,

يمكن أن نستنتج ما سبق

ان لتأثير الـ LPS تأثير امراضي عالي مشابه لتأثير الخلايا البكتيرية واكثر شدة , و يختلف تأثيره حسب تركيز الـ LPS حيث يكون التأثير اكثر في التركيز العالي 300 مايكروغرام \ 0.05 و اقل بالنسبة للتركيز الاقل 200 مايكروغرام \ 0.05 .

ونوصي بدراسة تأثير Lipid A في سميته الـ LPS , اجراء دراسة نسيجية لتأثير الـ LPS على اعضاء مختلفة مثل الكبد والطحال والرئتين وحسب موقع العزل بالنسبة للعضو المصاب .

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تأثير المستخلصات والبروتينات المعزولة من بذور البازاليا *Pisum sativum* في مستوى الاكسدة الفوقية للدهون و الكلوتاثايون في انسجة الفئران السليمة والمصابة بداء السكر والجهد التأكسدي المستحدث ببيروكسيد الهيدروجين

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ABSTRACT

This study was aimed to evaluate the included effect of cold , boiled aqueous extracts, proteinous precipitate obtained by acetone precipitation , proteinous compounds A and B which were isolated by gel filtration chromatophy and non-proteinous extracts , in normal , diabetic , exposed to oxidative stress induced by hydrogen peroxide male mice . The extracts were administrated intraperitoneally and their effects were compared with insulin . After one week of treatment the results indicated that the crude , proteinous precipitated, non-proteinous cold and boiled aqueous extracts, and the boiled proteinous compounds A,B at the doses of 750 , 500 , 15.75 , 5.9 , 730, 494 , 4.09 , 1.5 mg/Kg body weight respectively caused a significant increase in the level of glutathione while MDA content significantly decreased in the liver , kidney and heart tissues after the treatment with cold crude aqueous extract , the proteinous precipitate , non-proteinous extracts and the boiled proteinous compounds A,B in normal, alloxan – induced diabetic and exposed oxidative stress male mice .It was concluded that cold crude, non proteinous aqueous extract and proteinous precipitate, also the boiled A and B proteinous compounds from seeds of *Pisum sativum* have antioxidative effect in normal, diabetic and oxidative stress-exposed mice.

الخلاصة

هدفت الدراسة الى تقييم تأثير المستخلص المائي الخام البارد والمغلي والراسب البروتيني الناتج من الترسيب بالاسيتون والمركبات البروتينية المفصولة بتقنية كروماتوغرافيا الترشيح الهلامي والمستخلص غيرالبروتيني في ذكور الفئران السليمة والمصابة بداء السكر المستحدث بالالوكسان والمعرضة للجهد التأكسدي المستحدث ببيروكسيد الهيدروجين عن طريق الحقن بالتجويف البريتوني ومقارنتها مع تأثير الأنسولين . وأشارت النتائج بعد اسبوع من

تأثير المستخلصات والبروتينات المعزولة من بذور البازاليا *Pisum sativum* في مستوى الاكسدة الفوقية للدهون و الكلوتاثايون في انسجة الفئران السليمة والمصابة بداء السكر والجهد التأكسدي المستحدث بيبروكسيد الهيدروجين

ناهدة وإيمان

المعاملة الى ان المستخلص المائي الخام والراسب البروتيني وغير البروتيني البارد والمغلي والمركبين البروتينيين A و B المغليين ويجرع (750 و 500 و 15.75 و 5.9 و 4.09 و 1.5 و 730 و 494) ملغم/كغم وزن الجسم على التوالي ادت الى ارتفاع معنوي في مستوى الكلوتاثايون ، بينما انخفض مستوى المالدونداياليهايد معنويا في انسجة الكبد والكلية والقلب عند المعاملة بالمستخلص المائي الخام والراسب البروتيني وغير البروتيني البارد والمركبين البروتينيين A و B المغليين في الفئران السليمة المصابة بداء السكر والمعرضة للجهد التأكسدي . استنتجت الدراسة ان المستخلص المائي الخام وغير البروتيني والراسب البروتيني البارد والمركبين البروتينيين A, B المغليين لبذور نبات البازاليا يمتلك تأثيرا مضادا للاكسدة في الفئران السليمة والمصابة بداء السكر والمعرضة للجهد التأكسدي.

المقدمة

تؤدي ارتفاع مستويات الجذور الحرة للوكسجين الى عدد من الامراض التي تصيب الانسان والحيوان ، حيث ان التراكيز العالية من هذه الاصناف تعمل على تلف وموت الخلايا واحداث طفرات وراثية وتغير في الكروموسومات والاصابة بالسرطان [1] ، كما انها تؤدي الى بيروكسدة (زناخة) الدهن في الاغشية الخلوية مسببة بذلك موت الخلايا [2] . ويقوم الكائن الحي بازالة تأثير هذه الجذور والاصناف من خلال بعض الانزيمات وموانع الاكسدة [3] . ان من مضادات الاكسدة التي تصنع داخل الجسم (مضادات الاكسدة الأيضية) فتشمل الكلوتاثايون (GSH) الذي يعد عاملا مهما في منع الأذى الناتج عن جهد التأكسدي فضلا عن انه من الكاسحات الرئيسية للجذور الحرة متحولاً بذلك الى حالته المؤكسدة (GSSG) [4] .

إن عملية بيروكسدة الدهن هي احدى التفاعلات الناتجة عن الجهد التأكسدي [5] وتحدث بيروكسدة الدهن في العديد من الحالات المرضية مثل داء السكر وامراض الكبد وتصلب الشرايين والسكتة الدماغية والاورام السرطانية [2] . وقد اثبتت الدراسات الحديثة أن داء السكر التجريبي المستحدث بوساطة الالوكسان او الستريبتوزوتوسين يصاحبه تغيرات واضحة في مضادات الاكسدة الموجودة في مختلف الانسجة كالقلب والكبد والكلية والبنكرياس [6] .

ينتمي نبات البازاليا الى العائلة البقولية وهذه العائلة تنتمي إلى رتبة الورديات [7] ، وهو عبارة عن محصول سنوي متسلق يتألف من جذر رئيسي متفرع ، الساق يختلف حسب الصنف [8] الازهار والاثمار قرنية تحتوي على البذور الكروية. وتوجد حبوب البازاليا داخل وعاء خضري [9] ، يحتوي النبات على القلويدات وكومارينات والتربينويدات ، والفلافونيدات

وستيرويدات [10]، فضلا عن الماء والبروتين والدهون وكاربوهيدرات [11]، لقد اشار [12] الى ان البذور الخضراء غير الناضجة تحتوي على انوسيتول ، كولين وأيضا تحتوي الحبوب على اللكتين و تراجونيلين ومركبات نتريل الامين [8]. لوحظ ان قشرة او غطاء البذرة تحتوي على التانين [13].

إن الهدف من البحث هو دراسة تأثير المستخلصات المائية الخام الباردة والمغلية والبروتينية وغير البروتينية والمركبات البروتينية المعزولة من بذور البازاليا وفعاليتها في التقليل من تكوين الجذور الحرة في الحيوانات المصابة بداء السكر المستحدث بالالوكسان والمعرضة للجهد التاكسدي المستحدث ببيروكسيد الهيدروجين وذلك من خلال قياس مستوى الكلوتاثاينون والمالوندايديهايد في انسجة الكبد والكلية والقلب .

المواد وطرائق العمل

النبات المستعمل

تم الحصول على بذور نبات البازاليا *Pisum sativum* من الأسواق المحلية في مدينة الموصل وذلك في الشهر الخامس من عام 2005 ، ووضعها في اكياس بلاستيكية ، وضعت بعدها في المجمدة لحين استعمالها فيما بعد ، وصنفت في كلية التربية / قسم علوم الحياة .

الحيوانات المستخدمة

استخدمت في هذه الدراسة ذكور الفئران البيض السليمة male Albino mice المجهزة من كليتي (الطب،التربية/جامعة الموصل) وتقاربت اوزانها بين (30-35 غم) وضعت في اقفاص خاصة معدة ومجهزة لهذا الغرض ، وزودت بالماء والعلف الحيواني الخاص بها باستمرار واخضعت جميع الحيوانات للظروف ذاتها من ضوء طبيعي ودرجة حرارة (25)°م.

النظام المستخدم في تقسيم الحيوانات

وزنت الفئران قبل يوم واحد من حقنها بالمستخلصات والمواد المستخدمة في الدراسة الحالية ووزعت عشوائيا على (10) مجموعات سليمة و (10) مجموعات مصابة بداء السكر المستحدث بالالوكسان و(10) مجموعات معرضة للجهد التاكسدي المستحدث ببيروكسيد الهيدروجين ، تضم كل مجموعة (4) فئران ، فضلا عن ان هناك مجموعة لكل من الفئران السليمة والمصابة بداء السكر والمعرضة للجهد التاكسدي عدت مجموعة سيطرة (Control) حقنت بـ(0.5) سم³ من المحلول الملحي الفسلجي فقط [14] ومجموعة اخرى لكل من الفئران السليمة ، المصابة بداء السكر والمعرضة للجهد التاكسدي حقنت بالانسولين (10) وحدة دولية /كغم من وزن الجسم .

تأثير المستخلصات والبروتينات المعزولة من بذور البازاليا *Pisum sativum* في مستوى الاكسدة الفوقية للدهون و الكلوتاثايون في انسجة الفئران السليمة والمصابة بداء السكر والجهد التأكسدي المستحدث بيبيروكسيد الهيدروجين

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حقن الحيوانات السليمة

حقنت الفئران في التجويف البريتوني بجرع مقدارها (1.5 , 4.09 , 4.3 , 10.1) ملغم/كغم) من وزن الجسم بالمركبات البروتينية المفصولة بتقنية الترشيح الهلامي [15] في حين حقنت مجموعات اخرى بالمستخلص الخام والمواد غير البروتينية ومواد الرواسب البروتينية الخام ويجرع مقدارها (1.5 , 4.09 , 4.3 , 10.1) ملغم/كغم) من وزن الجسم على التوالي .

استحداث داء السكر

استخدمت ذكور الفئران البيض (male Albino mice) التي تقاربت اوزانها بين (30-35) غم ، قسمت عشوائيا على (12) مجموعة تضم كل مجموعة (4) فئران ، فضلا عن مجموعة سيطرة سليمة ، حقنت المجموعات (12) بمادة الالوكسان في التجويف البريتوني (Intraperitoneally) [16] بعد تجويعها لمدة (24) ساعة قبل احداث داء السكر فيها [17] . كانت الجرعة المعطاة من الالوكسان بمقدار (180 ملغم/كغم) من وزن الجسم والمحضرة آنيا [18] باذابتة في (0.5) سم³ من المحلول الملحي الفسلجي واعطيت محلول الكلوكوز (5%) مع ماء الشرب بعد الحقن بساعتين ولمدة يوم واحد لتجنب هلاكها من جراء النقص الحاد في السكر ، ثم سمح للفئران بتناول كفايتها من العلف والماء ، وتم التأكد من حدوث داء السكر بفحص الادرار يوميا ولمدة اسبوع بواسطة الشريط الكاشف (Test – Tape (R) , Eli – Lilly and Co., USA) .

حقن الحيوانات المصابة بداء السكر التجريبي

بعد التأكد من حدوث داء السكر في الحيوانات وزعت الفئران المصابة بداء السكر عشوائيا إلى (10) مجاميع تضم كل مجموعة (4) فئران . وزنت الفئران ، ثم حقنت في التجويف البريتوني يوميا ولمدة اسبوع بكل من المستخلص المائي الخام (البارد والمغلي) ، المواد غير البروتينية ، مواد الرواسب البروتينية الخام والمركبات البروتينية المفصولة بتقنية الترشيح الهلامي العائدة لهما بجرع مقدارها (1.5 , 4.09 , 4.3 , 10.1 , 5.9 , 15.75 , 494 , 730 , 500 , 750) ملغم/كغم) من وزن الجسم على التوالي . فضلا عن (3) مجاميع تضم كل مجموعة (4) فئران وكما يأتي :

أ. مجموعة سيطرة سليمة حقنت في التجويف البريتوني بـ (0.5) سم³ من المحلول الملحي الفسلجي (Normal saline) ولمدة اسبوع.

- ب. مجموعة مصابة بداء السكر المستحدث بالالوكسان متروكة من غير معاملة .
 ج. مجموعة مصابة بداء السكر المستحدث بالالوكسان حقنت بالانسولين تحت الجلد (10) وحدة /كغم ولمدة اسبوع.

حقن الحيوانات المعرضة للجهد التأكسدي المستحدث ببيروكسيد الهيدروجين

- استخدمت ذكور الفئران البيض ووزنت قبل بدء التجربة وقسمت عشوائيا إلى (13) مجموعة تضم كل مجموعة (4) فئران وكما يأتي:
 أ. مجموعة السيطرة تركت تتناول العلف والماء دون معاملة لمدة (15) يوما.
 ب. مجموعة عرضت للجهد التأكسدي باعطائها ببيروكسيد الهيدروجين (0.5%) مع ماء الشرب ولمدة (15) يوما.
 ج. مجموعة عرضت للجهد التأكسدي المستحدث ببيروكسيد الهيدروجين (0.5%) لمدة (15) يوما، مع حقنها في اليوم السابع ويومياً ولمدة اسبوع بالانسولين تحت الجلد بجرعة (10) وحدة /كغم .

د. المجاميع من (4-13) عرضت للجهد التأكسدي المستحدث ببيروكسيد الهيدروجين بنسبة (0.5%) لمدة (15) يوما ، مع حقنها في اليوم السابع ويومياً ولمدة اسبوع في التجويف البريتوني بكل من المستخلص المائي الخام (البارد والمغلي) ، المواد غير البروتينية ، مواد الرواسب البروتينية الخام والمركبات البروتينية المفصولة بتقنية الترشيح الهلامي العائدة لهما بجرع مقدارها (1.5 , 4.09 , 4.3 , 10.1 , 5.9 , 15.75 , 494 , 730 , 500 , 750) ملغم/كغم من وزن الجسم على التوالي .

الحصول على العينات النسيجية

نهاية كل تجربة خدرت الحيوانات بالايثر لبضع ثوانٍ ثم اخذت العينات النسيجية (القلب و الكبد و الكلية) وضعت في المحلول الملحي الفسلجي البارد (كلوكوز، كلوريد الصوديوم) ، بعدها لغت بورق الألمنيوم ووضعت في المجمدة لحين الحاجة (تقدير مستوى الكلوتاثايون والمالوندايالديهيد).

تقدير مستوى الكلوتاثايون في الانسجة

قدر مستوى الكلوتاثايون في انسجة القلب والكبد والكلية بطريقة المان المحورة [19].

تقدير مستوى المالوندايالديهيد في الانسجة

استخدمت الطريقة المتبعة من الباحثين [20] لتقدير مستوى المالوندايالديهيد في الانسجة . اذ يعتمد التحليل على التفاعل بين المالوندايالديهيد وحامض الثايوباربيتيوريك (TBA) .

تأثير المستخلصات والبروتينات المعزولة من بذور البازاليا *Pisum sativum* في مستوى الاكسدة الفوقية
لدهون و الكلوتاثايون في انسجة الفئران السليمة والمصابة بداء السكر والجهد التأكسدي المستحدث
ببيروكسيد الهيدروجين

ناهدة وإيمان

التحليل الاحصائي :

حللت نتائج مستوى الكلوتاثايون والمالونديالديهيد احصائيا وذلك باستخدام تحليل
التباين الاحادي One way analysis of variance كما تم تحديد الاختلافات الخاصة بين
المجاميع باستخدام اختبار دنكن Duncan [21] وكان مستوى التمييز الاحصائي المقبول
عند 5% ($P < 0.05$).

النتائج والمناقشة

تأثير داء السكر المستحدث بالالوكسان على بيروكسدة (زناخة) الدهن ومستوى الكلوتاثايون
في انسجة الكبد والكلية والقلب لذكور الفئران

أدى استحداث داء السكر بالالوكسان في ذكور الفئران انخفاضاً معنوياً في مستوى
الكلوتاثايون في انسجة الكبد والقلب والكلية كما مشار اليه في الجداول (1,2) ، وتتطابق هذه
النتائج مع الانخفاض الذي لاحظته [22] ، وكذلك مع نتيجة الانخفاض الذي لاحظته [23] في
مستوى الكلوتاثايون في أنسجة الكبد والقلب والكلية والبنكرياس في الارانب المصابة بداء السكر
المستحدث بالالوكسان ، وقد اشار [24] الى انخفاض مستوى الكلوتاثايون في انسجة الكبد
والكلية والقلب والبنكرياس في الجرذان المصابة بداء السكر المستحدث بالالوكسان ، يعزى
السبب في انخفاض مستوى الكلوتاثايون في انسجة الفئران المصابة بداء السكر الى زيادة هدم
الكلوتاثايون او انخفاض تصنيعه [25].

واظهرت الدراسة الحالية وكما موضحة النتائج في الجداول (1,2) ان مستوى
المالونديالديهيد ارتفع معنوياً في انسجة الكبد والكلية والقلب لذكور الفئران المصابة بداء السكر
المستحدث بالالوكسان ، وهذا يتفق مع نتائج [22] ، وكذلك مع نتائج [23] ، حيث لاحظ ارتفاع
مستوى المالونديالديهيد معنوياً في انسجة الكبد والكلية والقلب والبنكرياس في ذكور الارانب
المصابة بداء السكر المستحدث بالالوكسان ، وقد اشار [24] الى ان استحداث داء السكر في
ذكور الجرذان أدى ارتفاعاً معنوياً في مستوى المالونديالديهيد في انسجة الكبد والكلية والقلب
والبنكرياس عند المقارنة مع مجموعة السيطرة السليمة . في حين اشار [26] الى وجود ارتفاع
معنوي في مستوى المالونديالديهيد في انسجة الكبد والدماغ والعضلات لذكور الجرذان المصابة
بداء السكر المستحدث بالستريزوتوسين ، فضلاً عن ذلك لوحظت زيادة معنوية في مستوى
المالونديالديهيد في انسجة الكبد والكلية والدماغ لذكور الجرذان المصابة بداء السكر المستحدث
بالستريزوتوسين ، وهذه الزيادة المعنوية في مستوى زناخة الدهن (المالونديالديهيد) في تلك

الانسجة المدروسة عند مقارنتها مع مجموعة السيطرة السليمة ربما يعود سببها الى احتواء هذه الانسجة تراكيز عالية نسبياً من الاحماض الدهنية القابلة للتأكسد بسهولة [27] .

جدول 1: تأثير المستخلص المائي الخام وغيرالبروتيني البارد والمغلي لبذور نبات البازاليا في مستويات الكلورثاينون والمالوندايالديهايد في انسجة الكبد والكلى والقلب في ذكور الفئران المصابة بداء السكر المستحدث بالالوكسان

المعاملات			الكلورثاينون (نانومول/غم)			المالوندايالديهايد (نانومول/غم)		
			الكبد	الكلى	القلب	الكبد	الكلى	القلب
فئران سليمة معاملة بالمحلول الملحي الفسلجي (سيطرة سليمة C)			f ±5160.08 52.50	cd ±1978.05 49.01	Cd ±2564.17 59.40	bc ±426.12 47.34	C ±600.32 96.89	de 493.58 38.46±
فئران مصابة بداء السكر المتروكة من دون معاملة (سيطرة مصابة C ⁺)			a ±3708.43 64.87	a ±1713.41 59.49	A ±2181.43 77.42	h ±614.95 13.58	F ±820.51 64.10	h 727.56 54.49±
فئران مصابة بداء السكر + الاتسولين (10 وحدات دولية /كغم)			f ±5183.88 45.04	cd ±1990.88 13.79	D ±2587.97 29.74	b ±418.28 21.53	C ±580.50 34.18	d 480.76 25.64±
فئران مصابة بداء السكر + المستخلص المائي الخام البارد (750 ملغم/كغم)			def ±4834.85 53.65	de ±2161.6 56.94	e ±2992.53 89.24	bcde ±458.54 13.15	bc ±543.80 11.25	c 426.27 3.20±
فئران مصابة بداء السكر + المستخلص المائي المغلي (500 ملغم/كغم)			bcd ±4489.79 24.76	abc ±1879.99 42.90	bcd ±2474.93 47.60	efg ±497.43 12.22	df ±788.05 11.89	fg 570.92 25.64±
فئران مصابة بداء السكر + المستخلص غير البروتيني البارد (730 ملغم/كغم)			ef ±5049.03 80.99	fg ±2431.30 67.65	f ±3325.69 172.53	bcd ±432.04 10.04	ab ±485.03 8.06	ab 355.76 16.02±

تأثير المستخلصات والبروتينات المعزولة من بذور البازاليا *Pisum sativum* في مستوى الاكسدة الفوقية للدهون و الكلوتاثايون في انسجة الفئران السليمة والمصابة بداء السكر والجهد التأكسدي المستحدث ببيروكسيد الهيدروجين

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ef	df	def	cd	abc	cde	فئران مصابة بداء السكر + المستخلص غير البروتيني المغلي (494 ملغم/كغم)
538.46 6.41±	±759.87 29.25	±480.76 6.78	±2534.42 47.59	±1899.83 18.16	±4600.84 70.37	

الحروف المختلفة عمودياً تعني وجود فرق معنوي عند مستوى احتمالية (0.05)

تشير القيم اعلاه الى المعدل ± الانحراف القياسي

جدول 2: تأثير الرواسب البروتينية والمركبات البروتينية المفصولة منها لبذور نبات البازاليا في مستويات الكلوتاثايون والمالوندايديهايد في انسجة الكبد والكلية والقلب في ذكور الفئران المصابة بداء السكر المستحدث بالالوكسان

المالوندايديهايد (نانومول/غم)			الكلوتاثايون (نانومول/غم)			المعاملات
الكلية	القلب	الكبد	الكلية	القلب	الكبد	
de ±493.58 38.46	C ±600.32 96.89	bc ±426.12 47.34	cd ±2564.17 59.40	cd ±1978.05 49.01	f ±5160.08 52.50	فئران سليمة معاملة بالمحلول الملحي الفسولجي (سيطرة سليمة C)
h ±727.56 54.49	F ±820.51 64.10	h ±614.95 13.58	a ±2181.43 77.42	a ±1713.41 59.49	a ±3708.43 64.87	فئران مصابة بداء السكر المتروكة من دون معاملة (سيطرة مصابة C ⁺)
d ±480.76 25.64	C ±580.50 34.18	b ±418.28 21.53	d ±2587.97 29.74	cd ±1990.88 13.79	f ±5183.88 45.04	فئران مصابة بداء السكر + الانسولين (10 وحدات دولية /كغم)
bc ±387.81 9.61	Ab ±511.21 4.80	bcd ±453.84 17.95	e ±3091.22 43.01	ef ±2300.42 184.85	def ±4957.80 95.43	فئران مصابة بداء السكر + الراسب البروتيني للمستخلص المائي البارد (15.75 ملغم/كغم)
g ±612.17 28.84	Def ±808.58 7.78	g ±531.62 1.96	b ±2367.84 11.89	abc ±1786.24 41.14	b ±4109.03 119.18	فئران مصابة بداء السكر + الراسب البروتيني للمستخلص المائي المغلي (5.9 ملغم/كغم)

g ±599.35 28.84	Df ±801.27 1.57	fg ±515.38 5.13	bc ±2427.33 47.59	abc ±1808.60 72.37	bc ±4394.6 79.22	فئران مصابة بداء السكر+المركب البروتيني A المفصول من الراسب للمستخلص المائي البارد (10.1 ملغم/كغم)
h ±720.97 36.03	Ef ±817.51 6.52	h ±601.56 10.29	a ±2201.26 11.9	a ±1757.04 36.35	a ±3771.9 44.75	فئران مصابة بداء السكر+المركب البروتيني B المفصول من الراسب البروتيني للمستخلص المائي البارد (4.3 ملغم/كغم)
a ±314.9 52.08	A ±449.78 20.60	a ±240.16 73.16	g ±3611.26 89.24	g ±2526.49 84.41	g ±5671.73 57.63	فئران مصابة بداء السكر+المركب البروتيني A المفصول من الراسب البروتيني للمستخلص المائي المغلي (4.09) ملغم/كغم)
de ±506.40 12.82	c ±598.28 11.25	cdef ±471.79 17.95	cd ±2570.17 53.54	bc ±1955.35 56.22	cde ±4767.42 41.78	فئران مصابة بداء السكر+المركب البروتيني B المفصول من الراسب البروتيني للمستخلص المائي المغلي (1.5 ملغم/كغم)

الحروف المختلفة عمودياً تعني وجود فرق معنوي عند مستوى احتمالية (0.05)
تشير القيم اعلاه الى المعدل ± الانحراف القياسي

تأثير الجهد التأكسدي المستحدث ببيروكسيد الهيدروجين على مستوى الكلوتاثاينون والمالوندايالديهايد في الأنسجة المدروسة لذكور الفئران

أدى استحداث الجهد التأكسدي كما موضح في الجداول (4,3) من خلال المعاملة ببيروكسيد الهيدروجين (0.5%) مع ماء الشرب انخفاضاً معنوياً في مستوى الكلوتاثاينون في أنسجة الكبد والكلية والقلب لذكور الفئران ، وهذا يتفق مع نتائج [22] الذي كانت دراسته على نبات الكرفس ، وكذلك مع نتائج [28] ، اذ لوحظ انخفاض معنوي في مستوى الكلوتاثاينون في أنسجة الابهر والقلب والكبد لاثاث الجرذان البالغة بعد معاملتها ببيروكسيد الهيدروجين (0.5%)

تأثير المستخلصات والبروتينات المعزولة من بذور البازاليا *Pisum sativum* في مستوى الاكسدة الفوقية
للدّهون و الكلوتاثايون في انسجة الفئران سليمة والمصابة بداء السكر والجهد التأكسدي المستحدث
ببيروكسيد الهيدروجين

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، في حين اشارت الباحثة [29] الى ارتفاع معنوي في مستوى الكلوتاثايون في نسيج الكلية ولم
يؤد تغيراً معنوياً يذكر في انسجة الكبد والبنكرياس والقلب في افراخ الدواجن المعرضة للجهد
التأكسدي المستحدث بببيروكسيد الهيدروجين (0.5%) لمدة ثلاثة اسابيع مقارنة مع مجموعة
السيطرة السليمة . وجد ان الانخفاض في مستوى كلوتاثايون الانسجة (الكبد ، الكلية ، القلب)
في ذكور الفئران قد يكون نتيجة لحدوث الجهد التأكسدي الناتج من تجريع احد اصناف
الايوكسجين الفعالة التي تتمثل بببيروكسيد الهيدروجين مما أدى الى استنزاف الكلوتاثايون من تلك
الانسجة وهذا ما اكدته [30] ، ورافق هذا الانخفاض في مستوى الكلوتاثايون في هذه الانسجة
ارتفاعاً معنوياً في مستوى المالوندايديهايد في الانسجة المدروسة ، وهذا يتفق مع نتائج [22] ،
وكذلك مع نتائج [28] ، اذ لوحظ ارتفاع معنوي في مستوى المالوندايديهايد في انسجة الابهر
والقلب والكبد لاناث الجرذان البالغة المعاملة بببيروكسيد الهيدروجين ، فضلاً عن ذلك لوحظت
زيادة معنوية في مستوى المالوندايديهايد في انسجة الكبد والكلى والبنكرياس والقلب في افراخ
الدواجن المعاملة بببيروكسيد الهيدروجين [29] . وقد تعزى هذه الزيادة في مستوى
المالوندايديهايد في الانسجة المدروسة الى عدم قابلية هذه الانسجة لمقاومة الجهد التأكسدي
المستحدث تجريبياً ، وهذه الزيادة في محتويات المالوندايديهايد تشير الى زيادة في بيروكسدة
الدهن في هذه الانسجة [31].

الجدول 3: تأثير المستخلص المائي الخام وغير البروتيني البارد والمغلي لبذور نبات البازاليا
في مستويات الكلوتاثايون والمالوندايديهايد في انسجة الكبد والكلى والقلب في ذكور الفئران
المعرضة للجهد التأكسدي بوساطة بيروكسيد الهيدروجين

المعاملات			الكلوتاثايون (نانومول/غم)			والمالوندايديهايد (نانومول/غم)		
الكبد	الكلى	القلب	الكبد	الكلى	القلب	الكبد	الكلى	القلب
c ±5165.69 218.68	bcd ±1951.39 91.23	bcd ±2538.39 83.57	b ±416.12 58.44	a ±583.32 53.4	ab ±485.03 38.64	فئران سليمة معاملة بالمحلول الملحي الفسلجي (سيطرة سليمة C)		
a ±3156.94 61.84	a ±1439.74 154.68	a ±1981.11 48.92	i ±894.22 29.94	c ±1105.76 80.12	f ±960.82 56.23	فئران معاملة بببيروكسيد الهيدروجين (0.5%) مع ماء الشرب فقط (سيطرة معرضة للجهد التأكسدي C ⁺)		

ab ±482.97 1.98	a ±565.16 58.72	b ±409.93 7.34	bcd ±2558.23 40.04	bcd ±1983.12 39.49	c ±5211.64 82.70	فرنار معاملة بيبروكسيد الهيدروجين (0.5%) مع ماء الشرب+الانسولين (10 وحدات دولية ملغم/ كغم)
ab ±478.62 13.34	a ±511.74 81.48	de ±538.19 31.19	de ±2724.98 110.85	cd ±2165.56 94.44	c ±4941.92 56.22	فرنار معاملة بيبروكسيد الهيدروجين (0.5%) مع ماء الشرب+المستخلص المائي الخام البارد (750 ملغم/كغم)
cd ±641.02 12.82	bc ±1036.25 5.6	g ±607.9 20.16	b ±2225.57 66.11	abc ±1784.81 78.02	b ±3974.03 83.44	فرنار معاملة بيبروكسيد الهيدروجين (0.5%) مع ماء الشرب+المستخلص المائي الخام المغلي (500 ملغم/كغم)
a ±429.48 29.37	a ±483.97 6.41	c ±475.95 6.98	de ±2974.65 47.73	d ±2300.41 91.54	c ±4989.53 184.46	فرنار معاملة بيبروكسيد الهيدروجين (0.5%) مع ماء الشرب+المستخلص غير البروتيني البارد (730 ملغم/كغم)
c ±602.66 6.41	bc ±1019.99 11.14	g ±599.88 16.13	bc ±2260.75 71.13	abc ±1808.6 35.69	b ±4021.77 94.45	فرنار معاملة بيبروكسيد الهيدروجين (0.5%) مع ماء الشرب+المستخلص غير البروتيني المغلي (494 ملغم/كغم)

الحروف المختلفة عموديا تعني وجود فرق معنوي عند مستوى احتمالية (0.05)

تشير القيم اعلاه الى المعدل ± الانحراف القياسي

تأثير المستخلصات والبروتينات المعزولة من بذور البازاليا *Pisum sativum* في مستوى الاكسدة الفوقية
لدهون و الكلوتاثايون في انسجة الفئران السليمة والمصابة بداء السكر والجهد التأكسدي المستحدث
ببيروكسيد الهيدروجين

ناهدة وإيمان

الجدول 4: تأثير الروا سب البروتينية والمركبات البروتينية المفصولة منها لبذور نبات البازاليا
في مستويات الكلوتاثايون والمالوندايديهايد في انسجة الكبد والكلى والقلب في ذكور الفئران
المعرضة للجهد التأكسدي

المعاملات			الكلوتاثايون (نانومول/غم)			المالوندايديهايد (نانومول/غم)		
القلب	الكلى	الكبد	القلب	الكلى	الكبد	القلب	الكلى	الكبد
ab ±485.03 38.64	a ±583.32 53.4	b ±416.12 58.44	bcd ±2538.39 83.57	bcd ±1951.39 91.23	C ±5165.69 218.68	افئران سليمة معاملة بالمحلول الملحي الفسلجي (سيطرة سليمة C)		
f ±960.82 65.23	c ±1105.76 80.12	i ±894.22 29.94	a ±1981.11 48.92	a ±1439.74 154.68	a ±3156.94 61.84	فئران معاملة بببيروكسيد الهيدروجين (0.5%) مع ماء الشرب فقط (سيطرة معرضة لجهد التأكسدي C ⁺)		
ab ±482.97 1.98	a ±565.16 58.72	B ±409.93 7.34	bcd ±2558.23 40.04	bcd ±1983.12 39.49	c ±5211.64 82.70	فئران معاملة بببيروكسيد الهيدروجين (0.5%) مع ماء الشرب+الانسولين (10 وحدات دولية /كغم)		
a ±461.53 19.23	a ±499.99 11.55	Cd ±508.01 9.74	de ±2901.28 89.16	cd ±2189.36 154.1	c ±4957.8 85.22	فئران معاملة بببيروكسيد الهيدروجين (0.5%) مع ماء الشرب+الراسب البروتيني للمستخلص المائي البارد (15.75 ملغم/كغم)		
e ±749.99 44.87	bc ±1087.21 43.38	H ±695.25 50.58	b ±2141.77 30.22	ab ±1588.47 39.01	b ±3902.78 128.70	فئران معاملة بببيروكسيد الهيدروجين (0.5%) مع ماء الشرب+الراسب البروتيني للمستخلص المائي المغلي (5.9 ملغم/كغم)		
de ±721.15 48.08	bc ±1061.12 61.11	G ±631.94 9.65	b ±2189.57 53.56	ab ±1677.71 54.52	b ±3938.48 94.44	فئران معاملة بببيروكسيد الهيدروجين (0.5%) مع ماء الشرب+المركب البروتيني A المفصول من الراسب البروتيني للمستخلص المائي البارد (10.1 ملغم/كغم)		
f ±956.66	c ±1100.22	I ±885.92	a ±1984.17	a ±1452.62	a ±3162.56	فئران معاملة بببيروكسيد الهيدروجين (0.5%) مع ماء		

4.1	18.26	22.79	101.08	28.57	58.70	الشرب+المركب البروتيني B المفصول من الراسب البروتيني للمستخلص المائي البارد (4.3 ملغم/كغم)
a ±397.43 12.82	a ±469.01 8.06	A ±324.25 7.9	e ±3307.78 106.84	e ±2962.79 32.48	d ±5378.66 60.93	فئران معاملة ببيروكسيد الهيدروجين (0.5%) مع ماء الشرب + المركب البروتيني A المفصول من الراسب البروتيني للمستخلص المائي المغلي (4.09 ملغم/كغم)
bc ±557.69 25.64	a ±592.94 16.02	Bc ±572.11 22.43	bc ±2332.15 41.02	bc ±1887.93 32.05	b ±4299.43 30.03	فئران معاملة ببيروكسيد الهيدروجين (0.5%) مع ماء الشرب+المركب البروتيني B المفصول من الراسب البروتيني للمستخلص المائي المغلي (1.5 ملغم/كغم)

الحروف المختلفة عموديا تعني وجود فرق معنوي عند مستوى احتمالية (0.05)
تشير القيم اعلاه الى المعدل \pm الانحراف القياسي

تأثير المستخلص المائي الخام وغيرالبروتيني البارد والمغلي على مستويات الكلوتاثاينون
والمالوندايديهايد في الأنسجة المدروسة لذكور الفئران السليمة والمصابة بداء السكر
والمعرضة للجهد التأكسدي
* الكلوتاثاينون :

من خلال المعاملة بالمستخلص المائي الخام وغيرالبروتيني البارد لبذور نبات البازاليا لوحظ
حدوث ارتفاع في مستوى الكلوتاثاينون في أنسجة الكبد والكلية والقلب لذكور الفئران السليمة
والمصابة بداء السكر والمعرضة للجهد التأكسدي وكما موضح في الجداول (3,1,5) وهذا يتفق
مع نتائج [22] ،

ان قدرة هذا المستخلص في رفع مستوى الكلوتاثاينون في الأنسجة المدروسة ربما تعزى الى
احتوائه لنشاط مضاد للاكسدة من خلال تنشيط مضادات الاكسدة الانزيمية [25] ، كما أدت
المعاملة بالمستخلص المائي الخام وغيرالبروتيني المغلي لبذور نبات البازاليا زيادة معنوية في
مستوى الكلوتاثاينون في أنسجة الكبد والقلب في حين احدثت ارتفاع غير معنوي في مستوى
الكلوتاثاينون في نسيج الكلية لذكور الفئران السليمة والمصابة بداء السكر والمعرضة للجهد

تأثير المستخلصات والبروتينات المعزولة من بذور البازاليا *Pisum sativum* في مستوى الاكسدة الفوقية
لدهون و الكلوتاثايون في انسجة الفئران السليمة والمصابة بداء السكر والجهد التأكسدي المستحدث
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التأكسدي ، وقد يعزى السبب الى قدرة هذا المستخلص على تنشيط فعالية انزيم كلوتاثايون
سينثيتيز GSH Synthetase [32].

* المألونداياليديهايد :

لوحظ حدوث انخفاض معنوي في مستوى المألونداياليديهايد في انسجة الكبد والكلى والقلب لذكور
الفئران السليمة والمصابة بداء السكر والمعرضة للجهد التأكسدي خلال المعاملة بالمستخلص
المائي الخام وغيرالبروتيني البارد كما مشار اليه في الجداول (3,1,5) ، وهذا يتفق مع نتائج
دراسة [22]، كذلك أدت المعاملة بالمستخلص المائي الخام وغيرالبروتيني المغلي لبذور نبات
البازاليا انخفاضاً معنوياً في مستوى المألونداياليديهايد في انسجة القلب والكبد في حين أدت تغيراً
غيرمعنوي في مستوى المألونداياليديهايد في نسيج الكلية ، . وقد يعزى ذلك الى احتواء هذه
المستخلصات على مادة الصابونين التي تمتلك تأثير مضاد للأكسدة [33], 34

الجدول 5: تأثير المستخلص المائي الخام وغيرالبروتيني البارد والمغلي لبذور نبات البازاليا في
مستويات الكلوتاثايون والمألونداياليديهايد في انسجة الكبد والكلى والقلب في ذكور الفئران
السليمة

المعاملات	الكلوتاثايون (نانومول/غم)			المألونداياليديهايد (نانومول/غم)		
	الكبد	الكلى	القلب	الكبد	الكلى	القلب
فئران سليمة معاملة بالمحلول الملحي الفسلجي (سيطرة سليمة C)	a ±5203.71 44.97	a ±1971.22 83.91	a ±2449.76 24.77	h ±422.01 51.51	f ±582.3 18.22	g ±499.99 23.11
فئران سليمة +الانسولين (10 وحدات دولية/كغم)	ef ±7654.85 20.78	cd ±2605.82 28.78	bcd ±2935.02 53.09	ab ±200.99 4.78	bcd ±331.99 21.94	cd ±332.47 24.54
فئران سليمة + المستخلص المائي الخام (750 ملغم/كغم)	e ±7071.82 36.50	de ±2827.93 24.94	bcd ±2974.68 62.91	de ±268.68 2.13	abc ±302.34 46.92	bc ±294.87 29.37

فئران سليمة + المستخلص المائي الخام المغلي (500 ملغم/كغم)	cd ±6056.45 27.37	ab ±2144.13 51.92	bc ±2831.90 42.89	f ±307.56 10.33	ef ±415.06 14.42	ef ±391.02 23.11
فئران سليمة + المستخلص غير البروتيني البارد (730 ملغم/كغم)	ef ±7551.73 70.98	e ±3010.37 39.25	cd ±3291.98 74.94	bc ±224.57 3.22	a ±252.66 51.7	ab ±267.09 22.51
فئران سليمة + المستخلص غير البروتيني المغلي (494 ملغم/كغم)	cd ±6215.11 49.33	abc ±2316.28 32.16	bcd ±2859.66 46.71	ef ±294.06 10.41	ef ±391.01 90.25	e ±378.2 25.64

الحروف المختلفة عمودياً تعني وجود فرق معنوي عند مستوى احتمالية (0.05)
تشير القيم اعلاه الى المعدل \pm الانحراف القياسي

تأثير الراسب البروتيني البارد والمغلي والمركبات البروتينية المفصولة منه على مستويات
الكلوتاثايون والمالوندايالديهيد في الأنسجة المدروسة في الفئران السليمة والمصابة بداء
السكر والمعرضة للجهد التأكسدي
* الكلوتاثايون :

أدت المعاملة بالراسب البروتيني المغلي والمركب البروتيني A المفصول من الراسب
البروتيني للمستخلص المائي البارد كما موضح في الجداول (4,2,6) ارتفاعاً معنوياً في مستوى
الكلوتاثايون في أنسجة الكبد والقلب في حين أدت الى زيادة غير معنوية في نسيج الكلية في
ذكور الفئران السليمة والمصابة بداء السكر المستحدث بالالوكسان والمعرضة للجهد التأكسدي ،
في حين احدثت المعاملة بالراسب البروتيني البارد والمركبين البروتينيين B,A المفصولين من
الراسب البروتيني للمستخلص المائي المغلي ارتفاعاً معنوياً في مستوى الكلوتاثايون في أنسجة
الكبد والقلب والكلية لذكور الفئران السليمة والمصابة بداء السكر والمعرضة للجهد التأكسدي في
الجدول المذكورة اعلاه. وقد يعزى ذلك الى زيادة فعالية انزيم كلوتاثايون ريدكتيز الذي يعمل
على اختزال الكلوتاثايون المؤكسد الى الشكل المختزل باستخدام NADPH عاملاً مختزلاً [35]،
اما المركب البروتيني B البارد لم يؤد فرقاً معنوياً في مستوى الكلوتاثايون في الانسجة المدروسة
لذكور الفئران السليمة والمصابة بداء السكر المستحدث بالالوكسان والمعرضة للجهد التأكسدي .

تأثير المستخلصات والبروتينات المعزولة من بذور البازاليا *Pisum sativum* في مستوى الاكسدة الفوقية
لدهون و الكلوتاثايون في انسجة الفئران السليمة والمصابة بداء السكر والجهد التأكسدي المستحدث
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* المألوندايالديهيد :

انخفض مستوى المألوندايالديهيد معنويا في انسجة الكبد والقلب وعلى نحو غير معنوي
في نسيج الكلية لذكور الفئران السليمة والمصابة بداء السكر المستحدث بالالوكسان والمعرضة
للجهد التأكسدي في الجداول (2, 6,4) خلال المعاملة بالراسب البروتيني المغلي والمركب
البروتيني A المفصول من الراسب البروتيني للمستخلص المائي البارد ، اما المعاملة بالراسب
البروتيني البارد والمركبين البروتينيين B,A المفصولان من الراسب البروتيني للمستخلص المائي
المغلي فقد أدت انخفاضاً معنوياً في مستوى المألوندايالديهيد في انسجة الكبد والكلى والقلب
لذكور الفئران السليمة والمصابة بداء السكر والمعرضة للجهد التأكسدي ، وقد يعزى السبب الى
ان هذه الرواسب والمركبات المفصولة منها تعمل على تنشيط مضادات الاكسدة الانزيمية مثل
سوبراوكسايد دسميوتز SOD ، و انزيم الكاتاليز CAT التي تسهم في ازالة اصناف الاوكسجين
الفعالة مما يؤدي بالتالي خفض عملية بيروكسدة (زناخة) الدهن المتمثلة بالمألوندايالديهيد
[34]، في حين لم يؤد المركب البروتيني B البارد الى أي فرق معنوي يذكر ، وهذا قد يشير الى
ان هذا المركب ليس له تأثير في عملية بيروكسدة الدهن .

الجدول 6: تأثير الرواسب البروتينية والمركبات البروتينية المفصولة منها لبذور نبات البازاليا
في مستويات الكلوتاثايون والمألوندايالديهيد في انسجة الكبد والكلى والقلب في ذكور الفئران
السليمة

المعاملات			الكلوتاثايون (نانومول/غم)			المألوندايالديهيد (نانومول/غم)		
الكبد	الكلى	القلب	الكبد	الكلى	القلب	الكبد	الكلى	القلب
a ±5203.71 44.97	a ±1971.22 83.91	a ±2449.76 24.77	h ±422.01 51.51	f ±582.3 18.22	g ±499.99 23.11	فئران سليمة معاملة بالمحلول الملحي الفلسجي (سـيطـرة سليمة C)		
ef ±7654.85 20.78	cd ±2605.82 28.78	bcd ±2935.02 53.09	ab ±200.99 4.78	bcd ±331.99 21.94	cd ±332.47 24.54	فئران سليمة +الانسولين (10 وحدات دولية/كغم)		
ef ±7329.62 65.22	de ±2950.22 74.30	bcd ±3121.43 65.48	cd ±251.21 1.98	ab ±284.85 27.64	ab ±279.67 42.29	فئران سليمة +الراسب البروتيني للمستخلص		

						المائي البارد (15.75 ملغم/كغم)
f ±421.67 17.44	ef ±418.58 70.67	g ±346.95 5.5	b ±2697.04 36.31	ab ±2074.34 50.09	bc ±5679.67 94.6	فئران سليمة +الراسب البروتيني للمستخلص المائي المغلي (5.9 ملغم/كغم)
ef ±399.56 22.51	ef ±447.11 20.83	g ±335.77 3.62	e ±2736.70 23.79	ab ±2090.2 43.98	bcd ±5846.25 47.65	فئران سليمة + المركب البروتيني A المفصول من الراسب البروتيني للمستخلص المائي البارد (10.1 ملغم/كغم)
g ±494.50 6.54	f ±574.58 24.9	h ±411.93 11.43	a ±2504.93 58.62	a ±1998.98 1.78	a ±5263.21 47.16	فئران سليمة + المركب البروتيني B المفصول من الراسب البروتيني للمستخلص المائي البارد (4.3 ملغم/كغم)
a ±249.99 12.82	a ±246.25 17.72	a ±186.96 8.82	d ±3339.57 36.99	f ±3466.49 40.86	f ±7876.96 49.81	فئران سليمة + المركب A المفصول من الراسب البروتيني للمستخلص المائي المغلي (4.09 ملغم/كغم)
de ±358.97 6.41	cd ±366.98 20.45	ef ±284.18 9.11	bcd ±2895.35 57.14	bc ±2403.54 30.33	d ±6464.98 32.44	فئران سليمة + المركب B المفصول من الراسب البروتيني للمستخلص المائي المغلي (1.5 ملغم/كغم)

الحروف المختلفة عموديا تعني وجود فرق معنوي عند مستوى احتمالية (0.05)

تشير القيم اعلاه الى المعدل ± الانحراف القياسي

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مما سبق يمكن أن نستنتج :

1. دلت النتائج وصول كل من مستوى الكلوتاثايون والمالوندايديهايد في نسيج الكبد الى مستوى الحد الطبيعي والتأثير المشابه للانسولين عند الحقن بالراسب البروتيني البارد في الفئران المصابة بداء السكر المستحدث بالالوكسان عند مقارنتها مع مجموعة السيطرة C . فضلاً عن قدرته على ائصال مستوى الكلوتاثايون في انسجة الكبد والكلية والقلب ومستوى المالوندايديهايد في انسجة الكلية والقلب الى المستوى الطبيعي في الفئران المعرضة للجهد التأكسدي فقط .
2. تشير النتائج الى ان حقن المركب البروتيني A المفصول من الراسب البروتيني المغلي بتقنية الترشيح الهلامي في التجويف البريتوني لذكور الفئران السليمة والمصابة بداء السكر المستحدث بالالوكسان والمعرضة للجهد التأكسدي بواسطة بيروكسيد الهيدروجين يؤدي حدوث اعلى ارتفاع في مستوى الكلوتاثايون واكثر انخفاضاً في مستوى المالوندايديهايد في نسيج الكبد مما في الانسجة الاخرى مقارنة بالمستخلصات المائية الخام وغيرالبروتينية والرواسب البروتينية والمركبات المفصولة منها وكذلك الانسولين .
3. امتلاك المستخلص غيرالبروتيني البارد تأثيراً مشابهاً للانسولين في رفع مستوى الكلوتاثايون في انسجة الكبد والكلية والقلب وخفض مستوى المالوندايديهايد في انسجة الكلية والقلب في الفئران المعرضة للجهد التأكسدي .

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انتاج نباتات القرع *Cucurbita pepo* من كالس الجذور الشعرية المحولة وراثياً بالسلالة R 1601 من بكتريا *A.rhizogenes* ومتابعة الفروقات المظهرية والمحتوى البروتيني

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ABSTRACT

This study succeeded in forming hairy roots by direct inoculation of the whole seedlings, shoots, hypocotyles, explants of *Cucurbita* with *Agrobacterium rhizogenes* R1601. The inoculated samples were cultured on agar solidified hormone-free medium. Genetic transformation of hairy roots was proved by detection the agropine in their tissue by using paper electrophoresis. The hairy root cultures of hypocotyles were able to initiate callus after 75 days of culture in agar solidified hormone-free medium. In addition, callus derived from hairy roots expressed its totipotentiality to regenerate shoots, all shoots were rooted easily in hormone- free MS medium and MS medium supplemented with 2.0mg/L IBA. The results shows the putative effects of genetic transformation on the morphological features of *C.pepo* plants regenerated from hairy root cultures. They include shortness of plants, small size and wrinkled leaves, with short internodes.

الخلاصة

نجحت الدراسة في تكوين نمط من الجذور الشعرية Hairy roots ناتجة من تلقيح بادرات القرع الكاملة والبادرات الفاقدة للجذور وقطع السيقان تحت الفلجية المستأصلة منها ببكتريا الاكروبيكتيريوم بالحقن المباشر . وزرعت العينات الملقحة في وسط MS الصلب الخالي من منظمات النمو , وتم التأكد من حدوث التحول الوراثي في مزارع الجذور الشعرية بالكشف عن الاوبينات باستعمال الترحيل الكهربائي Paper electrophoresis الذي أظهر ايجابية الكشف بانفصال بقع الاكروبين من هذه العينات . واستطاعت مزارع الجذور الشعرية المتكونة على السيقان تحت الفلجية استحداث الكالس بعد 75 يوماً في وسط MS الصلب الخالي من منظمات النمو، فضلاً عن تمايز كالمها بعد 25 يوماً وجذرت الافرع الخضرية الناتجة من كالس الجذور الشعرية جميعاً في وسط MS الصلب الخالي من منظمات النمو وكذلك المدعم بإضافة 2.0 ملغم/لتر IBA لوحده. وبينت نتائج هذه الدراسة حصول اختلافات في الصفات المظهرية لنباتات القرع الناتجة من كالس الجذور الشعرية المحولة وراثياً متمثلة بقلّة ارتفاع النباتات، وصغر حجم الاوراق، وتجدها، والتفافها الى الداخل، وقصر السلاميات، وزيادة عدد الافرع الناتجة من العقد .

انتاج نباتات القرع *Cucurbita pepo* من كالس الجذور الشعرية المحولة وراثياً بالسلالة R 1601 من بكتريا *A. rhizogenes* ومتابعة الفروقات المظهرية والمحتوى البروتيني

سنة ونزك

المقدمة

تتتمي نباتات القرع *Cucurbita pepo* L. الى العائلة القرعية Cucurbitaceae (1) وتضم هذه العائلة ما يقارب 90 جنساً و 700 نوعاً , يكثر انتشارها في المناطق الاستوائية وشبه الاستوائية من العالم (2) استخدمت البكتريا من جنس *Agrobacterium* في التحول الوراثي لنباتات العائلة القرعية Cucurbitaceae بوصفها نواقل كفاءة , فقد أنتجت نباتات خيار *Cucumis sativus* مباشرة من مزارع الجذور الشعرية (3), وتمكن (4) من انتاج نباتات خيار *Cucumber* محولة وراثياً في ثمانية اسابيع بأتباع تقانة الزراعة المرافقة *Cocultivation* التي تضمنت تحضين قطع الاوراق وأعناقها مع المعلق البكتيري للسلالة LBA 4404 من بكتريا *A. tumefaciens* مدة خمس دقائق وأنتجت نباتات حنظل *Citrullus colocynthis* محولة وراثياً بتحضين أجزاء من الفلق مع السلالة LB 4404 من بكتريا *A. tumefaciens* وزراعتها على وسط MS الحاوي على 0.5 مايكرومول BA و 5.0 مايكرومول IAA وبدأ استحداث الكالس على هذا الوسط بعد 10 أيام من الزراعة(5).

وفي دراسة أخرى أنتجت نباتات بطيخ *Cucumis melo* محولة وراثياً ناتجة من تحضين بكتريا *A. tumefaciens* مع قطع الأوراق المستأصلة من البادرات بعمر 10 أيام والنامية على وسط MS الصلب المحتوي على 1.0 مايكرومول BA و 1.0 مايكرومول 2ip وتكوينها الأفرع بواقع 73% واستجابت النباتات الناتجة لنظام التأقلم حين نقلها الى التربة (6) تُعد مزارع الجذور الشعرية *Hairy roots* نظاماً جيداً ومباشراً للحصول على نباتات خصبة ذات مواصفات وراثية معينة، ويتم الحصول على النباتات المحولة وراثياً باستعمال بكتريا *Agrobacterium rhizogenes* إما مباشرة من مزارع الجذور الشعرية بتكوين البراعم العرضية *Adventitious buds* أو على نحو غير مباشر باستحداث مزارع الكالس وتحفيزه على تكوين الافرع العرضية , فقد نجحت إحدى الدراسات في تكوين النباتات من البراعم العرضية للجذور الشعرية كما في نبات القرناييط *Brassica oleracea* بعد مرور 2-5 أشهر من إعادة زراعة الجذور الشعرية(7) , وأكدت دراسة أخرى التكوين المباشر للأفرع الخضرية من مزارع الجذور الشعرية لإحدى العوائل البقولية العلفية قرن الغزال *Lotus corniculatus* الملقحة بالسلالة 15834 بكتريا *A. rhizogenes*, ولحظت الدراسة زيادة أعداد الأفرع الخضرية المتكونة بتعرض مزارع الجذور الشعرية للضوء وقد جذرت على الوسط MS الخالي من منظمات النمو (8) . وسجلت دراسة أخرى أن نباتات السوس *Glucurrrhiza glabra* المحولة وراثياً بالحقن المباشر للأوراق الفتية بالسلالة K599 من بكتريا *A. rhizogenes* تكررراً للتحول الوراثي (TF) بلغ 47% في وسط MS و 30% في وسط NB و

20% في وسط B5 وبدأت الجذور الشعرية بالظهور في مواقع حقن الأوراق بعد مرور 25 يوماً من الزراعة ، ووجد تفوق الأوزان الطرية وللنباتات المحولة وراثياً على مثيلاتها في النباتات غير المحولة وراثياً (9).

وتهدف الدراسة إلى:

1- التعرف على استجابة بادرات القرع او اجزاءها حين تلقيحها ببكتريا *A.rhizogenes* على

تكوين الجذور الشعرية والنباتات المشتقة من كالسها .

2- مقارنة الصفات المظهرية بين نباتات القرع الناتجة من الكالس او الناتجة من كالس الجذور

الشعرية المحولة وراثياً والبذرية .

المواد وطرائق العمل

مصدر بذور القرع :

حُصل على بذور نباتات القرع *Cucurbita pepo L.* صنف (الكوسا) من الاسواق المحلية وتم التأكد من تصنيفها ونوعها من المختصين في معشب قسم علوم الحياة.

مصدر بكتريا *A.rhizogenes* R1601 :

استعملت السلالة R1601 من بكتريا *A. rhizogenes* الموجودة في مختبرات قسم علوم الحياة في كلية التربية وتنصف هذه السلالة بامتلاكها الدلائل الوراثية لصفة مقاومة المضادين الحيويين الكاناميسين $\text{Kana}^{\text{Res+}}$ والكاربنسلين $\text{Carb}^{\text{Res+}}$

تحضير لقاح البكتريا *A. rhizogenes* :

حضر معلق هذه البكتريا بنقل مستعمرة واحدة من مزرعة البكتريا النامية على سطح APM الصلب الى ورق سعة 100 مل يحتوي على 25 مل من وسط APM السائل المعقم، نقلت الدوارق الى الحاضنة الهزازة *Shaking incubator* حسب طريقة (10).

التلقيح المباشر للبادرات الكاملة أو أجزائها ببكتريا *A. rhizogenes* السلالة R1601 :

استعملت البادرات الكاملة السليمة المعقمة بعمر 15 يوماً والبادرات الخالية من المجموعة الجذرية والسيقان تحت الفلقية بطول 3-4 سم والاوراق ولقحت العينات النباتية المارة بغمر ابرة (Needle) السرنجة الطبية في لقاح البكتريا ووخزت البادرات وقطع السيقان تحت الفلقية في 3-5 مواقع في حين وخزت الاوراق في العرق الوسطي. وغرست الاجزاء الملقحة قائمة في قناني زجاجية سعة 100 مل تحتوي على 25 مل من وسط MS (11) الصلب الخالي من منظّمات النمو وبمعدل 2-1 قطعة /قنينة وحفظت العينات في غرفة الزروع بدرجة حرارة $25 \pm 2^\circ \text{C}$ وشدة اضاءة 200

انتاج نباتات الفرع *Cucurbita pepo* من كالس الجذور الشعرية المحولة وراثيا بالسلالة R 1601 من
بكتريا *A. rhizogenes* ومتابعة الفروقات المظهرية والمحتوى البروتيني

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لوكس (8) . وعدت البادرات وقطع السيقان والاوراق الملقحة بوخزها بالماء المقطر المعقم عينات
مقارنة .

ثم حسبت النسبة المئوية لتكرار التحول الوراثي وفق الصيغة الآتية :

$$\text{تكرار التحول الوراثي (TF)} = \frac{\text{عدد الوخزات المستجيبة لتكوين الجذور الشعرية}}{\text{العدد الكلي للوخزات}} \times 100$$

(9)

استحداث مزارع الجذور الشعرية :

استؤصلت الجذور الشعرية الفتية المتكونة في مواقع التلقيح بطول 1-3 سم ونقلت بشكل
خصلة كاملة الى اطباق بتري زجاجية قطر 9 سم تحتوي على وسط MS الصلب الخالي من
منظمات النمو وسدت الاطباق باغطيئها، ثم سدت حافاتهما بالبارافيلم Parafilm وحفظت العينات
في الظروف المشار اليها .

إدامة مزارع الجذور الشعرية المحولة وراثياً :

اعيدت زراعة مزارع الجذور الشعرية الخالية من البكتريا كل 10-20 يوماً مع إزالة الجذور
الميتة عنها، وتقسيم المزرعة إلى 2-3 خصل، ونقل كل منها إلى طبق جديد يحتوي على وسط
MS الصلب الخالي من منظمات النمو، وحفظت العينات في الظروف السابقة نفسها .

الترحيل الكهربائي Electrophoresis للكشف عن الاوبينات في مزارع الجذور الشعرية :

استعملت الطريقة القياسية (12) للكشف عن الاوبينات Opines في مزارع الجذور الشعرية،
ومقارنتها بجذور البادرات السليمة غير الملقحة .

استحداث مزارع الكالس من الجذور الشعرية :

نقلت مجموعة من الجذور الشعرية بطول 2-3 سم ووضعت على سطح 25 مل من وسط
MS الصلب الخالي من منظمات النمو وفي الظروف المشار اليها (13).

تكوين الافرع الخضرية من كالس الجذور الشعرية :

نقلت قطع الكالس المستحدثة من مزارع الجذور الشعرية الى وسط MS الصلب الخالي من
منظمات النمو، لتكوين الأفرع الخضرية.

تجذير الافرع الخضرية الناتجة من كالس الجذور الشعرية المحولة وراثيا :

استؤصلت الأفرع الخضرية بطول 2-4 سم الناتجة من كالس الجذور الشعرية، وغرست
قواعدها قائمة في 25 مل من وسط MS الصلب الخالي من منظمات النمو أو الحاوي على 2.0
ملغم /لتر من IBA وحفظت العينات في الظروف السابق ذكرها .

نقل النباتات الناتجة من كالس الجذور الشعرية المحولة وراثياً الى التربة :

رُفعت مجموعة هذه النباتات التي تمتلك مجموعة جذرية جيدة بعمر 20 يوماً من وسط التجذير ، نقلت بعناية الى التربة كما ذكر سابقاً .

مقارنة عدداً من الصفات المظهرية بين النباتات الناتجة من البذور والنباتات الناتجة من كالس الجذور الشعرية المحولة وراثياً :

قورنت مجموعة من الصفات بين النباتات الناتجة من البذور والنباتات الناتجة من كالس الجذور الشعرية المحولة وراثياً وبالمرحلة العمرية نفسها ثلاثة اسابيع، وشملت صفات : ارتفاع النباتات وعدد الافرع وعدد العقد وأطوال السلاميات وعدد الأوراق ومساحة الورقة وأطوال الجذور وعددها .

حساب العدد الكروموسومي :

قدر العدد الكروموسومي في القمم النامية لجذور النباتات الناتجة من الجذور الشعرية المحولة وراثياً حسب طريقة الهرس (14) .

تقدير المحتوى البروتيني :

قدر البروتين الكلي بطريقة فولن (15) المحورة عن طريقة (16)، بالاعتماد على قياس الكثافة الضوئية عند الطول الموجي 650 نانوميتر طيفياً .

النتائج والمناقشة

نشوء الجذور الشعرية من التلقيح بالحقن المباشر للبادرات الكاملة أو أجزائها ببيكتريا *A. rhizogenes* R1601 :

لحظت النتائج الأولية لتلقيح بادرات القرع الكاملة بعمر 15 يوماً أو أجزائها (البادرات الفاقدة للجذور ، قطع السيقان تحت الفلقية والأوراق) ببيكتريا *A. rhizogenes* ، والتي حقنت في أكثر من موقع في هذه الاجزاء ، وزرعت قائمة في وسط MS الصلب الخالي من منظمات النمو، لحظت تحمل هذه العينات النباتية عملية التلقيح واحتفاظها بحيويتها واستجابتها بتكوين مجموعة من الجذور العرضية في مواقع التلقيح.

وقد كانت استجابة قطع السيقان تحت الفلقية أفضل من استجابة البادرات الفاقدة للجذور والبادرات الكاملة، إذ سجلت نسبة تكوينها الجذور الشعرية 76% في حين بلغت نسبة تكوينها في البادرات الفاقدة للجذور والبادرات الكاملة 44 و 50% على التوالي (الجدول 1) . في حين لم تستجب الاوراق المستأصلة من البادرات نفسها لعملية التلقيح، ولم تظهر عليها أية علامات.

انتاج نباتات القرع *Cucurbita pepo* من كالس الجذور الشعرية المحولة وراثيا بالسلالة R 1601 من بكتريا *A.rhizogenes* ومتابعة الفروقات المظهرية والمحتوى البروتيني

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جدول 1: تكوين الجذور الشعرية على بادرات القرع *C. pepo* الكاملة أو أجزائها الملقحة بالحقن

المباشر ببكتريا *A. rhizogenes*

الاجزاء النباتية	عدد القطع المستجيبة	تكوين الجذور الشعرية %	معدل عدد الجذور الشعرية/قطعة	مدة تكوينها (يوم)
البادرات الكاملة (المقارنة)	25 0	50 0	3 0	7 0
البادرات الفاقدة للجذور (المقارنة)	22 0	44 0	4 0	8 0
السيقان تحت الفلقية (المقارنة)	38 0	76 0	6 0	5 0

عدد المكررات 50 عينة نباتية/ معاملة , المقارنة تمثل الاجزاء المحقونة بالماء المقطر .

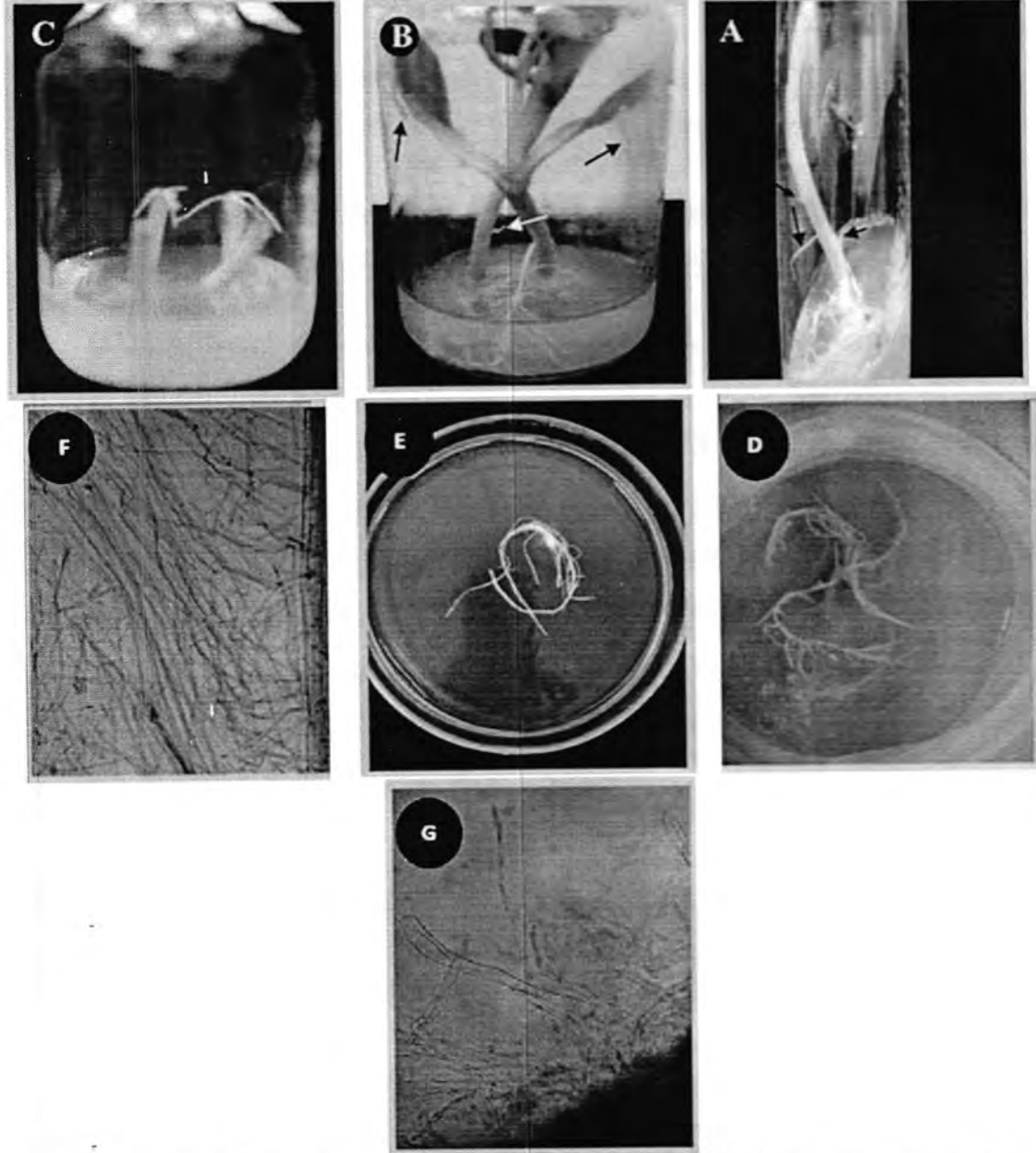
تكوين الجذور الشعرية في مواقع الحقن المباشر :

ظهرت أولى علامات تكوين الجذور الشعرية في مواقع الحقن المباشر للبادرات الكاملة الملقحة ببكتريا *A. rhizogenes* والمزروعة في وسط MS الصلب الخالي من منظمات النمو بعد 7 أيام من تلقيحها (الشكل A.1) . واستغرق ظهورها على البادرات الفاقدة للجذور والملقحة من 9-7 أيام (الشكل B.1) وعلى قطع السيقان تحت الفلقية 5 أيام (الشكل C.1) . وعموماً كان ظهورها بهيئة تراكيب خيطية , رقيقة , بيضاء اللون , غزيرة الشعيرات الجذرية , سالبة الانتحاء الارضي negative geotropism ثم انها تطورت بعد ذلك الى كتلة بيضاء كثيفة ظهرت على أجزاء العينة الملقحة , مع احتفاظها بحيويتها ولونها طوال مدد الادامة . ومن الملاحظات المهمة أن لون البادرات الملقحة بالبكتريا والتي تكونت عليها جذوراً شعرية بدأ بالتغير الى الأخضر المصفر بعد مرور 25 يوماً من حقنها وزراعتها على الوسط الغذائي . وبينت النتائج ايضاً أن الاوراق الملقحة في مواقع مختلفة من العرق الوسطي لم تبد أية استجابة لتكوين الجذور الشعرية على الرغم من تحضينها المدة الزمنية نفسها مقترنة بتغير لون الاوراق الى البني المصفر بعد مرور 14 يوماً من تلقيحها بالبكتريا .

إنشاء مزارع الجذور الشعرية على وسط MS الصلب الخالي من منظمات النمو :

أوضحت نتائج نقل الجذور الشعرية المتكونة في مواقع الحقن على البادرات الكاملة وأجزائها بشكل انفرادي أو خصلة وبطول 1.5 سم/ جذر الى وسط MS الصلب الخالي من منظمات النمو اوضحت حدوث زيادة في معدل استطالتها الى 3.0 سم في الاسبوع الثاني من نقلها الى الوسط

الغذائي MS (الشكل D.1) مقارنة بالجذور العادية التي لم تظهر أية زيادة في معدل استطالتها في مدة التحضين نفسها (الشكل E. 1) وتميزت الجذور الشعرية بكثافة وغزارة الشعيرات عليها (الشكل F.1) مقارنة بالجذور الاعتيادية التي تميزت بقلة الشعيرات عليها (الشكل G.1).



شكل 1: تكوين مزارع الجذور الشعرية المحولة وراثياً المتكونة على بادرات القرع واجزائها حين

تلقيحها ببكتريا *A. rhizogenes* R1601 وإنشاء مزارع الجذور الشعرية

(A): بدايات نشوء الجذور الشعرية في مواقع تلقيح البادرات الكاملة (بعد 7 أيام) ببكتريا *A. rhizogenes*

(B): بدايات نشوء الجذور الشعرية على البادرات الفاقدة لمجاميعها الجذرية (بعد 9 أيام) في مواقع الحقن ببكتريا *A. rhizogenes*

انتاج نباتات القرع *Cucurbita pepo* من كاسس الجذور الشعرية المحولة وراثياً بالسلالة R 1601 من بكتريا *A. rhizogenes* ومتابعة الفروقات المظهرية والمحتوى البروتيني

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(C): نشوء الجذور الشعرية على أسطح قطع السيقان تحت الفلقية (بعد 5 أيام) من حقنها ببكتريا *A. rhizogenes*

(D): استحداث مزرعة الجذور الشعرية Hairy roots من الجذور المستأصلة في (C) بعد 40 يوماً على وسط MS الصلب الخالي من منظمات النمو.

(E): توقف نمو الجذور الاعتيادية المستأصلة من البادرات (بعد 40 يوماً) من نقلها على وسط MS الصلب الخالي من منظمات النمو.

(F): عينة من الجذور الشعرية في (D) تحت المجهر الضوئي (40X) لملاحظة كثافة الشعيرات الجذرية عليها .

(G): عينة من الجذور الاعتيادية تحت المجهر الضوئي (40X) لملاحظة قلة الشعيرات الجذرية عليها.

الكشف عن الاوبينات Opines في الجذور الشعرية بالترجيل الكهربائي

: Paper Electrophoresis

أشارت نتائج الترحيل الكهربائي Electrophoresis لعينة من مستخلص الجذور الشعرية المحملة على ورق الكروماتوغرافيا الى انفصال بقع من الاكروبين Agropine من الجذور الشعرية، مقابلة لبقعة الاكروبين القياسي Standard Agropine وغيابها في عينات المقارنة من الجذور الاعتيادية ، ويُفَد هذا الكشف على أغلبية مزارع الجذور الشعرية المتكونة اثناء العمل، وأعطت جميعاً أدلة واضحة لاجابية هذا الكشف . تؤكد نتائج هذا الاختبار مبدئياً حدوث التحول الوراثي في هذه الانسجة بدلالة تكون هذا النوع من الاوبينات في هذه الجذور . وتشير نتائج الجدول (2) الى قيم تكرار التحول الوراثي (TF) في العينات المختبرة.

جدول 2: تكرار التحول الوراثي في الجذور الشعرية المحولة وراثياً والمتكونة على بادرات القرع

A. rhizogenes الملقحة ببكتريا *C. pepo*

العينة النباتية	عدد القطع الملقحة	العدد الكلي للوخزات/قطعة	عدد الوخزات المكونة للجذور/قطعة	تكرار التحول الوراثي TF (%)
البادرات	10	8	5	62.50
(مقارنتها)	8	6	0	0
البادرات الفاقدة للجذور	8	4	2	50
(مقارنتها)	8	4	0	0
السيقان تحت الفلقية	15	8	6	75
* (مقارنتها)	10	7	0	0

* تمثل المقارنة : التلقيح بالماء المقطر المعقم .

استحداث الكالس من الجذور الشعرية المحولة وراثياً :

عُبرت الجذور الشعرية المحولة وراثياً عن طاقتها الكامنة باستحداثها للكالس حين زراعتها على وسط MS الصلب الخالي من منظمات النمو في ظروف اضاءة منخفضة 100 لوكس . الأضاءة العالية تثبط تكوين الجذور وتمثلت مراحل تكوينها للكالس بمباشرة هذه الجذور بالانتفاخ وزيادة اقطارها بعد مرور 30 يوما من زراعتها (الشكل A.2) على وسط MS الصلب متبوعاً باختفاء معالمها وتحولها كاملة الى كتلة خلوية غير متميزة من الكالس بعد مرور 75 يوما من نقلها على الوسط الغذائي . واستمر الكالس المتكون بنموه وزيادة حجمه طيلة مدة الادامة الدورية على هذا الوسط ، واتصف بقوامه المتماسك قليلا ولونه الابيض المصفر (الشكل B.2) ، مماثلاً في بنيته ولونه للكالس المشتق من قطع السيقان والاوراق المأخوذة من بادرات القرع .

وعموماً، تفوقت مزارع الجذور الشعرية المستأصلة من قطع السيقان تحت الفلجية في استعدادها وسهولة تكوينها للكالس على اوساط MS الصلبة الخالية من منظمات النمو مقارنة بمزارع الجذور الشعرية المستأصلة من البادرات الكاملة والبادرات الفاقدة للجذور ، ربما يعزى السبب إلى نشاط الأنسجة المرستيمية (الكامبيوم) في السيقان في حين فشلت الجذور الاعتيادية في تكوين الكالس حين زراعتها على الوسط نفسه MS الخالي من منظمات النمو .

تكوين الافرع الخضرية من كالس الجذور الشعرية المحولة وراثياً :

من النتائج البارزة والمهمة أن كالس الجذور الشعرية المحولة وراثياً اظهر قابلية على تكوين الافرع الخضرية ، فقد أبدت مزارع الكالس المشتق من الجذور الشعرية اثناء ادامتها الدورية كل 20-15 يوما على وسط MS الصلب الخالي من منظمات النمو قدرتها على تكوين تراكيب شبيهة بالأعضاء في ظروف النمو $(25 \pm 2^\circ \text{C})$ وشدة اضاءة 1500 لوكس /16 ساعة ضوء يومياً). تطورت الى اعضاء خضرية بعد 15 يوماً من إعادة الزراعة على الوسط الغذائي (الشكل C. 2) ثم تكشفت بعدئذٍ عن افرع خضرية كاملة تحمل 2-3 ورقة /فرع بعد مرور 10 أيام اخرى (الشكل D. 2). وتمكنت هذه الافرع من الاستمرار في نموها على الوسط الغذائي نفسه الى حين بلوغها حجماً مناسباً يضمن نجاح نقلها الى وسط التجذير. وقد اشارت النتائج الى أن مزارع الجذور الشعرية المستأصلة من قطع السيقان تحت الفلجية امتلكت قابلية بارزة على استحداث الكالس وتكوين الافرع الخضرية بواقع 60 % (الجدول 3) مقارنة بمزارع الجذور الشعرية الناشئة عن تلقيح البادرات الفاقدة للجذور والبادرات الكاملة إذ سجلت 33.33 و 40% على التوالي وبلغ عدد الافرع الخضرية المتكونة 2-3 /قطعة كالس .

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جدول 3: تكوين الأفرع الخضرية من الكالس المشتق من الجذور الشعرية المحولة وراثياً الناشئة على بادرات القرع *C.pepo* الكاملة والفاقة للجذور وقطع السيقان تحت الفلقية حين تلقيحها

ببكتريا *A. rhizogenes*

منتشأ مزارع الجذور الشعرية	قطع الكالس المستحدث من مزارع الجذور الشعرية	العدد الكلي لقطع الكالس المكونة للأفرع الخضرية	المجموع الكلي للأفرع الخضرية	إنتاج الأفرع الخضرية (%)
البادرات الكاملة	5	2	4	40
البادرات الفاقدة للجذور	3	1	2	33.33
السيقان تحت الفلقية	10	6	13	60
المقارنة*	0	0	0	0

* تمثل المقارنة الجذور الاعتيادية لبادرات القرع *C. pepo*.

تجذير الأفرع الخضرية الناتجة من تمايز كالس الجذور الشعرية المحولة وراثياً :

أظهرت الأفرع الخضرية جميعاً الناتجة من تمايز كالس الجذور الشعرية المحولة وراثياً ببكتريا *A.rhizogenes* اظهرت سهولة واضحة في تكوينها للجذور.

جدول 4: تجذير مجموعة الأفرع الخضرية المتميزة من كالس الجذور الشعرية المحولة وراثياً

من بادرات القرع *C. pepo* والملقحة ببكتريا *A. rhizogenes*

التجذير %	العدد الكلي للأفرع الخضرية المكونة للجذور	عدد الأفرع الخضرية المتكونة من كالس الجذور الشعرية		أوساط التجذير
100	3		3	MS بدون منظمات
100	5		5	IBA+2.0ملغم/لتر

فقد باشرت الأفرع جميعاً بتكوين جذورها بعد 10 أيام من نقلها الى وسط التجذير MS الصلب الخالي من منظمات النمو و 7 أيام في وسط التجذير MS الحاوي على 2.0 ملغم/لتر IBA (الجدول 4) .

وتراوح أطوال الجذور المتكونة بين 1-4 وتراوح أعدادها بين 6-8 جذر (الشكل 2.E).

نقل النباتات الناتجة من كالس الجذور المحولة وراثياً الى التربة واقلمتها :

أشارت النتائج الى تحمل نباتات القرع الناتجة من كالس الجذور الشعرية المحولة وراثياً عملية نقلها الى التربة في سنادين وتغطيتها بأغطية بلاستيكية شفافة مثقبة في ظروف المختبر للأيام الثلاثة الاولى ، ثم رفعت بعد ذلك هذه الأغطية عنها مع متابعة نموها ، وقد أظهرت قابليتها على تحمل الظروف البيئية خارج المختبر واستمرارها بالنمو (الشكل F.2) .

مقارنة عدد من الصفات المظهرية بين نباتات القرع *C.pepo* الناتجة من كالس الجذور الشعرية المحولة وراثياً مع النباتات البذرية

امتازت مجموعة نباتات القرع الناتجة من كالس الجذور الشعرية المحولة وراثياً بقصر ارتفاعاتها وصغر حجم أوراقها وتجدها والتفافها للداخل، ولونها الغامق قياساً بالنباتات البذرية (المقارنة) فضلاً عن حصول زيادة في عدد العقد ، وقصر السلاميات وفي قطر سيقانها وأفرعها الخضرية المتكونة عليها (الشكل G.2) .

جدول 5: الاختلافات المظهرية بين مجموعتين من نباتات القرع *C. pepo* المتميزة من كالس الجذور الشعرية المحولة وراثياً ومجموعة النباتات البذرية بعمر ثلاثة اسابيع

الصفات	النباتات الناتجة من كالس الجذور الشعرية المحولة وراثياً	النباتات البذرية
ارتفاع النباتات (سم)	1.58 ± 4.0	1.58 ± 7.0
عدد الأفرع الخضرية	1.29 ± 5.0	0.70 ± 2.0
عدد العقد	1.29 ± 5.0	0.70 ± 2.0
أطوال السلاميات (سم)	0.38 ± 1.0	0.79 ± 3.0
عدد الاوراق	1.29 ± 5.0	1.58 ± 4.0
مساحة الورقة (سم ²)	0.17 ± 0.72	0.50 ± 5.43
طول الجذور (سم)	0.70 ± 2.0	0.70 ± 5.0
عدد الجذور	1.58 ± 7.0	2.34 ± 12.0

الأرقام تمثل معدلات القيم لخمسة نباتات \pm الانحراف القياسي (SD)

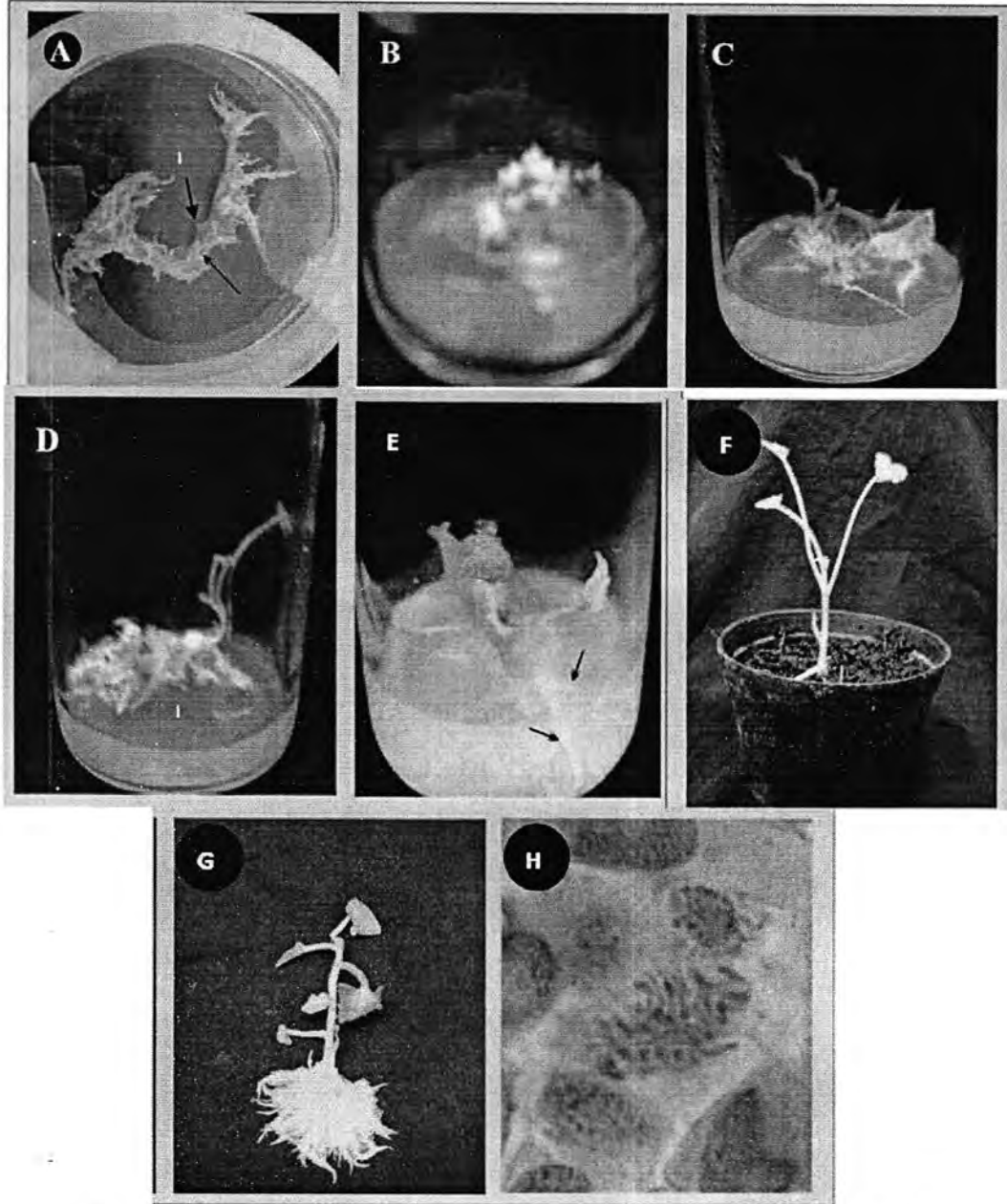
حساب العدد الكروموسومي في قمم جذور نباتات القرع *C. pepo* الناتجة من كالس الجذور الشعرية المحولة وراثياً :

أوضحت البيانات الناتجة عن فحص التحضيرات المجهرية المؤقتة لحساب العدد الكروموسومي في قمم جذور نباتات القرع الناتجة عن كالس الجذور الشعرية المحولة وراثياً أوضحت اختلافات واضحة في أعداد الكروموسومات ، إذ سجل عدد الكروموسومات في قمم

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جذور النباتات المحولة وراثياً $2n = 46$ (الشكل H.2), في حين إن عدد الكروموسومات $2n = 40$ في قمم جذور نباتات القرع الناتجة عن البذور .



شكل 2: إنتاج نباتات القرع من كالس الجذور الشعرية المحولة وراثياً ببكتريا

A. rhizogenes R1601

(A) بداية تحفز الجذور الشعرية على تكوين بادئات الكالس في وسط MS خلال 30 يوماً.

(B): تكوين الكالس من الجذور الشعرية خلال 75 يوماً من زراعتها على وسط MS الصلب.

(C): بداية ظهور الافرع الخضرية من الكالس في (B) بعمر 15 يوماً على وسط MS الصلب الخالي من منظمات النمو.

- (D): تطور الافرع الخضرية في (C) خلال 25 يوماً من زراعتها على وسط MS .
- (E) استئصال الافرع الخضرية الناتجة من كالس الجذور الشعرية وتجذيرها في وسط MS الخالي من منظمات النمو بعد 10 أيام من زراعتها .
- (F) نباتات القرع الناتجة من كالس الجذور الشعرية المحولة وراثياً بعد 7 أيام من نقلها الى التربة.
- (G) نباتات القرع الناتجة من كالس الجذور الشعرية المحولة وراثياً لا حظ كثافة المجموعة الجذرية وصغر حجم الاوراق والتفافها .
- (H) الكروموسومات في خلايا قمة جذور في النبات (G) تحت المجهر الضوئي (40X) لاحظ الجزء المؤشر.

تقدير المحتوى البروتيني في نباتات القرع *C. pepo* الناتجة من كالس الجذور الشعرية المحولة وراثياً والنباتات البذرية :

أظهرت نتائج تقدير المحتوى البروتيني في جذور نباتات القرع الناتجة من كالس الجذور الشعرية المحولة وراثياً حصول زيادة واضحة في المحتوى البروتيني قياساً بعينات المقارنة (الجدول 6) في حين حصل نقصان في المحتوى البروتيني في أوراق نباتات القرع الناتجة عن كالس الجذور الشعرية المحولة وراثياً مقارنةً بمحتواه في أوراق النباتات البذرية .

جدول 6 : تقدير المحتوى البروتيني في جذور وأوراق نباتات القرع *C. pepo* الناتجة من كالس الجذور الشعرية المحولة وراثياً مع محتواه في جذور النباتات البذرية واوراقها

العينة	ملغم بروتين/ غم وزن طري للنسيج النباتي
جذور النباتات الناتجة من كالس الجذور الشعرية المحولة وراثياً	9.5
جذور النباتات الناتجة من البذور	4.6
أوراق النباتات الناتجة من كالس الجذور الشعرية المحولة وراثياً	3.5
أوراق النباتات الناتجة من البذور	8.2

ان الاستجابة البارزة لقطع السيقان تحت الفلقة عند تلقحها ببكتريا *A. rhizogenes* قياساً باستجابة البادرات الكاملة والبادرات الفاقدة للجذور المستأصلة منها قد يعزى الى تباين أعمار أو أعداد الخلايا أو كليهما التي استجابت للتلقيح بهذه البكتريا (17)، او الى كفاءة انتقال قطع T-DNA من بلازميد Ri الى المادة الوراثية للخلايا النباتية (18)، وعموماً فان التباين في الفترة اللازمة لظهور الجذور الشعرية المحولة وراثياً على العينات المختلفة ، قد يعزى الى نوعية الجزء النباتي طالما ان السلالة المستخدمة في التلقيح هي نفسها (19)، في حين استغرقت فترات اطول كما في نباتات البنجر السكري *Beta vulgaris* (10) وعنيد الذيب *Solanum nigrum* (13)، في حين استلزم تكوين الجذور الشعرية على قطع السيقان تحت الفلقة والاوراق لبادرات الناردين *Valeriana sisymbriifolium* 10 أيام من الحقن بالسلالة 15834 من بكتريا *A. rhizogenes*

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(20). وللنوع النباتي اثر مهم في تحديد المدة اللازمة لظهور الجذور الشعرية التي سجلت 21 يوما لنشوتها على قطع السيقان تحت الفلجية لنباتات المغد *Solanum dulcamara* (21).

اظهر استعمال السيفوتاكسيم Cefotaxime كفاءته للتخلص الكامل من البكتريا *A. rhizogenes* في مزارع الجذور الشعرية ، وأشارت دراسة اخرى الى نجاح المضاد الحيوي عينه في ازالة البكتريا نفسها من مزارع الجذور الشعرية لنباتات *Solanum dulcamara* (22).

ومن المحتمل ان يعزى تكوين الجذور الشعرية المحولة وراثيا للكالس في وسط MS الخالي من منظمات النمو الى التغيرات في المحتوى الداخلي للهرمونات نتيجة انتقال T-DNA من الناقل البكتيري واقتنائها بالمادة الوراثية لخلايا هذه الجذور (9). و ربما يعد النجاح الذي حققته هذه الدراسة في انتاج نباتات كاملة من الكالس مسارا قصيرا في الحصول على (النباتات المحولة وراثيا) ، فقد ذكرت احدى الدراسات تكوين الأفرع الخضرية من كالس مزارع الجذور الشعرية المحولة وراثيا لنباتات الحنظل (5) و تكوين الافرع الخضرية من كالس الجذور الشعرية المحولة وراثيا لنوعين من البقوليات فول الصويا *Glycine max* ونوع من اللوبيا *Vigna angularis* وتجديرها في الوسط MS الخالي من منظمات النمو (23).

وقد اكدت الدراسة الحالية ظهور اختلافات مظهرية في نباتات القرع الناتجة من كالس الجذور الشعرية المحولة وراثيا، هذا الامر يتعلق بفعل الجينات المحمولة على الحامض T-DNA التي من المفترض تداخلها مع المادة الوراثية في الخلايا (17). مما سبق نستنتج

1. الحصول على نباتات قرع ناتجة من كالس الجذور الشعرية المحولة وراثيا مما يؤشر الى مسارات قصيرة في التحول الوراثي المعروفة عادة باستغراقها مدداً اطول.
2. ان الاختلافات في مجموعة الصفات المورفولوجية لنباتات القرع الناتجة من كالس الجذور الشعرية المحولة وراثيا من المتوقع ان تعزى الى حدوث التحول الوراثي .

ونوصي بـ :

1. اختبار سلالات اخرى من بكتريا الاكروبيكتيريوم لهذا النوع من الدراسة للوقوف على أثر السلالات المختلفة من البكتريا عينها .
2. إجراء دراسات مستقبلية تتناول تقانة الزراعة المرافقة Cocultivation للمعلقات الخلوية مع بلازميدات Ri في الحصول على نباتات القرع المحولة وراثيا ، ودراسة صفاتها المظهرية والتشريحية .

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13. الطائي، شفاء مهدي صالح، بكتريا الاكروبيكتيريوم

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دراسة العوامل المؤثرة في أستخلاص الجيلاتين

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ABSTRACT

Ossien was produced from cow bones by acidic treatment through several successive steps . Gelatine was extracted letter from ossein to be used in bacteriological diagnosis. Many effected parameters have been investigated to study the gelatin extraction .These parameters included effect of hydrochloric acid concentration , period of extraction and times of water extraction . The results showed that using (2%) of (HCL) for (4) hours at (60) c were the optimal conditions for gelatin extraction ,this have been acheived through three successive water extraction . Extracted gelatin was detected by used turbidity technique with tannic acid , solidity and liquification tests . The results revealed , that extracted gelatin is completely identical with standard gelatin. Turbidity was formed with tannic acid and solidity and clarity were also similar to the standard gelatin. Liquification of nutrient gelatin medium was abserved after the inoculation by *Proteus mirabilis* bacterium, while it remained solid after the inoculation by *Escherichia coli* bacterium, compared with standard gelatin.

الخلاصة

أنتج الأوسين من عظام البقر بواسطة المعاملة الحامضية بعدة خطوات متعاقبة بعدها أستخلص الجيلاتين من الأوسين لأستخدامه في التشخيص البكتريولوجي . درست عدد من العوامل المؤثرة في استخلاص الجيلاتين ومنها ، تأثير تركيز حامض الهيدروكلوريك المستخدم ، والفترة الزمنية وعدد مرات الأستخلاص . بينت النتائج إن استخدام الحامض بتركيز (2%) واستخلاص لفترة (4) ساعات بدرجة حرارة (60)°م وثلاث مراحل متعاقبة من الأستخلاص المائي هي الظروف المثلى للأستخلاص. أجريت أختبارات للكشف عن الجيلاتين المستخلص ومقارنته بالجيلاتين القياسي من خلال أستخدام أختبارات تقنية العكورة مع حامض التانيك والصلابة وأماعة الجيلاتين ، وأظهرت النتائج مطابقة الجيلاتين المستخلص تماما مع الجيلاتين القياسي من خلال تكون العكورة في أختبار حامض التانيك لكليهما ، و كذلك أظهر الجيلاتين المستخلص صلابة وشفافية مطابقة للقياسي . لوحظ تميع وسط الجيلاتين المغذي بعد تلقّحه ببكتريا *Proteus mirabilis* وبقاءه صلبا بعد تلقّحه ببكتريا *Escherichia coli* مقارنة بالقياسي في أختبار أماعة الجيلاتين.

المقدمة

الجيلاتين بروتين ذائب في الماء ناتج من التحلل الجزئي للكولاجين . يوجد الكولاجين في الجلود والعظام وهو عبارة عن البروتين الرابط للأنسجة ويحتوي على نسبة عالية من الأحماض الأمينية (البرولين والهيدروكسي برولين والجليسين) (1). عند تعرض البروتينات الذائبة لعوامل غير طبيعية مثل الحرارة ، الحامضية أو القاعدية ، تراكيز الأملاح العالية ، المذيبات فإنه سوف يسبب ذلك تمسخ (denaturation) لها وعموماً فإن البروتينات الممسوخة (denatured) تكون غير فعالة بايولوجيا (2).

يتكون الجيلاتين من مزيج من البروتينات الذائبة ذات الأوزان الجزيئية العالية التي لها القدرة على تكوين هلام قوي في الوسط السائل (3) . عادة ما تكون مصادر الجيلاتين هي عظام الأبقار وجلود الخنازير فضلاً عن إنتاجها من جلود الأسماك بعد المخاوف التي طرأت في استخدام الجيلاتين البقري لاسيما بعد تفشي مرض جنون البقر (4). يعتبر الجيلاتين وجبة غذائية جيدة للمرضى وذلك لأنه فاتح للشهية وسهل الهضم (1). يستخدم الجيلاتين في الصناعات الصيدلانية إذ يستخدم في تكوين معظم أقراص الأدوية ومستحضرات العيون والتحاميل وأدوية الحروق والجروح الجلدية العميقة وحتى في بعض الصمامات القلبية والأنسجة المزروعة في الأسنان . ويستخدم في عمليات التصنيع الغذائي حيث يدخل في صناعة الألبان كعامل مجلتن ، وصناعة الآيس كريم وفي صناعة العصائر (5,6). هناك ثلاثة أنواع من طرائق تصنيع الجيلاتين تتضمن الطريقة القاعدية والحامضية والأنزيمية وهي تشترك في عدة عوامل منها أن الأواصر بين الجزيئات وداخل الجزيئات (وهي التي تثبت الكولاجين وتمنع ذوبانيته) يجب كسرها الأواصر لكي ينتج الجيلاتين والجيلاتين الناتج من هذه الطرائق له مديات مختلفة من نقاط التعادل الكهربائي (7) . نظراً لأهمية الجيلاتين في تحضير الأوساط الزرع البكتريولوجية لأستخدامها في الدراسات التشخيصية والتخميرية ، فقد هدف هذا البحث لتحضير الجيلاتين من العظام بأعتقاد الطريقة الحامضية ثم دراسة العوامل المؤثرة في أستخلاص الجيلاتين المستخدم للتشخيص البكتريولوجي .

المواد وطرائق العمل

- 1- تحضير العظام :- نظفت العظام وغسلت بالماء جيداً ، ثم كسرت الى قطع صغيرة بحجم (0.5-4) سم . إزيلت الدهون وذلك بوزن (400غم) من العظام المهيأة وإضيف لها (1 لتر) من كحول الايثانول ووضعت في جهاز الهزاز Shaker للمزج جيداً ، ثم أزيل الأيثانول منها وغسلت جيداً بالماء العادي .

2- إزالة الأملاح Demineralization: عوملت العظام بحامض الهيدروكلوريك للتخلص من الأملاح (Demineralization) وإنتاج الأوسين لأكمال عملية الأستخلاص عليها وإنتاج الجيلاتين حسب ماورد في (9) .

3- الاستخلاص :- إضيف حامض الهيدروكلوريك بتركيز (0.0, 0.5, 1.0, 1.5, 2.0) % بحجم ضعف وزن العظام ووضعت في جهاز الهزاز لمدة (18) ساعة ، ثم غسلت العظام جيدا من الحامض بالماء العادي ثم بعدها بالماء المقطر .

- إضيف ماء مقطر ذو رقم هيدروجيني (6.0) وبحجم ضعف وزن العظام ، ثم سُخن بدرجة حرارة (60 م °) وفترات زمنية (4,8,23) ساعة وتكرر عدد مرات الاستخلاص الفترات الزمنية نفسها .
- رشح المستخلص الناتج بأستخدام أوراق الترشيح ثم عقم الجيلاتين المستخلص بجهاز الموصدة (Autoclave) بدرجة حرارة (120 م °) وتحت ضغط (1.5) جو . ثم جفد بجهاز التجفيد (lyophilizer).

4-الكشف عن الجيلاتين

1- اختبار الصلابة وقوة الجيل:- أجرى هذا الاختبار بدرجة حرارة ما بين (10-60) م ° حسب ما ورد في (9).

2- اختبار العكرة مع حامض التانيك :- اضيف بضع قطرات من حامض التانيك بتركيز (2%) الى محلول الجيلاتين المحضر بتركيز (5 %) طبقا لماورد في (9) .

3 - اختبار اماعة الجيلاتين :- حضر وسط الجيلاتين المغذي بالاعتماد على الطريقة المذكورة في (8) : ثم لقع بالجراثيم *E.coli* و *P.mirabilis* ثم وضعت النماذج في الحاضنة بدرجة حرارة (37) م لمدة (24) ساعة.

النتائج والمناقشة

1- دراسة تأثير حامض الهيدروكلوريك :- . أظهرت نتائج قياس الرقم الهيدروجيني بعد معاملة الأوسين بتركيز مختلفة من حامض الهيدروكلوريك لأستخلاص الجيلاتين كما موضح في جدول رقم (1).

جدول 1: قيم الرقم الهيدروجيني pH للمستخلص بعد المعاملة بحامض الهيدروكلوريك

التركيز %	0.0	0.5	1.0	1.5	2
pH	3.6	3.5	3.2	3.1	3.0

إذ لوحظ انخفاض قيمة الرقم الهيدروجيني p H بزيادة تركيز الحامض وذلك لتأثير تركيز الحامض إذ يتناسب مع انخفاض الرقم الهيدروجيني وزيادة الحمضية .فالمعاملة الحامضية هي

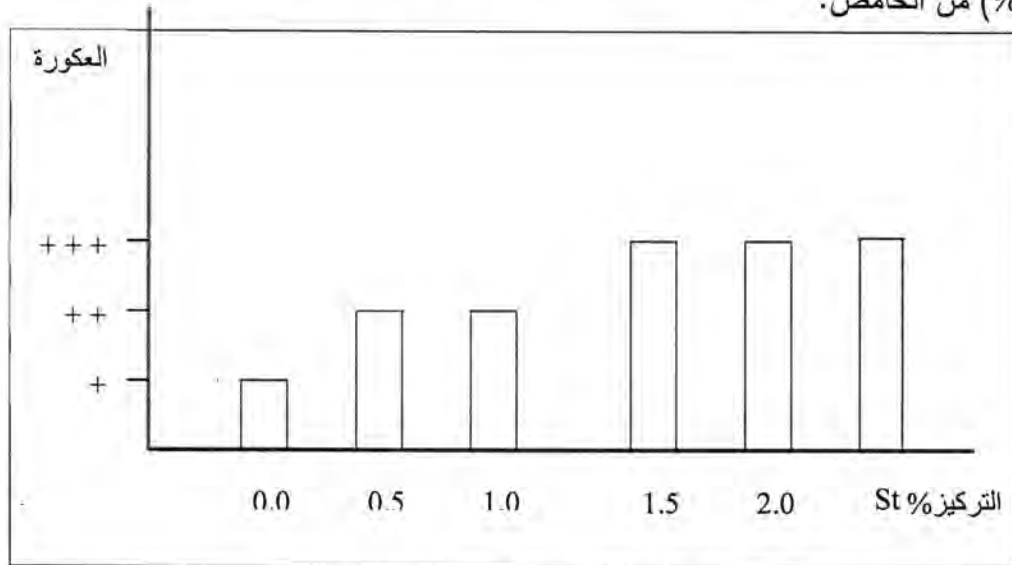
دراسة العوامل المؤثرة في أستخلاص الجيلاتين

حسنة وسعاد وسوسن وصبا

غالبا ماتكون مناسبة لكسر الأواصر التساهمية الموجودة في الأوسين (10) . أورد عدد من الباحثين إلى أستخلاص الجيلاتين عند درجة حرارة الغرفة بأستخدام هيدروكسيد الصوديوم المخفف (pH: 11) وحامض الهيدروكلوريك (pH: 2.0 - 2.6) كلا على حدة (11). فيما استخلص الجيلاتين من جلد السمك بعد تعريضه للاذابة بحامض الخليك بتركيز (0.05) مولاري (12) . استخلص الجيلاتين من قبل (13) باستخدام حامض الكبريتيك بتركيز (0.01) مولاري وكان الرقم الهيدروجيني يتراوح بين (2.5 - 3.0) .

1- اختبار العكورة مع حامض التانيك Tannic acid

اجري الاختبار لجميع النماذج مقارنة بالجيلاتين القياسي أعطت جميع النماذج نتيجة ايجابية بتكون العكورة مع حامض التانيك مقارنة بالجيلاتين القياسي كما مبين بالشكل رقم (1). لقد تكون راسب أصفر عند إضافة حامض التانك الى الجيلاتين الذي يترسب بشكل دقائق صغيرة تستقر في قعر الأنبوبة ،ويؤدي زيادة حامض التانك الى ذوبان الراسب . يعد هذا الأختبار هو ضمن تفاعلات الترسيب بالكواشف الحامضية لأختبار الجيلاتين أذ تحمل هذه الكواشف شحنة كبيرة سالبة تعادل شحنة البروتين (الجيلاتين) الموجبة لتكوين ملح غير ذائب ، تكون الكواشف الحامضية أكثر كفاءة في الرقم الهيدروجيني الحامضي (9) وهذا يفسر تكون عكورة عالية في النموذج ذو التركيز (2%) من الحامض.



شكل 1 : اختبار العكورة مع حامض التانيك

2-الصلابة

الصفة المفيدة والفريدة لمحلول الجيلاتين المائي هو قابليته على التحول الأرجاعي من الهلام الى السائل (gel-to- sol) (8) ، أعطت النماذج المحضرة باستخدام حامض الهيدروكلوريك بالتركيز (1.5 - 2.0) جيل متصلب مشابه للجيلاتين القياسي الموضحة في جدول رقم (2)، أما

تركيز (0.5 %) أعطى جيل اقل صلابة من الجيلاتين القياسي أما النموذج (0.0) أعطى جيل ضعيف جدا اقل من نموذج ذا تركيز (0.5 %). إذ أن البروتينات عند تعرضها للحامض فان ذلك يؤثر على تركيب البروتينات خاصة على التراكيب الثلاثية والرباعية والبروتينات الناتجة تكون غير فعالة بايولوجيا (14) وتسمى هذه العملية الدنترة (Denaturation) ومن نتائج هذه العملية تصبح البروتينات سهلة الهضم بسبب تكسر الأواصر الببتيدية (1).

جدول 2 : نتائج اختبار الصلابة لنماذج الجيلاتين الناتج بعد المعاملة بتركيز متدرجة من الحامض

القياسي	2.0	1.5	1.0	0.5	0.0	التركيز
متصلب	متصلب	متصلب	متصلب	اقل صلابة	غير متصلب	الصلابة

3- اختبار اماعة الجيلاتين

يعتبر فحص اماعة الجيلاتين من الفحوصات التشخيصية البكتريولوجية (15) إذ أنه يشخص قابلية البكتريا على افراز الأنزيمات المحللة للجيلاتين؛ ومن الضروري عدم تعرض الوسط إلى درجات الحرارة العالية لفترة طويلة لأنه يؤدي إلى تحلل الجيلاتين الجزئي مما يؤدي إلى عدم تصلبه عند التبريد (16).

جدول 3 : نتائج اختبار اماعة الجيلاتين لنماذج الجيلاتين المحضرة

سيطرة (بدون زرع)	<i>P.mirabilis</i>	<i>E.coli</i>	نموذج الجيلاتين
جيل	سائل	جيل	0.0
اقل صلابة	سائل	اقل صلابة	0.5
صلب	سائل	صلب	1.0
صلب	سائل	صلب	1.5
صلب	سائل	صلب	2.0
صلب	سائل	صلب	القياسي

من خلال النتائج المبينة في جدول رقم (3) لوحظ ان جميع النماذج اعطت نتائج ايجابية لنمو الجراثيم بالمقارنة مع الجيلاتين القياسي لكلا النوعين من الجراثيم فقد كان نموذج الجيلاتين المحضر باستخدام حامض الهيدروكلوريك (2 %) اكثرهم تطابقا مع الجيلاتين القياسي من حيث صلابة الجيلاتين وثباتيته ثم يأتي بالمرتبة الثانية تركيز (1.5 %) .

يتضح من نتائج الاختبارات ان افضل تركيز لاستخدام حامض الهيدروكلوريك في استخلاص الجيلاتين هو تركيز (2 %)، وذلك لانه بعض العوامل يمكنها تغيير الخواص الطبيعية والكيميائية

دراسة العوامل المؤثرة في أستخلاص الجيلاتين

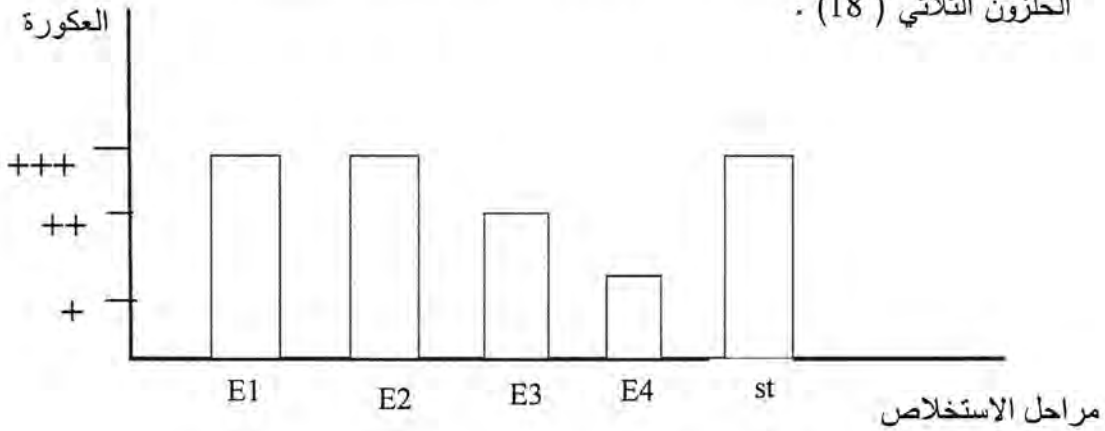
حسنة وسعاد وسوسن وصبا

والبايولوجية للبروتين دون ان يسبب ذلك في تحطيم او كسر الرابطة الببتيدية للبروتين ومن هذه العوامل هي الحوامض (1). تؤثر تغييرات الرقم الهيدروجيني على الحالة الأيونية للبروتين ، فعند تعرض البروتين لقيم من الرقم الهيدروجيني المتطرفة (العالية والمنخفضة) فإن ذلك يؤثر على حالة الشحنة للبروتين (الجلياتين) وتتغير وضعيته وقد يؤدي الى مسخ البروتين (17). وتنفذ جزيئات البروتين التراكيب الثلاثية والرباعية (2). لذلك تم اختيار هذه التراكيز من الحامض ضمن مديات لا تؤثر على مسخ البروتين .

2 - دراسة تأثير عدد مراحل الاستخلاص

استخلص الجيلاتين من الأوسين بعدة مراحل من الاستخلاص التي ذكرت في طرائق العمل . اوضحت نتائج اختبارات الجيلاتين الناتج لكل استخلاص مايلي :-

1 - اختبار العكورة مع حامض التانيك Tannic acid - : اجري الاختبار لجميع النماذج المستخلصة مقارنة مع الجيلاتين القياسي واعطى النتائج المبينة في الشكل رقم (2). اظهرت نتائج العكورة ان مرحلتي الاستخلاص الاول والثاني كانت متطابقة مع عكورة الجيلاتين القياسي ، اما مرحلة الاستخلاص الثالث والرابع فكانت اقل عكورة من الجيلاتين القياسي . جزيئة الكولاجين متألفة من ثلاثة سلاسل الفا (Three α chains) ملتفة لذلك يدعى الكولاجين (ثلاثي الحلزون) الذي يعطي تركيباً ثلاثي الابعاد بسبب الاواصر الهيدروجينية داخل السلسلة ، فمسخ الأوسين يسبب فصل كلي أو جزئي للسلاسل بسبب تحطم الأواصر الهيدروجينية مسببة فقدان لهيئة الحلزون الثلاثي (18) .



E1 = مرحلة الاستخلاص الاول
E2 = مرحلة الاستخلاص الثاني
E3 = مرحلة الاستخلاص الثالث
E4 = مرحلة الاستخلاص الرابع
St = القياسي

شكل 2: اختبار العكورة مع حامض التانيك

2- اختبار الصلابة :- أوضحت نتائج اختبار الصلابة المبينة في جدول رقم (5) أن مرحلة الاستخلاص الاول والثاني كانت متطابقة للجيلاتين القياسي من حيث الصلابة والشفافية بعد التبريد ، أما المرحلة الثالثة من الاستخلاص فهي مشابهة للجيلاتين القياسي غير أنها متصلبة بدرجة أقل وشفافة ، وأنتجت المرحلة الرابعة جيلاتين غير متصلب وشفاف . فالمعاملة الحرارية فوق (40) م° ولعدة مرات تحطم الاواصر الهيدروجينية وتفتح عدد اخر من الاواصر التساهمية مؤديا الى عدم ثبات الحلزون وينتج عن ذلك التحول هو زيادة ذوبان الجيلاتين (19) . عمليات الاستخلاص يمكن أن تؤثر على طول السلاسل الببتيدية والصفات الوظيفية (Functional properties) للجيلاتين (20) .

جدول 5 : نتائج اختبار الصلابة للجيلاتين المستخلص بارب مراحل استخلاص متتالية

الجيلاتين	الصلابة بعد التبريد	درجة حرارة
القياسي	متصلب شفاف	سائل
E1	متصلب شفاف	سائل
E2	متصلب شفاف	سائل
E3	متصلب اقل من القياسي وشفاف	سائل
E4	غير متصلب جيل خفيف جداول شفاف	سائل

3- اختبار اماعة الجيلاتين :- بينت نتائج اختبار اماعة الجيلاتين الموضحة في جدول(7) أن جميع النماذج كانت ايجابية للنمو البكتيري ، لأحتواء وسط الجيلاتين على مصدر الكربون (الكاربوهيدرات) ومصدر النتروجين (الأحماض الأمينية والنوية)وهي المواد التي يحتاجها الكائن المجهرى لتوليد الطاقة والبناء الحيوي (8) ، بالمقارنة مع الجيلاتين القياسي فقد كان النموذجان E1 وE2 مطابقين لوسط الجيلاتين القياسي من حيث الصلابة في حالة البكتريا *E.coli* التي ليس لها فعالية محللة للبروتين ، اما البكتريا *P.mirabilis* التي لها فعالية محللة للبروتين بأننتاجها لأنزيم (Gelatinase) (11). فقد كانت جميع النماذج الملقحة بها سائلة بعد تبريدها . والنموذج E3 فقد كان أقل صلابة من القياسي . فقد استخدم الجيلاتين ضمن مزيج من عدة مواد تتضمن (السكرورز والحليب والبطاطا الحلوة) كوسط تخميري لبكتريا اللبن (Yogurt bacteria) (21) .

جدول 6 : نتائج اختبار اماعة الجيلاتين لنماذج مراحل الاستخلاص

الجيلاتين	<i>E.coli</i>	<i>P.mirabilis</i>	المسيطر
E1	متصلب	سائل	متصلب
E2	متصلب	سائل	متصلب
E3	اقل صلابة	سائل	اقل صلابة
E4	جيل	سائل	جيل

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القياسي	متصلب	سائل	متصلب
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3- دراسة تأثير الفترة الزمنية للاستخلاص

أظهرت نتائج قياس الرقم الهيدروجيني لنماذج الجيلاتين المستخلص بفترة زمنية مختلفة المبينة في جدول (7) أن الرقم الهيدروجيني للمستخلص (A) مقارب للمستخلص (B) وكذلك الأرقام الهيدروجينية لبقية الاستخلاصات كانت متقاربة أيضا ،وبعد اكمال مرحلة الاستخلاص الاولى اهتم النموذج المعامل لمدة (23) ساعة .وذلك لتعرض الجيلاتين للحرارة لفترة طويلة، مما أدى الى التحلل الجزئي للجيلاتين مما يؤدي الى عدم تصلبه عند التبريد (15) .أستخلص الجيلاتين من قبل (22) بمرحلتين (كل مرحلة تستغرق ساعتين) بواسطة التحريك المستمر وبحجم واحد لتر من الماء وبدرجات حرارة (56، 65) م° لكل المرحلتين .

جدول 7 : قيم الرقم الهيدروجيني لنماذج الجيلاتين المستخلص

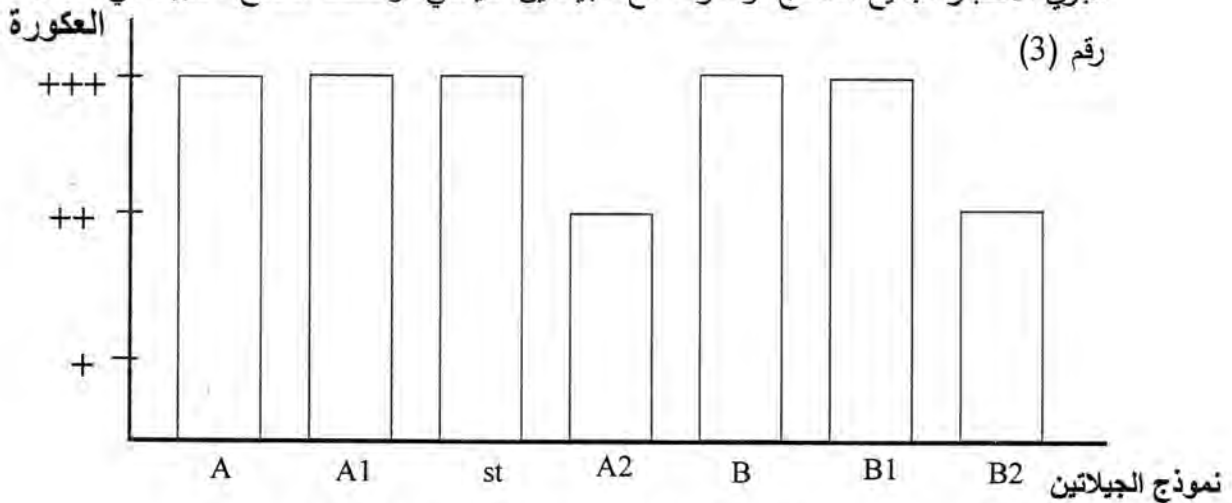
النموذج	A	A1	A2	B	B1	B2
PH	3.2	3.4	3.5	3.3	3.4	3.4

A = استخلاص اول لمدة 4 ساعة
A1 = استخلاص ثاني لمدة 4 ساعة
A2 = استخلاص ثاني لمدة 8 ساعة
B = استخلاص اول لمدة 8 ساعة
B1 = استخلاص ثاني لمدة 4 ساعة
B2 = استخلاص ثاني لمدة 8 ساعة

وأجريت الاختبارات على نماذج الجيلاتين المستخلص وهي :

1-اختبار العكورة مع حامض التانيك

أجري الاختبار لجميع النماذج ومقارنته مع الجيلاتين القياسي، واعطت النتائج المبينة في الشكل العكورة رقم (3)



شكل 3 : اختبار العكورة مع حامض التانيك

نتائج ايجابية لاختبار العكورة مع حامض التانيك وكانت نماذج الاستخلاص الاول لمدة (4-8) ساعة والاستخلاص الثاني لمدة (4 ساعة) اعطى نتيجة مطابقة للجلاتين القياسي اما نموذج الاستخلاص الثاني لمدة 8 ساعة اعطى نتيجة عكورة اقل من النماذج الاخرى مقارنة بالجلاتين القياسي . وذلك لانه عند الاستخلاص الثاني بدا تأثير درجة الحرارة بزيادة الفترة الزمنية لتعرض بروتين الجيلاتين للحرارة مما يؤدي الى التحلل الجزئي لبروتين الجيلاتين (17). زيادة درجة الحرارة فوق المثلى يؤدي الى مسخ البروتين (الجيلاتين) ويعزى ذلك الى زيادة الطاقة الحركية للجزيئات الى ان تصل فيه الى حد تتجاوز فيه حاجز الطاقة فتؤدي الى تكسير الاواصر الثانوية المحافظة على تركيب البروتين وبالتالي فقدان التركيب الرابعي والثانوي (14) .

2 - اختبار الصلابة

لقد كان محلول الجيلاتين سائلا في درجات حرارية اعلى من (35 م°) وبعد التبريد اعطت نماذج الجيلاتين المستخلص النتائج المبينة ادناه في جدول رقم (8) .

جدول 8 : نتائج اختبار الصلابة للجيلاتين وتأثير الفترة الزمنية للاستخلاص

الجيلاتين	الصلابة بعد التبريد	الصلابة قبل التبريد
A	صلب شفاف	سائل
A1	صلب شفاف	سائل
A2	جيل اقل صلابة	سائل
B	صلب شفاف	سائل
B1	صلب شفاف	سائل
B2	جيل اقل صلابة	سائل
St	صلب	سائل

اذ لوحظ ان نماذج الاستخلاص الاول لمدة (4, 8) ساعة والاستخلاص الثاني لمدة (4 ساعة) كانت مطابقة للجيلاتين القياسي من حيث الصلابة والشفافية ، اما نماذج الاستخلاص الثاني لمدة (8 ساعة) كانت اقل صلابة مقارنة مع الجيلاتين القياسي ،ومن النتائج أعلاه ظهر أن استخلاص الجيلاتين بفترة زمنية مجموعها (16) ساعة وبدرجة حرارة (60 م°) أنتج جيلاتين مطابق للقياسي ، وهذه النتيجة مقارنة لما ذكره (23) أذ استخلص الجيلاتين باستخدام الماء الحار وبدرجة حرارة (50 م°) ولمدة (18) ساعة . قوة الجل ونقطة ذوبان الجيلاتين هي من الصفات الفيزيائية

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الرئيسية له ، وهذا يحكم عليه من خلال الوزن الجزيئي وتفاعل معقدات الأحماض الأمينية المكونة له ونسبة سلاسل الفا وبيتا الموجودة في الجيلاتين (24).

3- اختبار أمانة الجيلاتين : أعطت نتائج الزرع البكتريولوجي لفحص أمانة الجيلاتين وجود النمو البكتيري في جميع النماذج وبعد التبريد كانت النتائج كما مبين في الجدول رقم (9). أذ لوحظ وجود تميع للجيلاتين في جميع النماذج الملقحة بالبكتريا (*P. mirabilis*) مقارنة بالقياسي ، لأنها تملك القابلية على إفراز أنزيم (Gelatinase) المحلل للجيلاتين ، أما النماذج المنقحة بالبكتريا (*E. coli*) والتي لا تفرز هذا الأنزيم فبقيت النماذج (A, A1, B, B1) صلبة مقارنة بالقياسي، وكان النموذجين (A2, B2) أقل صلابة من النموذج القياسي ويمكن اعتبارهما كببتون جيلاتيني، فالبيتون الجيلاتيني يجهز النتروجين والأحماض الأمينية والفيتامينات في الأوساط الزرعية المايكروبيولوجية ويوصى بأستخدامه في أوساط اختبار المضادات الحيوية وفي الدراسات التخمرية ، ويكون مناسباً عند أستخدامه كمصدر غذائي وحيد في تحضير الأوساط الزرعية للأحياء المجهرية التي تكون غير نحسة في متطلباتها الغذائية (8).

جدول 9 : نتائج اختبار أمانة الجيلاتين وتأثير الفترة الزمنية للأستخلاص

سيطرة	<i>P. mirabilis</i>	<i>E. coli</i>	نموذج الجيلاتين
صلب	سائل	صلب	A
صلب	سائل	صلب	A1
أقل صلابة	سائل	أقل صلابة (جيل)	A2
صلب	سائل	صلب	B
صلب	سائل	صلب	B1
أقل صلابة	سائل	أقل صلابة	B2
صلب	سائل	صلب	St

مما سبق نستنتج ما يلي:

- 1- أن التركيز الأمثل لحامض الهيدروكلوريك عند أستخلاص الجيلاتين هو (2%) .
- 2- الفترة الزمنية المثلى لأستخلاص الجيلاتين هي (4 ساعات) لكل مرحلة مقارنة بالفترات الزمنية الأخرى قيد الدراسة.
- 3- ثلاث مراحل من الأستخلاص لمدة (4 ساعات) بدرجة حرارة (60 م°) هي أفضل مراحل أستخلاص الجيلاتين .

ونوصي بـ :

- 1- اعتماد ظروف الاستخلاص المثلى قيد الدراسة في استخلاص الجيلاتين من العظام الحيوانية .
- 2- إنتاج الجيلاتين بكميات كبيرة باستخدام منظومات إنتاجية كبيرة بأعتماد هذه الطريقة لإنتاج الجيلاتين المستخدم في الأوساط الزرع البكتريولوجية.
- 3- إجراء دراسات تطبيقية أخرى على الجيلاتين لمعرفة صفاته الفيزيائية والكيميائية الأخرى.
- 4- إجراء دراسات لاستخلاص الجيلاتين من مصادر أخرى مثل جلود الحيوانات.

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تحضير الجيلاتين من عظام الحيوانات للإستعمالات البكتريولوجية

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ABSTRACT

The production of gelatin and its using in bacteriological diagnosis have been studied .The gelatin had been produced from bones by numbers of stages Bones preparation and cleaning , remove of fats, Demineralization, extraction and drying of gelatin. The conditions that effected gelatin production have been studied like acid concentration, volume and the duration of treatment at first stage of gelatin preparation (Demineralization). The results showed that the optimal conditions for gelatin production are 9% acid solution, 1/2 (wt./vol.) ratio of bone to acid and period of treatment (5 days) which are identical to the standard gelatin .When nutrient gelatin medium were prepared from produced and standard gelatin then inoculated with *Proteus mirabilis* bacterium and *Escherichia coli* bacterium, the test results were showed their similarity in bacteriological diagnosis.

الخلاصة

تم دراسة إنتاج مادة الجيلاتين (Gelatin) والاستعماله في التشخيص البكتريولوجي، فقد تم إنتاجه من العظام بعدة خطوات، وتم دراسة الظروف المؤثرة في إنتاجه ومنها تأثير تركيز وحجم الحامض المستخدم والمدة الزمنية للمعاملة للمرحلة الأولى من تحضير الجيلاتين وهي مرحلة إزالة المعادن (Demineralization). بينت النتائج أن استخدام الحامض بتركيز 9% وبحجم ضعف وزن العظام المستخدمة ولمدة خمسة ايام، أنتج جيلاتين مطابق للجيلاتين القياسي. عند تحضير الوسط الزرعي البكتريولوجي (وسط الجيلاتين المغذي) وباستخدام الجيلاتين المحضر والقياسي وتلقيحه بالجرثومة *Proteus mirabilis* والجرثومة *Escherichia coli* وبعد فترة الحضان، أظهر الاختبار تشابه النتائج لوسط الجيلاتين المحضر مع الجيلاتين القياسي في التشخيص البكتريولوجي.

المقدمة

الجيلاتين خليط من الببتيدات المشتقة من البروتين التركيبي للكولاجين المكون الرئيسي للانسجة الرابطة (Cconnective tissues)، والمكون من املاح معدنية بنسبة 1- 2 % وبروتينات 84-90% والنسبة المتبقية ماء(1). يتكون الجيلاتين من مزيج من البروتينات الذائبة ذات الأوزان الجزيئية العالية التي لها القدرة على تكوين هلام قوي في الوسط السائل (2). كمية

تحضير الجيلاتين من عظام الحيوانات للإستعمالات البكتريولوجية

سعاد وحسنة

الانتاج العالمي للجيلاتين هو حوالي 300,000 طن للسنة، يصنع الجيلاتين على المستوى التجاري كناتج عرضي لصناعة اللحوم والجلود (3). توجد ثلاثة طرائق مختلفة لتحضير المواد الخام لأستخلاص الجيلاتين هي الحامضية، والقاعدية والأنزيمية. الطريقة الحامضية أسرع من القاعدية. الجيلاتين المستحصل بالطريقة الحامضية يسمى نوع A أما المستحصل بالطريقة القاعدية فيسمى نوع B. الطريقة الأنزيمية لها فوائد عديدة بالمقارنة مع الطريقة القاعدية فهي تستغرق وقت أقصر وغالبا إنتاجية 100 % والصفات الفيزيائية للجيلاتين المنتج تكون أفضل (4). يستخدم الجيلاتين في الصناعات الصيدلانية أذ يستخدم في تكوين معظم أقراص الأدوية ومستحضرات العيون والتحاميل وأدوية الحروق والجروح الجلدية العميقة وحتى في بعض الصمامات القلبية والأنسجة المزروعة في الأسنان ويستخدم في عمليات التصنيع الغذائي حيث يدخل في صناعة الألبان والمرطبات وصناعة العصائر (5).

المواد وطرائق العمل

- 1- تحضير العظام : نظفت عظام الابقار وغسلت جيداً بالماء، ثم كسرت الى قطع صغيرة بحجم 0.5 - 4 سم وازيلت الدهون بوزن 400غم من العظام المهيأة واضيفت لها 1لتر من كحول الايثانول ووضعت في جهاز الهزاز (Shaker) للمزج جيداً، ثم ازيل الايثانول فيها وغسلت جيداً بالماء العادي (6).
- 2- ازالة الاملاح (Demineralization) : عوملت العظام بحامض الهيدروكلوريك HCL بالتراكيز المذكورة ادناه للتخلص من الاملاح وانتاج الاوسين (Ossien) لاكمال عملية الاستخلاص عليها وانتاج الجيلاتين (6).
- دراسة حجم حامض الهيدروكلوريك : استخدم حامض الهيدروكلوريك بتركيز 7% وبحجم ضعف وزن العظام وحجم ثلاثة اضعاف وزن العظام والمدة الزمنية للمعاملة الحامضية كانت ل(7 و 14) يوم لكل نموذج.
- دراسة تحديد المدة الزمنية : استخدم حامض الهيدروكلوريك بتركيز 7% والمدة الزمنية للمعاملة الحامضية هي (3، 5، 7) يوم .
- دراسة تحديد تركيز حامض الهيدروكلوريك : استخدم حامض الهيدروكلوريك بالتراكيز (5، 7، 9، 14)% لمدة 5 يوم .
- 3- الاستخلاص : استخلص الجيلاتين من الـ (Ossien) الناتج بعد المعاملة الحامضية حسب ماورد في (6).

4- الكشف عن الجيلاتين :

- اختبار الصلابة وقوة الجيل: اجري هذا الاختبار بدرجة حرارة مابين (10- 60) م° حسب ماورد في مصدر (6).
- اختبار العكرة مع حامض التانيك: اضيفت بضع قطرات من حامض التانيك بتركيز 2% الى محلول الجيلاتين المحضر بتركيز 5% طبقاً لما ورد في (6).
- اختبار تسهيل الجيلاتين : حضر وسط الجيلاتين المغذي بالاعتماد على الطريقة المذكورة في (7) ثم لقح بالجراثيم *Proteus mirabilis* و *Escherichia coli* التي مصدرها مختبر الصحة المركزي واجري الاختبار حسب ماورد في (7).

النتائج والمناقشة

1- دراسة تحديد حجم الحامض

لتحديد الحجم الافضل لحامض الهيدروكلوريك في مرحلة ازالة المعادن (demineralization) يحضر حامض الهيدروكلوريك بتركيز 7 % و اضافته لنماذج العظام المكسرة والمنظفة والمزال عنها الدهون وتقسيمها بحجوم مختلفة ضعف وزن العظام وثلاثة اضعاف وزن العظام لمدة 7 يوم و 14 يوم لكل نموذج . تم قياس الـ pH في بداية الدراسة لكل نموذج وفي كل يوم وفي نهاية المرحلة وكانت نتائج قياس الـ pH كما مبين في جدول رقم (1) :

جدول 1 : نتائج قياس الـ pH لخمس ايام الاولى من التجربة

يوم الجيلاتين	1	2	3	4	5
A	0.9	1.3	1.4	1.4	1.5
B	0.9	1.3	1.4	1.4	1.5
C	0.0	0.7	0.9	1.1	1.2
D	0.0	0.5	0.8	0.9	1.1

A : حجم ضعف وزن العظام والمدة 7 أيام B: حجم ضعف وزن العظام والمدة 14 يوم

C: حجم ثلاث أضعاف والمدة 7 أيام D: حجم ثلاث أضعاف والمدة 14 يوم

لوحظ زيادة في قيمة الـ PH خلال فترة التجربة لجميع النماذج مع ملاحظة النموذجين D, C قيم الـ PH لهما أقل من النموذجين B, A إذ اول قراءة PH لهما 0.0 وهذا يتطابق مع مدى قياس الـ PH إذ تتراوح قيم الـ PH من 0.0 - 14.0 وعند قيمة الـ PH 0.0 هذا يعادل تركيز حامض الهيدروكلوريك M1 اما عند قيمة الـ PH 14.0 هذا يعادل تركيز هيدروكسيد الصوديوم M1 حسب ماورد في (8). ما يفسر ارتفاع قيم الـ PH لجميع النماذج هو تأثير حامض الهيدروكلوريك لازالة

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الاملاح من العظام وانتاج الأوسين (Ossien) فالمعاملة الحامضية هي غالباً ماتكون مناسبة لكسر الأواصر الموجودة في الكولاجين (9).

تم قياس الوزن للنماذج بعد انتهاء هذه المرحلة لوحظ نقصان وزن العظام في جميع النماذج بنسب مختلفة اذ ان النماذج المعاملة بحجم ثلاثة اضعاف فقدت وزن اكثر من العظام المعاملة بحجم ضعف وزن العظام كما موضح في جدول رقم(2). وذلك لتأثير حامض الهيدروكلوريك وأزالته للاملاح إذ يتناسب نقصان الوزن مع انخفاض قيم الرقم الهيدروجيني وزيادة الحامضية ، فالمعاملة الحامضية هي غالباً ماتكون مناسبة لكسر الأواصر التساهمية الموجودة في الكولاجين (9). محاليل الحوامض المخففة تستخدم لازالة املاح الكالسيوم والاملاح المشابهة (4) .

جدول 2: وزن النماذج بعد المعاملة بالحامض (غم)

النموذج	A	B	C	D
الوزن غم	95	91	82	76

A: حجم ضعف وزن العظام والمدة 7 أيام
B: حجم ضعف وزن العظام والمدة 14 يوم
C: حجم ثلاثة أضعاف والمدة 7 أيام
D: حجم ثلاثة أضعاف والمدة 14 يوم

وبعد اتمام استخلاص الجيلاتين لجميع النماذج اجريت الاختبارات الآتية :

1- اختبار العكرة مع حامض التانيك (Tannic acid)

اجري الاختبار لجميع النماذج مقارنةً بالجيلاتين القياسي اعطت جميع النماذج نتيجة ايجابية بتكون العكرة مع حامض التانيك لكن نموذج A اكثرهم تطابقاً مع النموذج القياسي كما في جدول رقم (3)، إذ يتكون راسب عند اضافة حامض التانيك الى الجيلاتين ويترسب بشكل دقائق صغيرة تستقر في قعر الانبوبة، وعند زيادة حامض التانيك سوف يذوب الراسب. هذا الاختبار ضمن تفاعلات الترسيب بالكواشف الحامضية لاختبار الجيلاتين إذ تحمل هذه الكواشف شحنة كبيرة سالبة تعادل شحنة البروتين الموجبة لتكوين ملح غير ذائب وتكون الكواشف الحامضية أكثر كفاءة في الرقم الهيدروجيني الحامضي (6). إذ ان البروتينات عند تعرضها للحامض فان ذلك يؤثر على تركيب البروتينات خاصة على التراكيب الثلاثية والرباعية والبروتينات الناتجة تكون غير فعالة بايولوجياً (10) .

جدول 3: نتائج اختبار العكرة مع حامض التانيك

النموذج	A	B	C	D	St
العكرة	+++	++	++	+	+++

A: حجم ضعف وزن العظام والمدة 7 أيام
B: حجم ضعف وزن العظام والمدة 14 يوم
C: حجم ثلاثة أضعاف والمدة 7 أيام
D: حجم ثلاثة أضعاف والمدة 14 يوم

St: النموذج القياسي (Standard sample)

2 - اختبار الصلابة

الصفة المفيدة والفريدة لمحلول الجيلاتين المائي هو قابليته على التحول الارجاعي من الهلام الى السائل (gel to sol) (7) عند إجراء اختبار الصلابة لمحلول الجيلاتين بتركيز 5% بالمقارنة مع الجيلاتين القياسي أعطت النتائج المبينة في جدول رقم (4) إذ اعطت جميع النماذج نتائج ايجابية مطابقة لنموذج الجيلاتين القياسي وكان النموذج A اكثرهم تطابقاً مع نموذج الجيلاتين القياسي . إذ ان البروتينات عند تعرضها للحامض فإن ذلك يؤثر على تركيب البروتينات خاصة على التراكيب الثلاثية والرابعة والبروتينات الناتجة تكون غير فعالة بايولوجياً (11) .

جدول 4: نتائج اختبار الصلابة

النموذج	A	B	C	D	St
الصلابة	متصلب وشفاف	متصلب وشفاف	متصلب وشفاف	متصلب وشفاف	متصلب وشفاف

A: حجم ضعف وزن العظام والمدة 7 أيام B: حجم ضعف وزن العظام والمدة 14 يوم

C: حجم ثلاثة أضعاف والمدة 7 أيام D: حجم ثلاثة أضعاف والمدة 14 يوم

St : النموذج القياسي (Standard sample)

3- اختبار تسييل الجيلاتين (Liquefaction of gelatin) :

يبين جدول رقم (5) نتائج الزرع البكتريولوجي لإختبار تسييل الجيلاتين إذ ان هذا الاختبار هو احد الاختبارات البكتريولوجية المستخدمة في التشخيص البكتريولوجي (12). إذ انه يشخص قابلية البكتريا على إفراز الانزيمات المحللة للجيلاتين ، من الضروري عدم تعرض الوسط الى درجات الحرارة العالية لفترة طويلة لانه يؤدي الى تحلل الجيلاتين الجزئي مما يؤدي الى عدم تصلبه عند التبريد (13). بتحضير وسط الجيلاتين المغذي وتلقيحه بالجراثيم *E.coli* و *P.mirabilis* وبعد الحضان بدرجة حرارة 37م° لمدة 18- 24 ساعة.

لوحظ ان جميع النماذج اعطت نتائج ايجابية لنمو الجراثيم مقارنة مع الجيلاتين القياسي لكلا النوعين من الجراثيم فقد كان النموذج A اكثرهم تطابقاً مع الجيلاتين القياسي من حيث صلابة الجيل وثباتيته وذلك بعض العوامل يمكنها تغيير الخواص الطبيعية والكيميائية والبايولوجية للبروتين دون ان يسبب ذلك في تحطيم او كسر الرابطة الببتيدية للبروتين من هذه العوامل الحوامض (11). تؤثر تغييرات الرقم الهيدروجيني على الحالة الأيونية للبروتين . فعند تعرض البروتين لقيم من الرقم الهيدروجيني المتطرفة العالية او المنخفضة فإن ذلك يؤثر على حالة الشحنة للبروتين وتتغير وضعيته وقد يؤدي ذلك الى مسخ البروتين (14). تفقد جزيئات البروتين التراكيب الثلاثية والرابعة (2).

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جدول 5: نتائج اختبار تسييل الجيلاتين

Control	<i>P.mirabilis</i>	<i>E.coli</i>	النموذج
صلب	سائل	صلب	A
صلب	سائل	صلب	B
صلب	سائل	صلب	C
صلب	سائل	صلب	D
صلب	سائل	صلب	St

Control : بدون زرع بكتريولوجي
A: حجم ضعف وزن العظام والمدة 7 أيام
B: حجم ضعف وزن العظام والمدة 14 يوم
C: حجم ثلاثة أضعاف والمدة 7 أيام
D: حجم ثلاثة أضعاف والمدة 14 يوم
St: النموذج القياسي (Standard sample)

تحديد المدة الزمنية

بالاعتماد على نتائج التجربة السابقة اجريت تجربة لتقليل المدة الزمنية لمرحلة المعاملة الحامضية هي (3، 5، 7) يوم وتركيز الحامض المستعمل هو 7% وبحجم ضعف وزن العظام وعند اكمال عمليات الاستخلاص للجيلاتين لجميع النماذج أجريت الاختبارات التالية:

1- اختبار العكرة مع حامض التانيك:

اجري الاختبار لجميع النماذج المستخلصة مقارنة بالجيلاتين القياسي اعطت النتائج المبينة في جدول رقم (6).

جدول 6: نتائج اختبار العكرة مع حامض التانيك لدراسة تأثير المدة الزمنية للمعاملة الحامضية

St	C	B	A	النموذج
+++	+++	+++	++	العكرة

A : 3 يوم
B : 5 يوم
C : 7 يوم
St : النموذج القياسي (Standard sample)

اظهرت نتائج اختبار العكرة ان النموذج B هو أكثر النماذج تطابقاً مع الجيلاتين القياسي من حيث العكرة أما النموذج A فكان اقلها عكرة. جزيئة الكولاجين متألفة من ثلاثة سلاسل الفا (α - chains) ملفطة لذلك يدعى الكولاجين ثلاثي الحلزون الذي يعطي تركيباً ثلاثي الابعاد ببسبب الاواصر الهيدروجينية داخل السلسلة ، فمسخ الكولاجين يسبب فصل كلي او جزئي للسلاسل بسبب تحطم الأواصر الهيدروجينية مسببة فقدان لهيئة الحلزون الثلاثي (15).

2- اختبار الصلابة :

عند اجراء اختبار الصلابة لمحللول الجيلاتين بتركيز 5 % اعطت نتائج للنموذج (A) جيل ضعيف ، اما النموذجان B و C فكانا متصلبين لكن النموذج B اعطى جيل اكثر صلابة من النموذج C مقارنةً بالجيلاتين القياسي. وهذا يعني ان المدة 3 يوم غير كافية للمعاملة الحامضية للعظام وبذلك توصلنا الى ان مدة 5 يوم هي افضل مدة زمنية للمعاملة الحامضية . اذ ان البروتينات عند تعرضها للحامض فان ذلك يؤثر على تركيب البروتينات خاصة على التراكيب الثلاثية والرابعة والبروتينات الناتجة تكون غير فعالة بايولوجيا وتسمى هذه العملية الدنترة Denaturation . ومن نتائج هذه العملية تصبح البروتينات سهلة الهضم (16) .

جدول 7: نتائج اختبار الصلابة في دراسة تأثير المدة الزمنية للمعاملة الحامضية

النموذج	A	B	C	St
الصلابة	جيل ضعيف	متصلب	متصلب	متصلب

B : 5 يوم

A : 3 يوم

St : النموذج القياسي (Standard sample)

C : 7 يوم

3- اختبار تسييل الجيلاتين

بعد تلقیح وسط الجيلاتين المغذي بالجراثيم *P. mirabilis* و *E.coli* وبعد الحضان بدرجة حرارة 37°م لمدة 18-24 ساعة وبعد التبريد توضع النماذج في الثلاجة. بينت النتائج الموضحة في جدول رقم (8) بالمقارنة مع وسط الجيلاتين المغذي القياسي ووسط السيطرة بدون زرع بكتريولوجي . ان جميع النماذج كانت ايجابية للنمو الجرثومي لان وسط الجيلاتين المغذي يحتوي على مصدر الكربون (الكربوهيدرات) ومصدر النيتروجين (الأحماض الأمينية والنوية) وهي المواد التي يحتاجها الكائن المجهرى لتوليد الطاقة والبناء الحيوي (7)، بالمقارنة مع الجيلاتين القياسي كان النموذجان B و C مطابقين لوسط الجيلاتين القياسي ، اما النموذج A فكان الجيل ضعيف في حالة الجرثومة *E.coli* التي ليس لها فعالية محللة للبروتين اما الجرثومة *P. mirabilis* التي لها فعالية محللة للبروتين لانتاجها لانزيم (Gelatinase) المحلل للجيلاتين (13)، فقد كانت جميع النماذج الملقحة بها سائلة بعد تبريدها.

من نتائج الاختبارات نستنتج ان النموذج B افضل لتحضير جيلاتين مطابق للجيلاتين القياسي من حيث المواصفات المدروسة وأقل مدة زمنية . أما (6) فقد تم معاملة العظام لهذه المرحلة من تحضير الجيلاتين بحامض الهيدروكلوريك بتركيز 4-7% لمدة 10-14 يوم . اما في حالة الجلود فقد كانت المعاملة بحامض الهيدروكلوريك بتركيز 3% لمدة 10-30 ساعة (17).

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جدول 8: نتائج اختبار تسييل الجيلاتين لدراسة تأثير المدة الزمنية للمعاملة الحامضية

الجيلاتين	<i>E.coli</i>	<i>P.mirabilis</i>	Control
A	جيل ضعيف	سائل	جيل ضعيف
B	صلب	سائل	صلب
C	صلب	سائل	صلب
St	صلب	سائل	صلب

A : 3 يوم B : 5 يوم

C : 7 يوم St: النموذج القياسي (Standard sample)

تحديد التركيز لحامض الهيدروكلوريك

لتحديد التركيز الامثل لحامض الهيدروكلوريك تم تحضير التراكيز (5، 7، 9، 14)% وبحجم ضعف وزن العظام ولمدة 5 يوم لجميع التراكيز .

كانت النتائج عند اكمال عملية المعاملة الحامضية باستخدام تركيز 14% حامض الهيدروكلوريك لم يتبقى أي عظام فقد هضمت جميع العظام وكان الناتج محلول غامق جوزي اللون فهذا التركيز تم استبعاده فهو تركيز غير ملائم لتحضير الجيلاتين . عند تعرض البروتينات لظروف غير اعتيادية مثل درجة الحرارة، الحموضة القاعدية، تراكيز الملح العالية، فأنها تتمسخ خلال هذه العملية وتفقد جزيئات البروتينات مواصفاتها التركيبية (18). الكولاجين يتحطم خلال التحلل المائي ويمر بالمراحل: الجيلاتين، والبروتيز (Protease) والبيتونات (peptones) والبيتيدات المتعددة الى احماض امينية ، والاحماض الامينية الناتجة من تحلل الكولاجين والجيلاتين هي نفسها (11)، عند اكمال عملية المعاملة الحامضية والاستخلاص لبقية النماذج المعاملة بالحامض اجريت الاختبارات التالية:

1- اختبار العكرة مع حامض التانيك (Tannic acid)

اجري الاختبار لنماذج الجيلاتين المستخلص مقارنة مع الجيلاتين القياسي، أعطت جميع النماذج عكرة مع حامض التانيك، وكان نموذج الجيلاتين الذي أستخلص بتركيز 9% من حامض الهيدروكلوريك أكثرهم تطابقاً مع نموذج الجيلاتين القياسي كما مبين في الجدول رقم (9).

جدول 9: نتائج اختبار العكرة مع حامض التانيك لدراسة تأثير تركيز حامض الهيدروكلوريك

النموذج	5%	7%	9%	St
العكرة	++	++	+++	+++

St: النموذج القياسي (Standard sample)

2- اختبار الصلابة

عند إجراء اختبار الصلابة لمحلول الجيلاتين بتركيز 5% لنماذج الجيلاتين المستخلص مقارنة بالجيلاتين القياسي اعطت النتائج المبينة في جدول رقم (10) كانت جميع النماذج متصلبة لكن

النموذج المعامل لحامض الهيدروكلوريك 9% أكثرها تطابقاً مع الجيلاتين القياسي من حيث الصلابة واللون وخلوه من الشوائب. صلابة الجيل تعتمد على التركيز ودرجة الحرارة والرقم الهيدروجيني ومصدر الكولاجين (6).

جدول 10: نتائج اختبار الصلابة لدراسة تأثير التركيز الامثل لحامض الهيدروكلوريك

St	9%	7%	5%	النموذج
صلب	صلب	صلب	صلب	الصلابة

St: النموذج القياسي (Standard sample)

3- اختبار تسييل الجيلاتين

عند تحضير وسط الجيلاتين المغذي لجميع النماذج قيد الدراسة مع الجيلاتين القياسي وتلقيحه بالجرثومتين *E.coli* و *P.mirabilis* ونموذج سيطرة بدون تلقيح بالجرثائم ووضعه في الحاضنة بدرجة حرارة 37°م لمدة 18-24 ساعة، أعطت جميع النماذج نتائج ايجابية للنمو الجرثومي ومتقاربة من حيث فعالية تسييل الجيلاتين عند تلقيح الوسط بالجرثومة *P.mirabilis* وبقاء الوسط متصلب عند تلقيحه بالجرثومة *E.coli* وكان النموذج المحضر بتركيز 9% أكثر النماذج تطابقاً مع النموذج القياسي كما مبين في جدول رقم (11).

جدول 11: نتائج اختبار تسييل الجيلاتين لدراسة تأثير تركيز حامض الهيدروكلوريك .

Control	<i>P.mirabilis</i>	<i>E.coli</i>	الجيلاتين
صلب	سائل	صلب	5%
صلب	سائل	صلب	7%
صلب	سائل	صلب	9%
صلب	سائل	صلب	St

St: النموذج القياسي (Standard sample)

من خلال النتائج يتضح ان استخدام حامض الهيدروكلوريك بتركيز 9% لمدة 5 يوم أفضل تركيز لمرحلة المعاملة الحامضية للعظام لازالة المعادن (Demineralization) لتحضير الجيلاتين ، أما في المصدر (6) فقد تمت المعاملة الحامضية باستخدام حامض الهيدروكلوريك بتركيز 4-7% لمدة 10-14 يوماً. اما في حالة الجلود فقد كانت المعاملة لحامض الهيدروكلوريك بتركيز 3% لمدة 10-30 ساعة حسب ماورد في (17).

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دراسة تأثير بعض العوامل البيئية في نمو وإنتاجية طحلب *Microcystis* sp

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ABSTRACT

The research includes studying some of *Microcystis* sp. algae noticed on environmental factors (Illuminity tensity, temperature, pH, sailinty)and effectofit on *microcystis* sp algae in 25 C°good growth $24.427 \text{ cell} \times 10^3/\text{L}$ for the number cells and growth range 2.675 cell/ hour It become clear also that good increase in growth in Illuminity density $245 \mu\text{E}/\text{m}^2/\text{sec}$ and through the number of cells $42.421 \text{ cell} \times 10^3/\text{L}$ and growth range 2.872 cell/ hour under pH(7), The best concentration for sailinty 1.5 ppm and by increase the cellnumber $22.529 \text{ cell} \times 10^3/\text{L}$ and growth range 1.432 cell/hour. Observed that by the concentration 2 mg/L phosphate and 20 mg/L nitrate appeare high and good growth through $137.744, 61.233 \text{ cell} \times 10^3/\text{L}$. respectively and by growth range 3.674 ,2.357 cell/hour respectively when we comparative by the control.

الخلاصة

أهتم البحث دراسة بعض العوامل البيئية مثل (شدة الإضاءة ودرجة الحرارة والأس الهيدروجيني والملوحة) وتأثيرها على طحلب *Microcystis* sp، للطحلب نمو جيد في درجة حرارة 25 م° $24.427 \text{ خلية} \times 10^3/\text{لتر}$ كعدد للخلايا وبمعدل نمو 2.673 خلية/ساعة كذلك تبين ازدهار جيد للنمو بشدة إضاءة 245 مايكروأنشتاين/م²/ثا من خلال عدد الخلايا البالغ $42.421 \text{ خلية} \times 10^3/\text{لتر}$ وبمعدل نمو 2.872 خلية/ساعة تحت أس هيدروجيني 7، أما التركيز الأفضل للملوحة 1.5 ملغم/لتر بزيادة عدد الخلايا $22.529 \text{ خلية} \times 10^3/\text{لتر}$ وبمعدل نمو 1.432 خلية/ساعة وتبين تركيز 2 ملغم/لتر فوسفات و 20 ملغم/لتر نترات كثافة نمو عالية من خلال 137.744 و 61.238 $\text{خلية} \times 10^3/\text{لتر}$ على التوالي وبمعدل نمو 3.674 و 2.357 خلية/ساعة على التوالي مقارنة بالسيطرة.

المقدمة

تعتبر الطحالب من أهم مكونات السلسلة الغذائية لل Ecosystem لعدة أسباب منها لأنها تشكل القاعدة الأساس التي تستند عليها السلسلة الغذائية وتؤدي دورا كبيرا في أدائه التوازن بين الغازات في الطبيعة، فضلا عن قيمتها الغذائية التي استخدمت كغذاء جيد للحيوانات وبخاصة

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أمل وأحمد وبهجت وعبير وزهراء ولؤي

الأسماك [1] إذ تؤدي الطحالب دورا كبيرا في تخفيف حدة التلوث من خلال سحب المغذيات النباتية المتمثلة بالنيتروجين والفسفور التي تعتبر المكمل والداعم لأجهزتها الداخلية من دخول الفسفور في التركيب الخلوي للطحالب ويدخل في تركيب بروتوبلازم الخلايا كما تعمل هذه الطحالب على إنتاج الأوكسجين الذائب الذي يحسن من نوعية المياه. وتستطيع الطحالب أيضاً سحب الفسفور عندما يكون بتركيز عالية في وقت قصير وبكميات أكثر من حاجتها للنمو إذ يتبلر الفسفور بعد امتصاصه داخل خلية الطحالب بشكل متعدد الفوسفات Polyphosphate، ويدخل في عملية نقل الطاقة والنقل الأنزيمي من خلال مركب الادينوسين ثلاثي الفوسفات ATP ، ويتم إزالة الفوسفات في الطحالب عن طريق ظاهرة الاستهلاك الثري Luxury Consumption تستطيع الطحالب بسحب الفوسفات بشكل سريع وبكميات أكثر مما تحتاجه للنمو ثم تخزينه في خلاياها، كذلك النيتروجين يدخل في تصنيع الأحماض الأمينية والبروتينات ويؤدي النيتروجين دورا مهما في التركيب الخلوي للطحالب حيث يكون محدد لإنتاجية الطحالب في بعض البحيرات وخاصة عندما يكون تركيز الفوسفات عالي ، أن التمثيل الداخلي للنترات يتضمن عدد من التفاعلات منها الاختزال الاميني للامونيا إلى Glutamate يتبعها النقل الاميني لأحماض أمينية أخرى . أن سحب المغذيات يتم خلال نظام نقل أنزيمي متخصص يقع في غشاء الخلية وهو نظام مستهلك للطاقة المجهزة من قبل التنفس أو البناء الضوئي (3) ، ومن الجدير بالذكر أن الطحالب والنباتات تحتاج إلى بعض العناصر الثقيلة بتركيز ضئيلة جدا لإتمام عملية التركيب الكيميائي للمادة الحية . و تلعب بعض العوامل الفيزيائية مثل الحرارة وشدة الإضاءة دوراً هاماً في خفض تراكيز المغذيات. وعليه لا بد من الحاجة إلى طرائق معالجة مناسبة لمياه الفضلات للحفاظ على البيئة المائية من التلوث. لقد أثبتت الطحالب قدرتها في خفض نسبة الملوثات من مياه الفضلات وبالأخص المغذيات النباتية مثل النيتروجين والفسفور .

لذا يهدف البحث دراسة لبعض الصفات البيئية لطحلب *Microcystis* sp للأهمية الضرورية لهذا الطحلب لإفرازه السموم في البيئة المائية من خلال معرفة الظروف المثلى له لإفراز سمومه.

المواد وطرائق العمل

جمعت النماذج من مناطق في مدينة بغداد منها نهر ديالى ومنطقة الزعفرانية ، تم الحصول على العزلة بطريقة الزرع على وسط الاكار ، بعدها استزرعت العزلة في أوساط صلبة ولعدة مرات للحصول على عزلة نقية وإكثارها في وسط زرعي Chu-10 المحور من قبل (2). والمدرجة مكوناته في الجدول (1). حيث تم تعقيم الوسط الزرعي باستخدام جهاز التعقيم الموصدة Autoclave بدرجة 121 م وضغط 1.5 جو ولمدة 20 دقيقة وترك لليوم التالي ليبرد ثم تم قياس

الهيدروجيني (6.8) باستخدام جهاز قياس pH-meter نوع INOLOB ألماني الصنع بإضافة بعض قطرات من حامض الهيدروكلوريك وهيدروكسيد الصوديوم المخففين (0.01 عياري) لحين الوصول للدالة الحامضية.

جدول 1: مكونات الوسط الزراعي Chu-10 المحور من قبل [2]

الوزن (ppm)	الملح
10	MgSO ₄ .7H ₂ O
8	Na ₂ NO ₃
4	K ₂ HPO ₄
16	CaCl ₂
0.32	FeCl ₃
4	EDTA-Na ₂
30	NaCl
8	Na ₂ CO ₃
0.04	MnCl ₂ . 4H ₂ O
0.007	(NH ₄) ₆ Mo ₇ O ₂₄ .4H ₂ O
0.056	ZnSO ₄ .7H ₂ O
0.02	CuSO ₄ .5H ₂ O
0.01	CuCl ₂ .6H ₂ O
0.72	H ₃ BO ₃
5.7	Na ₂ SiO ₃

عرض طحلب *Microcystis* لثلاثة مستويات من شدة الإضاءة (190,220 ميكرواينشتاين، 245)م²/ثا كما تم دراسة تأثير ثلاثة درجات للحرارة (20 ، 25 ، 30) ± 2 م ودراسة تأثير ثلاث متغيرات من الحامضية (6، 7، 8) ودراسة تأثير ثلاثة تراكيز من الملوحة (1.5، 2، 3، 5) % واستخدمت مصابيح فلوريسنت Day light flourcesnt البالغة شدة إضاءة 245 ميكرواينشتاين/م²/ثا كمصدر للإضاءة وتم قياسها بجهاز Lux meter ولفترة ضوئية 16:8 (ضوء:ظلام).

كما تم قياس الملوحة بدلالة التوصيلية وفق الآتي :

$$S\% = (\text{Conductivity} - 14.78) / 1589.08 \dots\dots\dots(1)$$

استمرت التجارب لمدة (12) يوم لكل من الحرارة وشدة الإضاءة والحامضية والملوحة حسب من خلالها العدد الكلي للطحالب واعتبرت كل خلية للنوع *Microcystis* وحدة واحدة وكذلك تم حساب نسبة الإزالة للنترات والفوسفات. وتم حساب عدد الخلايا بواسطة شريحة haemocytometer المستخدمة في حساب عدد الخلايا كريات الدم وعبر عن النتائج بخلية/ملم باستخدام طريقة القطاع

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المستعرض وحسب الخطوات التالية :

- 1- حجم العينة في القطاع الواحد = طول القطاع × عرض القطاع × في عمق الشريحة
- 2- عدد القطاعات في (1 مل) من العينة = 1000 ÷ حجم العينة في القطاع الواحد
- 3- عدد الخلايا في (1 مل) من العينة = معدل عدد الخلايا في قطاع واحد × عدد القطاعات في (1 مل) من العينة .

واعتمدت معادلات [3]. في حساب معدل النمو (M) Growth rate

$$M = \frac{\ln(X_2/X_1)}{T_2 - T_1} \dots \dots \dots (2)$$

إذ أن M = معدل النمو .

X₂ = عدد الخلايا / مليلتر في زمن t₂ (خلية / مليلتر) .

X₁ = عدد الخلايا / مليلتر في زمن t₁ (خلية / مليلتر) .

T₂ = آخر يوم من التعريض للعنصر المستخدم .

T₁ = أول يوم من التعريض للعنصر المستخدم .

Doubling Time (G) ومن ثم حساب زمن التضاعف وبالإعتماد على (3) : وحسب المعادلة التالية:

$$G = \frac{\ln 2}{M}$$

تم حساب تركيز الفوسفات والنترات وطيلة فترة التجربة باستخدام جهاز الطيف الضوئي Spectrophotometer نوع Shimadzu -260A في طول موجي 860 نانوميتر للفوسفات و 543 نانوميتر للنترات والنترت وحسب الطرق التحليل القياسية رقم NO₃- B - 4500 و P - E - 4500 . [4].

النتائج والمناقشة

أوضحت النتائج من خلال الشكل (1) عند تعريض طحلب *Microcystis* لمدى من درجات الحرارة (20 , 25 , 30) م ± 2 أعطت درجة الحرارة 25 م أعلى معدل لعدد الخلايا 24,427 × 10³ خلية / مليلتر يقابله أعلى معدل نمو (2.673 خلية / ساعة) وأقل زمن تضاعف (17.02 خلية / ساعة) ، أما درجة الحرارة 30 م بلغ عدد الخلايا 10.324 × 10³ خلية / مليلتر وبمعدل نمو 1.920 خلية / ساعة وبزمن تضاعف 21.72 خلية / ساعة ، أما درجة حرارة 20 م بلغت به عدد الخلايا 8.837 × 10³ خلية / مليلتر وبمعدل نمو 1.783 خلية / ساعة وبزمن تضاعف 26.21 خلية / ساعة حسب جدول (2) وأظهر التحليل الإحصائي وجود فرق معنوي (p<0.05) بين معدل الخلايا ومعدل النمو وزمن التضاعف . إذ تتأثر الطحالب في البيئة المائية بالتغير الذي يحصل في درجات الحرارة من خلال تأثيرها في عملية البناء الضوئي والتنفس فضلا

عن تأثيرها في قدرتها للاستفادة من المغذيات في الوسط الذي توجد فيه. أما في هذه الدراسة تبين *Microcystis* sp أنه سجل أعلى معدل نمو عند درجة حرارة 25 °م وينخفض معدل الانقسام الخلايا بعد هذه الدرجة ودونها، يطابق ذلك لما أشار إليه [5] في دراسته أن للدرجة 25 °م الأفضل لنمو وانقسام الطحلب *S. acutus*. وأشار [6] معظم طحالب المياه العذبة تنمو بصورة جيدة في مدى من درجات الحرارة ما بين (22-30) °م، كما أتفقت هذه الدراسة مع دراسة [7] في دراسة النوعين من الطحالب الخضر *S. obliquus*، *C. vulgaris* من أن أفضل درجة نمو هي 25 °م . ويوضح الشكل (2) تعريض طحلب *Microcystis* لمستويات مختلفة من شدة الإضاءة (190 ، 220 ، 245) مايكروانشتاين / م² / ثا أعطت الشدة (245) مايكروانشتاين / م² / ثا أعلى عدد من الخلايا 42.421×10^3 خلية / مليلتر بمعدل نمو 2.872 خلية / ساعة بأقل زمن تضاعف 14.31 خلية/ساعة، أما الشدة (220) مايكروانشتاين / م² / ثا وصلت به عدد الخلايا أثناء مدة التجربة الى 18.772×10^3 خلية / مليلتر بمعدل نمو 1.942 خلية/ساعة وبزمن تضاعف 22.13 خلية/ساعة أما الشدة (190) مايكروانشتاين / م² / ثا بلغت عدد الخلايا 5.242×10^3 خلية / مليلتر بمعدل نمو 1.312 خلية/ساعة وبزمن تضاعف 35.20 خلية/ساعة جدول (3) . لوحظ أن طحلب *Spirogyra* sp. يعطي أعلى معدل نمو عند شدة 237 مايكروانشتاين / م² / ثا بينما كان أفضل معدل نمو لطحلب *Pithophora* sp. عند شدة إضاءة 500 مايكروانشتاين / م² / ثا (8) وبين التحليل الإحصائي وجود فرق معنوي ($p < 0.05$) بين مستويات لشدة الإضاءة في معدل النمو وزمن التضاعف . أما الشكل (3) يوضح زراعة طحلب *Microcystis* بأوساط زرعيه بتركيز مختلفة للحامضية (6، 7، 8) حيث أعطت pH=7 أفضل عدد خلايا 51.202×10^3 خلية / مليلتر وأعلى معدل نمو 3.229 خلية/ساعة بأقل زمن تضاعف 14.08 خلية/ساعة أما pH=8 أعطت عدد خلايا 23.725×10^3 خلية / مليلتر بمعدل نمو 2.542 خلية/ساعة وبزمن تضاعف 17.25 خلية / ساعة أما pH=6 بلغت بها عدد الخلايا 26.722×10^3 خلية / مليلتر ومعدل نمو 2.435 خلية/ساعة وبزمن تضاعف 16.76 خلية/ساعة وحسب جدول (4) وضح التحليل الإحصائي لا يوجد فرق معنوي بين (6 و 8 pH) بالنسبة لمعدل عدد الخلايا ومعدل النمو وزمن التضاعف ولكن يوجد فرق معنوي ($p < 0.05$) بالنسبة pH=7 . كما تبين أن أفضل حامضية لنمو *Microcystis* كانت عند pH=7 وهي مقاربة لدرجة حامضية الوسط الزرعي كانت 6.8 ، أن ذلك يبين للحامضية تأثير على معدل نمو الطحالب انخفاض معدل النمو عند زيادة وانخفاض pH عن 7. يوضح الشكل (4) نتائج طحلب *Microcystis* المنمى بأوساط زرعيه ذات تراكيز مختلفة من الملوحة (1.5 ، 2 ، 3 ، 5) ‰ . ان تركيز 1.5 سجل أعلى عدد من الخلايا 22.529×10^3 خلية / مليلتر وأعلى معدل نمو 1.432 خلية/ساعة وأقل زمن تضاعف 20.11 خلية/ساعة أما تركيز 2 أعطى عدد خلايا 16.233×10^3 خلية / مليلتر وبمعدل نمو بلغت 1.113 خلية/ساعة

دراسة تأثير بعض العوامل البيئية في نمو وإنتاجية طحلب *Microcystis* sp

أمل وأحمد وبهجت وعبير وزهراء ولؤي

وبزمن تضاعف 23.05 خلية/ساعة وتركيز 3 بلغت به عدد الخلايا 6.542×10^3 خلية / مليلتر وبمعدل نمو 1.062 خلية/ساعة وبزمن تضاعف 27.10 خلية/ساعة وبلغت عدد الخلايا لتركيز 5 وصلت الى 6.392×10^3 خلية / مليلتر وبمعدل نمو 1.034 خلية/ساعة وبزمن تضاعف 32.07 خلية/ساعة مقارنة بالسيطرة بلغت به عدد الخلايا 46.952×10^3 خلية / لتر وبمعدل نمو 2.443 خلية/ساعة وبزمن تضاعف 15.24 خلية/ساعة جدول (5) يوجد فرق معنوي لمعدل عدد الخلايا باحتمالية ($p < 0.05$) ولا يوجد فرق معنوي لمعدل النمو بين (1.5 و 2 %) كذلك لا يوجد فرق معنوي بين (3 و 5 %) لمعدل النمو، أما زمن التضاعف فلا يوجد فرق معنوي بين (1.5 و 3 و 5 %). لا يقتصر تأثير الطحلب بدرجة الحرارة وشدة الإضاءة والحمضية بل تتأثر بعوامل أخرى بمقاومتها للملوحة. إذ اثبت من خلال الدراسة أن أفضل ملوحة هي 1.5% فقد كان معدل النمو أفضل من درجة ملوحة 10.5 % التي قد تصل إليها مياه نهر صدام حيث أشار (11) إلى أن معدل النمو ينخفض عند الزيادة عن هذه الدرجة وخصوصاً عندما تكون درجة الملوحة 10 % حيث انخفض معدل النمو وعدد مرات التضاعف بشكل اكبر من ملوحة 5 % . ويلاحظ ارتفاع تراكيز الملوحة في نهر صدام بالمقارنة مع نهري دجلة والفرات وهي نتيجة طبيعية متأثرة من طبيعة النهر حيث يعزى ارتفاع التوصيلية إلى ارتفاع نسبة الأملاح في النهر وهي ناتجة عن زيادة تراكيز أملاح الكلورايد والأملاح الأخرى (9). ويوضح الشكل (5) زيادة أعداد الخلايا 137.744×10^3 /مليلتر ومعدل نمو 3.674 خلية / ساعة وبزمن تضاعف 12.31 خلية / ساعة بالنسبة لتركيز 2 ملغم / لتر فوسفات ، أما بقية التراكيز (5 ، 10 ، 20 ملغم / لتر فوسفات) كانت أقل استجابة للطحلب وعلى التوالي . ارتفاع أعداد الخلايا والوصول لقمة النمو للمزرعة في اليوم السابع للتجربة بعدها بدت بالاستقرار ومن ثم انخفاض ملحوظ بسبب قلة المغذيات لامتناس الطحالب له بدت التراكيز بالانخفاض أكثر بعد اليوم السابع للمعاملة وكان تركيز 2 ملغم / لتر فوسفات أكثر وضوحاً لانخفاضه بزيادة أعداد الخلايا الطحلبية حتى نهاية التجربة شكل (6) جدول (6) . وأظهر التحليل الإحصائي وجود فرق معنوي ($p < 0.05$) بين تراكيز الفوسفات لمعدل عدد الخلايا ومعدل النمو ، أما فحوصات النترات نلاحظها بتراكيز النترات من ضمنها 20 ملغم / لتر تميز عن بقية التراكيز بزيادة أعداد الخلايا 61.238×10^3 /مليلتر ومعدل نمو 2.357 خلية/ساعة وبزمن تضاعف 14.79 خلية/ساعة، أما بقية التراكيز أتضح تدرجت (10 ، 5 ، 2 ملغم/لتر نترات) الشكليين (7،8) ، بدت المزرعة بالاستقرار بالنسبة للنمو باليوم السابع للتجربة إذ أزدهرت المزرعة للتراكيز العالية من النترات وحسب الجدول (7) ، سجلت حالة أثراء عالية جدا في تركيز 2 ملغم/لتر فسفور - فوسفات و 20 ملغم/لتر نيتروجين - نترات أما بقية التراكيز فقد انخفضت كلما زاد تركيز الفوسفات عن 2 ملغم/لتر وكلما قل عن تركيز 20 ملغم/لتر نترات وهذا يطابق لما حصلت

عالية [10] تشير التحاليل الإحصائية إلى وجود فرق معنوي ($p < 0.05$) بين تركيزي (2 و 5 ملغم / لتر) ولا يوجد فرق معنوي بين تركيزي (10 و 20 ملغم / لتر) ، أشار (10) في دراسة إذ وجدت أن تركيز 1 ملغم / لتر فوسفات يؤدي إلى زيادة عالية في تركيز الصبغة وان هذه الاستجابة لتراكيز واطئة من الفسفور يمكن تفسيرها على أساس ما مخزون من العنصر في جسم الطحلب أكثر مما هو موجود في البيئة المحيطة تمتاز الطحالب بظاهرة الخزن أكثر من حاجتها Luxury storage ، وبعد أن تصل الخلايا إلى أقصى عدد تبدأ بالاستقرار النسبي أو الانخفاض ، أن توقف المزرعة عن النمو المستمر قد يعود لعدة أسباب منها استهلاك المغذيات لغرض النمو حيث تتناقص المغذيات تدريجياً لتصل أقل مستوى عندما يكون النمو بأقصى كثافة له . أو بسبب إفرازات الخلايا من المثبطات الذاتية حيث أصبح واضحاً من المصادر المتنوعة بأن أنواع معينة من الطحالب تنتج مواد تعتبر مثبطة لنموها مثل طحلب الـ *C. vulgaris* الذي يفرز مادة الـ Chlorellin [12]. أن نمو الطحلب يزداد طردياً مع زيادة تركيز النتروجين - نترات في الوسط الزراعي الحاوي على 20 ملغم / لتر نترات - نتروجين / لتر [3].

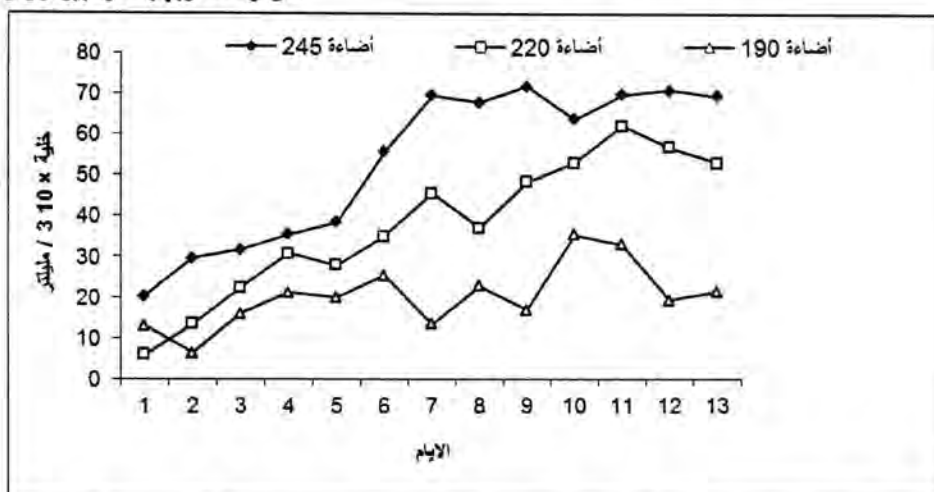
شكل 1: تأثير درجة الحرارة على طحلب *Microcystis sp* في وسط زرع مغذي بشدة إضاءة مثلي (245 مايكروانشتاين / م² / ثا)

جدول 2: تأثير درجة الحرارة على عدد الخلايا ومعدل النمو وزمن التضاعف لطحلب *Microcystis sp* في وسط زرع مغذي بشدة إضاءة مثلي (245 مايكروانشتاين / م² / ثا)

زمن تضاعف خلية / ساعة	معدل النمو خلية / ساعة	معدل عدد الخلايا خلية × 10 ³ / مليلتر	درجة الحرارة (م)
^a 0.673 ± 26.21	^c 0.006 ± 1.783	^c 0.756 ± 8.837	20
^c 1.733 ± 17.02	^a 0.300 ± 2.673	^a 2.189 ± 24.427	25
^b 0.952 ± 21.72	^c 0.205 ± 1.920	^b 1.150 ± 10.324	30

* الحروف المختلفة بين الأعمدة تدل على وجود اختلافات معنوية عند مستوى احتمالية ($P < 0.05$)

دراسة تأثير بعض العوامل البيئية في نمو وإنتاجية طحلب *Microcystis* sp أمل وأحمد وبهجت وعبير وزهراء ولؤي

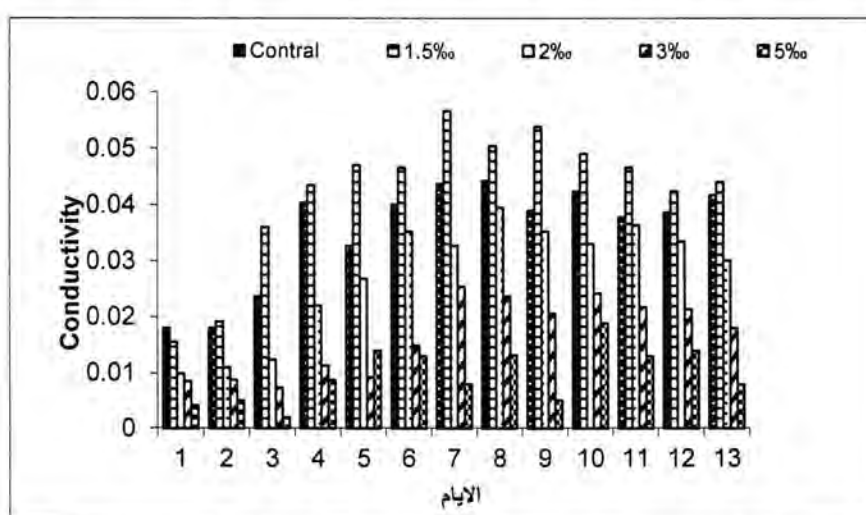


شكل 2: تأثير شدة الإضاءة على معدل نمو طحلب *Microcystis* sp في وسط زرع مغذي بدرجة حرارة مثلى (25 م°)

جدول 3: تأثير شدة الإضاءة على عدد الخلايا ومعدل النمو وزمن التضاعف لطحلب *Microcystis* في وسط زرع مغذي بدرجة حرارة مثلى (25 م°)

شدة الإضاءة مايكروانشتاين / م ² / ثا	معدل عدد الخلايا خلية × 10 ³ / مليلتر	معدل النمو خلية / ساعة	زمن تضاعف خلية / ساعة
245	^a 2.189 ± 42.421	^a 0.340 ± 2.872	^c 1.731 ± 14.31
220	^b 0.861 ± 18.772	^b 0.121 ± 1.942	^a 0.021 ± 22.13
190	^c 0.743 ± 5.242	^c 0.103 ± 1.312	^b 0.104 ± 35.20

*الحروف المختلفة بين الأعمدة تدل على وجود اختلافات معنوية عند مستوى احتمالية (P < 0.05)

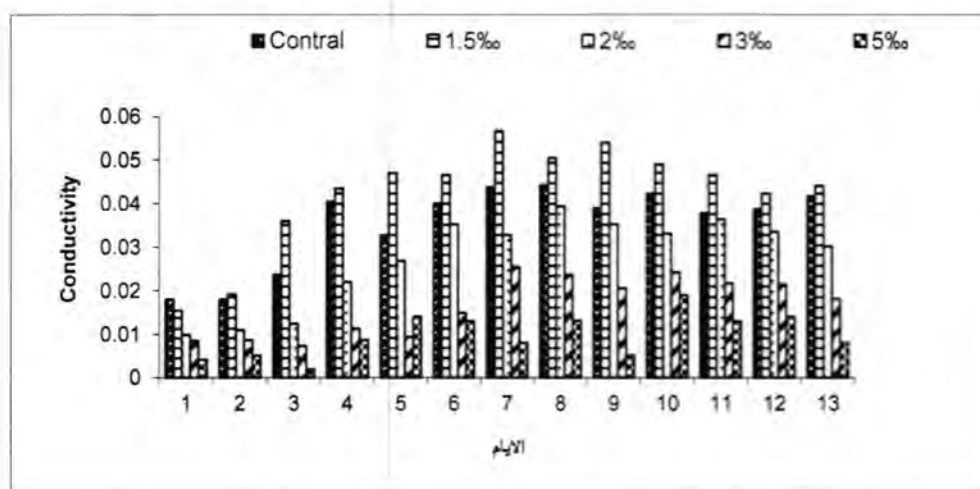


شكل 3: يوضح الأس الهيدروجيني وتأثيره على معدل نمو طحلب *Microcystis* sp في وسط زرع مغذي بدرجة حرارة مثلى (25 م°) وشدة إضاءة مثلى (245 مايكروانشتاين/م²/ثا)

جدول 4: تأثير الالاس الهيدروجيني على عدد الخلايا ومعدل النمو وزمن التضاعف لطحلب *Microcystis* في وسط زرع مغذي بدرجة حرارة مثلي 25 م وشدة إضاءة مثلي (245 مايكروانشتاين/م²/ثا)

زمن تضاعف خلية / ساعة	معدل النمو خلية / ساعة	معدل عدد الخلايا خلية $\times 10^3$ / مليلتر	pH – meter
^a 1.842 \pm 16.76	^b 0.563 \pm 2.435	^b 1.513 \pm 26.729	6
^b 1.557 \pm 14.08	^a 1.967 \pm 3.229	^a 2.453 \pm 51.202	7
^c 1.462 \pm 17.25	^b 0.471 \pm 2.542	^b 1.487 \pm 23.725	8

*الحروف المختلفة بين المعاملات تدل على وجود اختلافات معنوية عند مستوى احتمالية ($P < 0.05$)



شكل 4: يوضح تأثير الملوحة بدلالة التوصيلية على طحلب *Microcystis* لبعض تراكيزها في وسط زرع مغذي بدرجة حرارة مثلي 25 م وشدة إضاءة مثلي (245 مايكروانشتاين/م²/ثا)

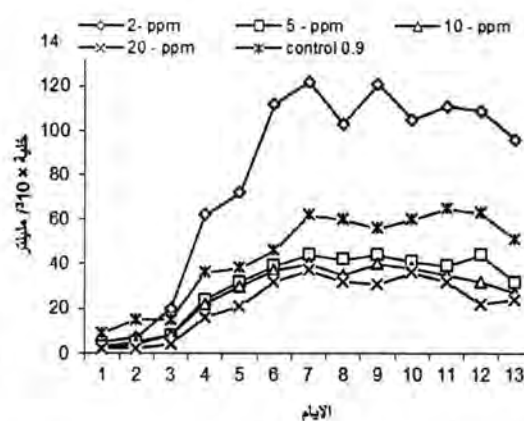
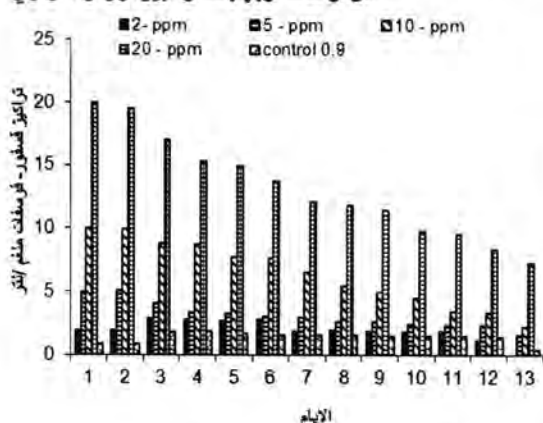
جدول 5: يوضح تراكيز مختلفة للملوحة واستجابة طحلب *Microcystis* لبعض تراكيزها في وسط زرع مغذي بدرجة حرارة مثلي 25 م وشدة إضاءة مثلي (245 مايكروانشتاين/م²/ثا)

زمن تضاعف خلية / ساعة	معدل النمو خلية / ساعة	معدل عدد الخلايا خلية $\times 10^3$ / مليلتر	تركيز ppm
^c 1.643 \pm 15.24	^a 0.300 \pm 2.443	^a 2.189 \pm 46.952	Control
^{bc} 0.687 \pm 20.11	^b 0.229 \pm 1.432	^b 0.96 \pm 22.529	1.5
^b 0.531 \pm 23.05	^b 0.229 \pm 1.213	^c 0.65 \pm 16.233	2
^b 1.205 \pm 27.10	^c 0.108 \pm 1.062	^d 0.173 \pm 6.542	3
^a 0.336 \pm 32.07	^c 0.104 \pm 1.034	^d 0.211 \pm 6.392	5

*الحروف المختلفة بين المعاملات تدل على وجود اختلافات معنوية عند مستوى احتمالية ($P < 0.05$)

دراسة تأثير بعض العوامل البيئية في نمو وإنتاجية طحلب *Microcystis* sp

أمل وأحمد وبهجت وعبيد وزهراء ونوي



الشكل 6: يوضح استجابة نمو طحلب *sp*

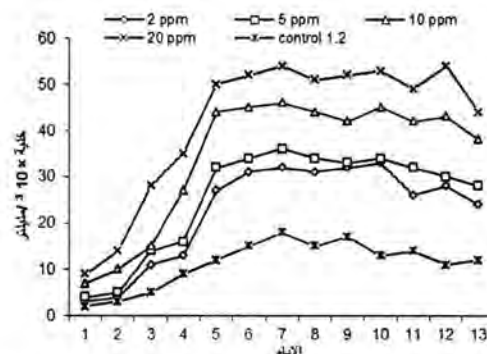
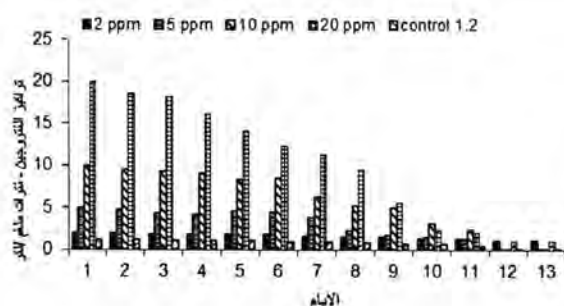
الشكل 5: تأثير تراكيز الفوسفات على معدلات

زيادة أعداد الخلايا لطحلب *Microcystis* *Microcystis* لبعض تراكيز فسفور- فوسفات

جدول 6: يوضح تأثير تراكيز الفسفور - فوسفات على معدل نمو طحلب *Microcystis* في وسط

زرعي مغذي بدرجة حرارة مثلي 25 م وشدة إضاءة مثلي (245 مايكروانشتاين/م²/ثا)

التركيز Ppm	معدل عدد الخلايا خلية $\times 10^3$ / مليلتر	معدل النمو خلية / ساعة	معدل زمن التضاعف خلية / ساعة	تركيز الفوسفات po_4 ppm
السيطرة	^b 0.762 \pm 89.110	^c 1.753 \pm 1.846	^a 0.460 \pm 15.14	^a 1.663 \pm 0.807
2	^a 2.689 \pm 137.744	^a 2.013 \pm 3.674	^{ab} 0.500 \pm 12.31	^a 1.741 \pm 0.592
5	^c 0.815 \pm 78.106	^c 1.683 \pm 1.822	^c 0.431 \pm 17.45	^{ab} 1.963 \pm 1.306
10	^d 0.373 \pm 64.634	^d 1.413 \pm 1.501	^d 0.348 \pm 19.55	^c 1.983 \pm 1.663
20	^e 0.185 \pm 50.549	^{cd} 1.143 \pm 1.475	^{ed} 0.311 \pm 20.77	^d 2.103 \pm 2.321



الشكل 8: يوضح استجابة نمو طحلب *sp*

الشكل 7: تأثير تراكيز النترات على معدلات زيادة

Microcystis لبعض تراكيز نيتروجين - نترات

أعداد الخلايا لطحلب *Microcystis* *sp*

جدول 7: يوضح تأثير تراكيز نيتروجين - نترات على معدل نمو طحلب *Microcystis* في وسط زرع مغذي بدرجة حرارة مثلي 25 م وشدة إضاءة مثلي (245 مايكروانشتاين/م²/ثا)

التركيز ppm	معدل عدد الخلايا خلية × 10 ³ / مليلتر	معدل النمو خلية / ساعة	معدل زمن لتضاعف خلية / ساعة	تركيز الفوسفات NO ₃ ppm
المسيطر	^a 0.762±17.831	^c 0.262±1.355	^a 0.867±21.99	^a 1.373 ±0.825
2	^b 1.483 ±36.669	^b 0.762±1.509	^b 0.732±17.83	^a 1.421 ±1.637
5	^c 1.174 ±41.757	^b 0.942±1.557	^b 0.736±17.95	^c 1.563 ±2.951
10	^d 2.459±52.846	^a 1.652±2.034	^c 0.642±15.70	^d 1.973 ±5.962
20	^d 2.661±61.238	^a 1.712±2.357	^c 0.681±14.79	^e 1.583 ±9.063

*الحروف المختلفة بين المعاملات تدل على وجود اختلافات معنوية عند مستوى احتمالية (P< 0.05)

أتضح من خلال الدراسة أن طحلب *Microcystis* sp. ينمو بظروف بيئية مثلي من درجة حرارة 25 م° وباس هيدروجيني pH=7 وبشدة إضاءة 245 مايكروانشتاين / م² / ثا وبملوحة مقدارها 1.5 ‰ أما التراكيز الأمثل بالنسبة للمغذيات من فسفور 2 ملغم/لتر وللنترات 20 ملغم/لتر التي حقق أفضل النتائج.

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دراسة السلوك الحجمي لبعض الأحماض الامينية في المحاليل المائية لهاليدات البوتاسيوم عند درجات حرارة مختلفة

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ABSTRACT

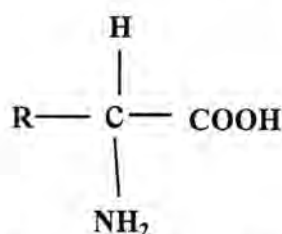
The study includes measurements of density (ρ) of Amino acid solution of different concentrations (range 0.1-0.8) mol . L⁻¹ in 0.4 mol . L⁻¹ Potassium halides solutions (KI ,KBr ,KCl) at different temperatures (298.15, 303.15, 308.15) K. from the density measurements it was calculated Apparent Molal Volumes (ϕ_v) and from this value were calculated Limiting Apparent Molal Volume(ϕ_v^*) and the Experimental $\text{slop}(S_v^*)$, Partial Molal Volume ($V_{1,2}$) for Amino acid solutions and partial molal volume limiting at infinity dilution these factors which indicate the strong solute – solvent or ion - hydrophilic interaction and weak solute – solute or ion - hydrophobic interaction .this results confirmed that the addition of amino acid to Potassium halides solutions is from Solvent Structure Maker type, which was confirmed by the expansibility molal volume(ϕ_E^*) values of the system.

الخلاصة

تم قياس الكثافة (ρ) للأحماض الامينية (الالانين و الثريونين واللايسين) بمدى من التراكيز (0.1-0.8) مول/ لتر في محلول 0.4 مولاري هاليدات البوتاسيوم (KI ,KBr ,KCl) عند درجات حرارة (298.15,303.15,308.15) كلفن . ومن خلال قياسات الكثافة تم حساب الحجم المولالي الظاهرية (ϕ_v) ومنها حسبت الحجم المولالي الظاهرية المحددة (ϕ_v^*) و الميل العملي (S_v^*) بالإضافة لحساب الحجم المولالي الجزئية ($V_{1,2}$) للأحماض الامينية والحجم المولالي الجزئية المحددة عند التخفيف إلى ما لا نهاية ($\bar{V}_{2,0}$) وقد أكدت اغلب هذه النتائج على قوة التأثيرات بين مذاب - مذيب أو ايون - محبة للماء وضعف التأثيرات من نوع مذاب - مذاب أو ايون - ايون أو ايون - غير محبة للماء مما يدل على ان إضافة الأحماض الامينية (الالانين و الثريونين واللايسين) لمحلول هاليدات البوتاسيوم من النوع المقوي لتركيب المذيب وهذا ماكدت عليه أيضا قيم التمدد المولالي الجزئي (ϕ_E^*) لهذا النظام.

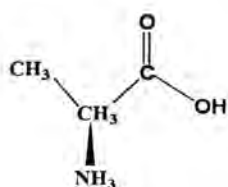
المقدمة

المحاليل الملحية تعمل على تحسين التركيب في البروتينات وخواصها مثل الذوبانية وفعالية الإنزيمات التي تتأثر بصورة كبيرة أيضا [2,1] التداخلات الناتجة بين البروتينات والأملاح تكون صعبة وذلك تبعا لتركيب المعقد للبروتينات [3] التي تعد من أكثر الجزيئات العضوية انتشارا في الأنظمة الحياتية إذ تؤدي أدوارا مهمة في جميع العمليات المتعلقة بوظائف الخلية لذلك سيتم دراسة الأحماض الامينية من نوع ألفا التي تعتبر اللبنة الأولية لبناء جميع البروتينات إذ تمتلك جميع الأحماض الامينية من خلال تركيبها الموضح في الشكل (1) دلائلا مشتركة وهي جذر الكربوكسيل و الأمين في ذرة كاربون ألفا [4]

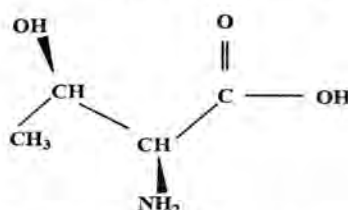


شكل 1: الصيغة التركيبية العامة للأحماض الامينية

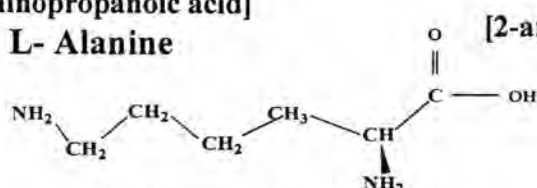
ان الأحماض الامينية قيد الدراسة موضحة [5] في الشكل (2) هي الالنين L-Alanine صيغته الجزيئية (C₃H₇NO₂) وهو حامض أميني ذو سلسلة جانبية لا قطبية او غير محبة للماء والثريونين L-Threonine صيغته الجزيئية (C₄H₉NO₃) وهو حامض أميني ذو سلسلة جانبية قطبية غير مشحونة واللايسين L-Lysine صيغته الجزيئية (C₆H₁₄N₂O₂) وهو حامض أميني ذو سلسلة جانبية موجبة الشحنة (قاعدية) [4].



[2-Aminopropanoic acid]
L- Alanine



[2-amino -3-hydroxy butanoic acid]
L- Threonine



[2,6 Diamino hexanoic acid]
L- Lysine

شكل 2: الصيغ التركيبية للأحماض الامينية قيد الدراسة

وعلى أساس المبدأ الشائع الشبيه يذيب الشبيه (Likes Dissolves Likes) فإذا كانت جزيئات المذاب (الأحماض الامينية) والمذيب (الماء + هاليدات البوتاسيوم) متشابهة بالتركيب والخصائص الكهربائية فسوف تتحقق ذوبانية عالية وذلك بسبب تجانس القوى التداخلية بين الجزيئات (Intermolecular Forces) وهذا ينطبق على محاليل هاليدات البوتاسيوم للأحماض الامينية قيد الدراسة [6].

هنالك دراسات عديدة تناولت الخواص الفيزيائية لمحاليل الأملاح والأحماض الامينية منها حيث قام Dhiman و Pamer [7] بتعيين الحجم المولارية الجزيئية لبعض المحاليل الملحية من خلال قياسات الكثافة عند درجات حرارة مختلفة إذ أكدت النتائج على التداخلات من نوع ايون-ايون و التداخلات من نوع ايون - مذيب ، وفي دراسة أخرى [8] تناولت تعيين كثافة محلول كلوريد المغنيسيوم لبعض الأحماض الامينية عند درجة حرارة 288.15 و 308.15 كلفن ومنها حسبت الحجم المولالية الظاهرية وأكدت النتائج على التداخلات من نوع مذاب- مذاب ثانوي . كما تناولت دراسة أخرى [9] الخواص الفيزيائية للأحماض الامينية في محاليل أملاح بيوتريت الصوديوم عند درجات حرارة 303.15, 308.15, 313.15 كلفن حيث حسبت الحجم المولالية الظاهرية والتمدد المولي إذ أكدت النتائج على ان إضافة الأحماض الامينية من النوع المقوي والمهدم لتركيب المذيب.

المواد وطرائق العمل

يحتوي الجدول (1) على مجموعة المواد الكيميائية المستعملة في البحث ودرجة نقاوتها ووزنها الجزيئي واسم الشركة المجهزة لها

جدول 1: المواد الكيميائية المستعملة في البحث

اسم المادة الكيميائية	الوزن الجزيئي/M.wt[5]	درجة النقاوة %	اسم الشركة المجهزة
Potassium Chloride	74.55	%99	BDH
Potassium Bromide	119.00	%99	BDH
Potassium Iodide	116.00	%99	BDH
L-Alanine	89.01	%99	Fluka
L-Threonine	119.12	%99	Fluka
L-Lysine	146.10	%99	Fluka

والماء المستعمل في عملية تحضير المحاليل غير أيوني له توصيلية كهربائية بحدود $(0.6 \times 10^{-6} \text{ S.Cm}^{-1})$.

دراسة السلوك الحجمي لبعض الأحماض الأمينية في المحاليل المائية لهاليدات البوتاسيوم عند درجات حرارة مختلفة

احمد

تحضير المحاليل

حضرت سلسلة من التراكيز بمدى (0.1 - 0.8) مول. لتر⁻¹ لكل الأحماض الأمينية (الالانين و الثريونين واللايسين) قيد الدراسة اذ تم إذابتها في محاليل 0.4 مولاري من هاليدات البوتاسيوم (KI, KBr, KCl) وذلك باستعمال ميزان حساس نوع (Sartorius) بدقة تصل إلى ± 0.0001 غرام.

قياس الكثافة

تم قياس الكثافة لمحاليل الملحبة للأحماض الأمينية قيد الدراسة عند درجات حرارة (308.15, 303.15, 298.15) كلفن باستعمال جهاز (Digital Densimeter Anton Paar) (Model DMA 60/601) بمنظم حراري تصل دقته إلى ± 0.1 . اذ يمكن الحصول على زمن التذبذب (t) من الجهاز ومن ثم يتم أيجاد ثابت الجهاز (k) وذلك عن طريق قياس قيمة (t) لكل من الماء والهواء على التوالي في درجة الحرارة اللازمة نفسها للقياس (308.15, 303.15, 298.15) كلفن ثم نطبق العلاقة الآتية:

$$k = \frac{\rho_{Water} - \rho_{Air}}{t_{Water} - t_{Air}} \quad \text{-----1}$$

اذ ان ρ_{Air} و ρ_{Water} كثافة الماء والهواء على التوالي t_{Air} و t_{Water} زمن التذبذب للماء والهواء على التوالي ومن خلال قيمة ثابت الجهاز يمكن حساب قيمة كثافة محاليل الأحماض الأمينية قيد الدراسة من خلال المعادلة الآتية :

$$\rho = k * t \quad \text{-----2}$$

ومن الجدير بالذكر انه يجب ترك الأنموذج في خلية القياس مدة عشر دقائق لكي يحصل توازن حراري بين الأنموذج والجهاز .

النتائج والمناقشة

تم في هذه الدراسة القياس العملي للأحماض الأمينية L-Lysine, L-Threonine, Alanine في محاليل 0.4 مولاري من هاليدات البوتاسيوم (KI, KBr, KCl) بثمانية تراكيز ضمن المدى (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8) مول. لتر⁻¹ وعند درجات حرارة (308.15, 303.15, 298.15) كلفن حيث يبين الجدول (2) قيم الكثافة العملية لمحاليل الأحماض الأمينية قيد الدراسة .

جدول 2: قيم الكثافة ρ (gm/cm^3) لمحاليل الأحماض الأمينية L-Lysine, L-Threonine, L-Alanine في محاليل 0.4 مولاري من هاليدات البوتاسيوم (KI, KBr) عند درجات حرارة (308.15, 303.15, 298.15) كلفن (KCl)

ρ (gm/cm^3)									
M- (mol.l ⁻¹)	Alanine+KCl			Threonine+KCl			Lysine+KCl		
	298.15	303.15	308.15	298.15	303.15	308.15	298.15	303.15	308.15
0	1.0162	1.0133	1.0094	1.0162	1.0133	1.0094	1.0162	1.0133	1.0094
0.1	1.0187	1.0159	1.0136	1.0210	1.0179	1.0142	1.0228	1.0196	1.0157
0.2	1.0209	1.0183	1.0162	1.0256	1.0226	1.0187	1.0290	1.0258	1.0219
0.3	1.0232	1.0208	1.0183	1.0304	1.0269	1.0230	1.0352	1.0322	1.0285
0.4	1.0255	1.0232	1.0208	1.0348	1.0311	1.0276	1.0416	1.0385	1.0348
0.5	1.0277	1.0256	1.0233	1.0373	1.0359	1.0321	1.0477	1.0452	1.0410
0.6	1.0303	1.0281	1.0257	1.0420	1.0404	1.0368	1.0539	1.0514	1.0473
0.7	1.0331	1.0305	1.0283	1.0462	1.0447	1.0411	1.0605	1.0576	1.0534
0.8	1.0356	1.0331	1.0309	1.0507	1.0489	1.0459	1.0665	1.0632	1.0599
M (mol.l ⁻¹)	Alanine+KBr			Threonine+ KBr			Lysine+ KBr		
	298.15	303.15	308.15	298.15	303.15	308.15	298.15	303.15	308.15
0	1.0224	1.0184	1.0164	1.0224	1.0184	1.0164	1.0224	1.0184	1.0164
0.1	1.0248	1.0209	1.0190	1.0270	1.0230	1.0212	1.0287	1.0247	1.0227
0.2	1.0273	1.0235	1.0215	1.0312	1.0276	1.0257	1.0349	1.0310	1.0289
0.3	1.0298	1.0260	1.0240	1.0358	1.0319	1.0304	1.0408	1.0372	1.0353
0.4	1.0321	1.0283	1.0265	1.0401	1.0361	1.0346	1.0471	1.0431	1.0416
0.5	1.0346	1.0306	1.0290	1.0443	1.0411	1.0392	1.0534	1.0493	1.0479
0.6	1.0370	1.0331	1.0314	1.0485	1.0457	1.0434	1.0597	1.0555	1.0542
0.7	1.0395	1.0356	1.0340	1.0533	1.0505	1.0476	1.0659	1.0614	1.0604
0.8	1.0421	1.0381	1.0364	1.0580	1.0549	1.0518	1.0723	1.0679	1.0670
M (mol.l ⁻¹)	Alanine+KI			Threonine+ KI			Lysine+ KI		
	298.15	303.15	308.15	298.15	303.15	308.15	298.15	303.15	308.15
0	1.0394	1.0364	1.0321	1.0394	1.0364	1.0321	1.0394	1.0364	1.0321
0.1	1.0420	1.0389	1.0347	1.0436	1.0410	1.0367	1.0457	1.0427	1.0380
0.2	1.0445	1.0414	1.0371	1.0484	1.0456	1.0408	1.0516	1.0489	1.0437
0.3	1.0470	1.0438	1.0396	1.0529	1.0498	1.0450	1.0582	1.0558	1.0500
0.4	1.0496	1.0463	1.0419	1.0575	1.0540	1.0494	1.0641	1.0613	1.0562
0.5	1.0521	1.0488	1.0445	1.0623	1.0588	1.0537	1.0703	1.0673	1.0624
0.6	1.0545	1.0513	1.0470	1.0664	1.0630	1.0579	1.0763	1.0727	1.0678
0.7	1.0570	1.0538	1.0496	1.0710	1.0672	1.0623	1.0809	1.0789	1.0737
0.8	1.0594	1.0563	1.0518	1.0758	1.0718	1.0664	1.0902	1.0852	1.0800

نلاحظ من الجدول (2) ان كثافة الأحماض الأمينية في محاليل هاليدات البوتاسيوم تزداد مع زيادة

التركيز المولارية للأحماض الأمينية قيد الدراسة وحسب التسلسل التالي :

L-Lysine > L-Threonine > L-Alanine

دراسة السلوك الحجمي لبعض الأحماض الأمينية في المحاليل المائية لهاليدات البوتاسيوم عند درجات حرارة مختلفة

أحمد

ولكنها تقل مع زيادة درجة الحرارة ويعزى ذلك إلى تكسر الأواصر الهيدروجينية بين جزيئات الماء نفسها في التركيب الجمعي للماء (Structure Bulk Water) وتكوين الماء في الحالة المكثفة [10](Dense).

ومن قياسات الكثافة تم حساب الحجم المولي الظاهري ϕ_v لمحاليل للأحماض الأمينية قيد الدراسة في محاليل 0.4 مولاري من هاليدات البوتاسيوم (KI ,KBr ,KCl) عند درجات حرارة مختلفة من خلال العلاقة الآتية [11]

$$\phi_v = \frac{1}{m} \left(\frac{1000 + mM_2}{\rho} - \frac{1000}{\rho_0} \right) \quad \text{-----} 3$$

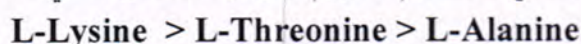
m مولالية المحلول (مول/كغم) ، M الوزن الجزيئي للأحماض الأمينية ρ كثافة محلول الحامض الأميني ، ρ_0 كثافة المذيب (محلول هاليدات البوتاسيوم) ودونت قيم الحجوم المولية الظاهرية لمحاليل الأحماض الأمينية مع هاليدات البوتاسيوم عند الدرجات الحرارة (298.15-303.15-308.15) كلفن في الجدول (3)

جدول 3 : قيم الحجوم المولية الظاهرية ϕ_v لمحاليل الأحماض الأمينية L-Lysine ,L- Threonine, L-Alanine في محاليل 0.4 مولاري من هاليدات البوتاسيوم (KI ,KBr ,KCl) عند درجات حرارة (308.15,303.15,298.15) كلفن

$(cm^3/mol) \phi_v$									
M (mol.l ⁻¹)	Alanine+KCl			Threonine+KCl			Lysine+KCl		
	298.15	303.15	308.15	298.15	303.15	308.15	298.15	303.15	308.15
0.1	248.53	219.87	181.76	277.64	277.97	211.08	303.75	275.29	237.45
0.2	167.27	153.15	134.31	196.05	196.62	163.40	221.81	207.91	189.42
0.3	140.06	130.77	118.37	168.50	169.18	147.18	193.92	184.86	172.80
0.4	126.35	119.48	110.29	154.48	155.22	138.81	179.56	172.93	164.07
0.5	118.06	112.62	105.35	146.03	146.62	133.58	170.63	165.38	158.51
0.6	112.44	107.98	102.00	140.12	140.73	129.93	164.39	160.12	154.53
0.7	108.36	104.61	99.53	135.80	136.40	127.20	159.68	156.14	151.47
0.8	105.26	102.02	97.63	132.42	133.06	124.99	156.01	153.02	148.94
M (mol.l ⁻¹)	Alanine+KBr			Threonine+ KBr			Lysine+ KBr		
	298.15	303.15	308.15	298.15	303.15	308.15	298.15	303.15	308.15
0.1	309.80	270.60	250.71	338.68	299.61	279.98	364.58	325.65	305.89
0.2	197.46	178.14	168.34	226.01	206.84	197.20	251.57	232.53	222.87
0.3	159.87	147.18	140.74	188.13	175.59	169.26	232.61	200.93	194.63
0.4	140.97	131.60	126.84	168.96	159.73	155.07	193.83	184.74	180.08
0.5	129.56	122.18	118.41	157.27	149.98	146.34	181.79	174.69	171.02
0.6	121.88	115.82	112.73	149.33	143.33	140.38	173.49	167.72	164.71
0.7	116.33	111.22	108.60	143.49	138.43	136.00	167.35	162.55	159.98

0.8	112.12	107.72	105.47	138.99	134.65	132.60	162.53	158.42	156.21
M	Alanine+ KI			Threonine+ KI			Lysine+ KI		
(mol.l ⁻¹)	298.15	303.15	308.15	298.15	303.15	308.15	298.15	303.15	308.15
0.1	477.29	447.99	405.23	505.40	476.05	433.72	530.83	501.46	459.22
0.2	279.99	265.54	244.46	307.90	293.45	272.65	332.88	318.53	297.87
0.3	214.07	204.58	190.74	241.72	232.25	218.65	266.38	256.99	243.57
0.4	181.02	174.01	163.78	208.39	201.42	191.42	232.73	225.84	216.01
0.5	161.11	155.58	147.52	188.19	182.73	174.91	212.22	206.85	197.71
0.6	147.76	143.23	136.61	174.59	170.13	163.75	198.31	193.97	186.18
0.7	138.18	134.36	128.76	164.73	161.00	155.64	188.26	184.52	179.32
0.8	130.94	127.65	122.84	157.21	154.03	149.47	180.23	177.24	172.81

نلاحظ من الجدول (3) ان قيم ϕ_v للأحماض الامينية L- Lysine, L-Threonine, Alanine في محاليل 0.4 مولاري من هاليدات البوتاسيوم (KI, KBr, KCl) تأخذ مسارين الأول تقل مع زيادة التركيز المولاري لجميع الأحماض الامينية قيد الدراسة وذلك لكون الطاقة الناتجة من عملية إذابة الأحماض الامينية في محاليل هاليدات البوتاسيوم غير كافية لإدخال جزيئات الحامض الاميني مع المذيب (الماء + هاليدات البوتاسيوم) على الرغم من زيادة درجة الحرارة [12] اما المسار الثاني فتأخذ قيم الحجوم المولالية التسلسل التالي:



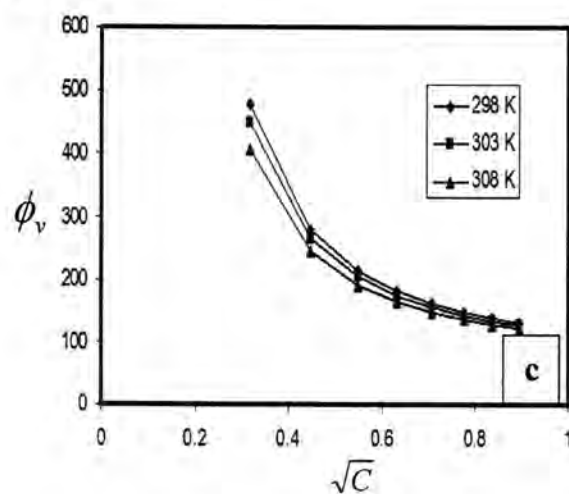
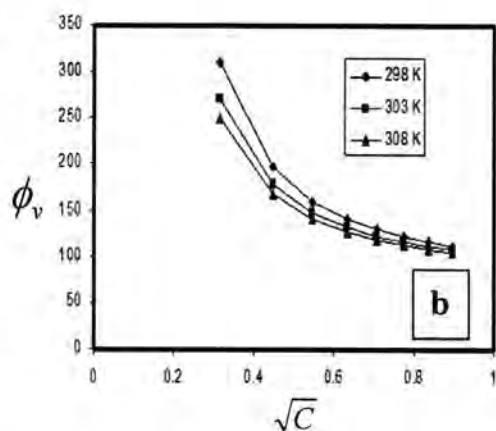
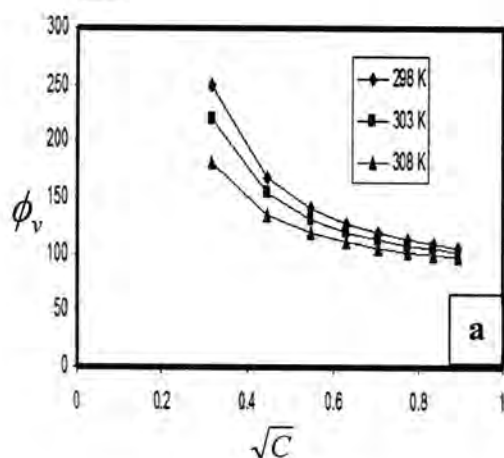
حسب الحامض الاميني وما يحتويه من مجاميع فعالة وحسب نوع هاليد البوتاسيوم (KI, KBr, KCl) ومقدار كهر وسليبيته. يمكن الرسم ما بين الحجوم المولالية الظاهرية والجذر التربيعي للتركيز المولاري (كما في الأشكال 1 و 2 و 3) وذلك من خلال العلاقة الآتية [13]

$$\phi_v = \phi_v^* + S_v^* \sqrt{C} \quad \text{-----} \quad 3$$

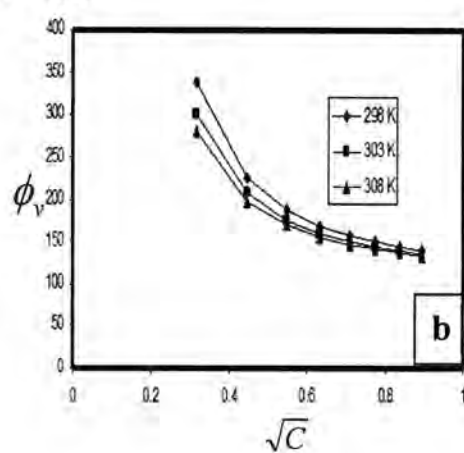
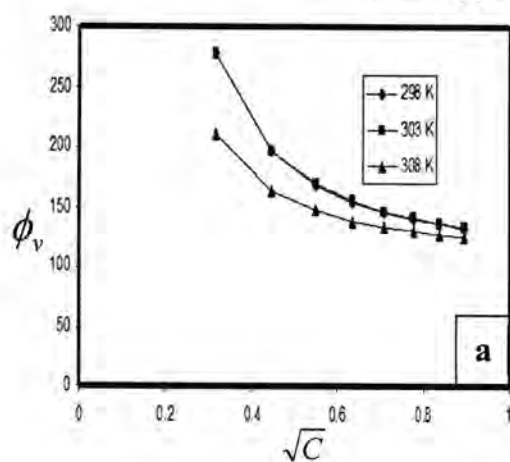
حيث أن ϕ_v^* = الحجم المولالي الظاهري المحدد وهو مقياس للتأثيرات من نوع مذاب - مذيب S_v^* = الميل العملي الذي يعتمد على الشحنة ونوع الملح وطبيعة المذيب وهو مقياس للتأثيرات من نوع ايون - ايون. وبالا اعتماد على معادلة Masson تم رسم ϕ_v مقابل \sqrt{C} كما في الإشكال (3 و 4 و 5) و بطريقة المربعات الصغرى (Least Squares Method) تم حساب ϕ_v^* و S_v^* حيث دونت في الجدول (4)

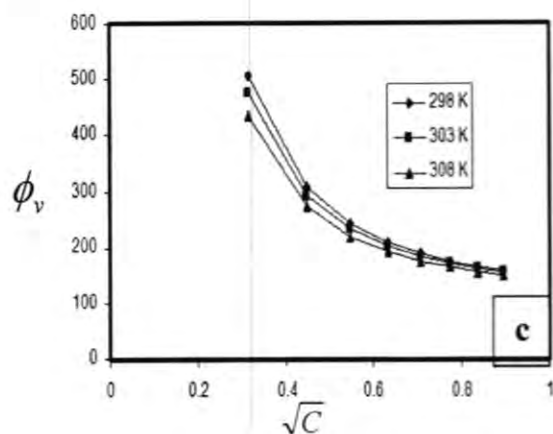
دراسة السلوك الحجمي لبعض الأحماض الأمينية في المحاليل المائية لهاليدات البوتاسيوم عند درجات حرارة مختلفة

أحمد

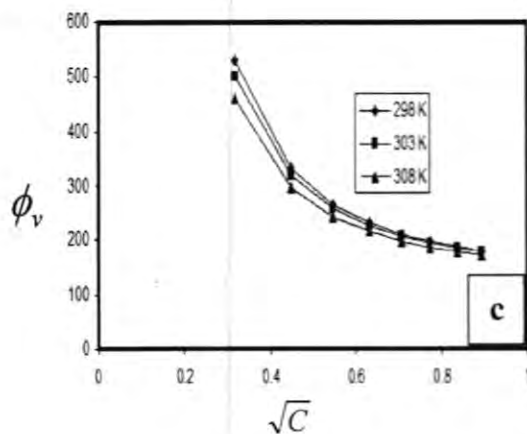
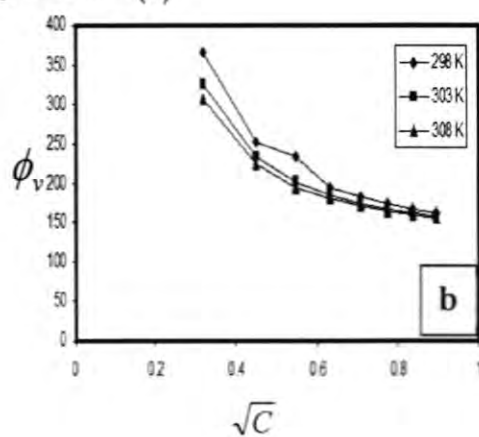
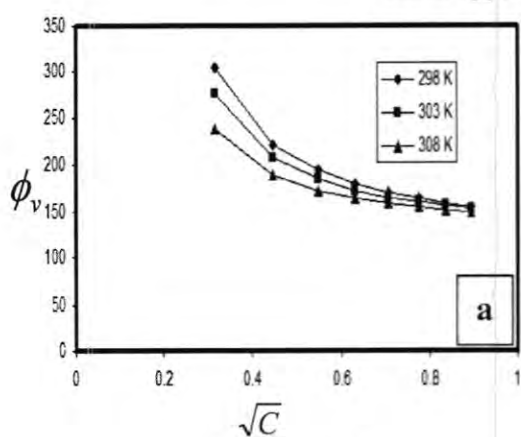


شكل 3: العلاقة بين \sqrt{C} و ϕ_v لحامض الانين في محاليل KCl (a) و KBr (b) و KI (c) عند درجات حرارة مختلفة





شكل 4: العلاقة بين \sqrt{C} و ϕ_v لحامض الثيونين في محاليل KCl (a) و KBr (b) و KI (c) عند درجات حرارة مختلفة



شكل 5: العلاقة بين \sqrt{C} و ϕ_v لحامض اللايسين في محاليل KCl (a) و KBr (b) و KI (c) عند درجات حرارة مختلفة

دراسة السلوك الحجمي لبعض الأحماض الامينية في المحاليل المائية لهاليدات البوتاسيوم عند درجات حرارة مختلفة

احمد

جدول 4: يبين قيم ϕ_v^* و S_v^* لمحاليل الأحماض الامينية L-Lysine, L-Threonine, L-Alanine في محاليل 0.4 مولاري من هاليدات البوتاسيوم (KI, KBr, KCl) عند درجات حرارة (308.15, 303.15, 298.15) كلفن

Temperature /K	Alanine+KCl		Threonine+KCl		Lysine+KCl	
	S_v^* ($cm^{3/2}/mol^{3/2}$)	ϕ_v^* ($cm^{3/2}/mol^{3/2}$)	S_v^* ($cm^{3/2}/mol^{3/2}$)	ϕ_v^* ($cm^{3/2}/mol^{3/2}$)	S_v^* ($cm^{3/2}/mol^{3/2}$)	ϕ_v^* ($cm^{3/2}/mol^{3/2}$)
298.15	-219.14	282.03	-222.46	314.26	-226.97	340.00
303.15	-180.32	247.53	-222.14	312.65	-188.14	305.71
308.15	-128.80	201.67	-132.26	232.27	-138.50	260.12
Temperature /K	Alanine+KBr		Threonine+ KBr		Lysine+ KBr	
	S_v^* ($cm^{3/2}/mol^{3/2}$)	ϕ_v^* ($cm^{3/2}/mol^{3/2}$)	S_v^* ($cm^{3/2}/mol^{3/2}$)	ϕ_v^* ($cm^{3/2}/mol^{3/2}$)	S_v^* ($cm^{3/2}/mol^{3/2}$)	ϕ_v^* ($cm^{3/2}/mol^{3/2}$)
298.15	-302.27	355.81	-305.72	385.90	-316.62	420.03
303.15	-249.11	308.61	-252.75	338.92	-256.66	366.33
308.15	-227.17	284.67	-225.88	315.19	-229.92	342.61
Temperature /K	Alanine+ KI		Threonine+ KI		Lysine+ KI	
	S_v^* ($cm^{3/2}/mol^{3/2}$)	ϕ_v^* ($cm^{3/2}/mol^{3/2}$)	S_v^* ($cm^{3/2}/mol^{3/2}$)	ϕ_v^* ($cm^{3/2}/mol^{3/2}$)	S_v^* ($cm^{3/2}/mol^{3/2}$)	ϕ_v^* ($cm^{3/2}/mol^{3/2}$)
298.15	-529.36	557.47	-532.61	613.57	-536.58	613.57
303.15	-489.62	522.19	-492.60	578.13	-496.43	578.13
308.15	-431.66	470.70	-434.88	527.49	-439.72	527.49

نلاحظ من الجدول (4) ان قيم S_v^* سالبة لكل الأحماض الامينية الثلاثة قيد الدراسة في محاليل 0.4 مولاري من هاليدات البوتاسيوم (KI, KBr, KCl) عند درجات حرارة (308.15, 303.15, 298.15) كلفن وذلك لكون المذيب المستعمل هو الماء الذي له ثابت عزل عالي [14] (78) حيث تكون الأملاح الذائبة فيه متأينة بشكل تام وهذا يؤدي إلى نشوء ما يسمى بنفوذية عالية للأيونات نفسها بعضها مع بعض وهذا يؤدي إلى تقليل التأثيرات من نوع أيون- أيون الذي بدوره يجعل كل قيم S_v^* سالبة هذا من جهة ومن جهة ثانية نلاحظ ان قيم ϕ_v^* موجبة وعالية وتأخذ التسلسل التالي



وذلك لان تعويض H بمجموعة مثيل في حامض Alanine تنتج تأثيرات متبادلة من نوع مجموعة محبة للماء - مجموعة صادة للماء وتأثيرات من نوع مجموعة صادة للماء - مجموعة صادة للماء

ولهذا يزداد الانقباض الكهربائي لجزيئات الماء وبالتالي نقصان قيم ϕ_v^* لحمض Alanine بينما تعويض H بمجموعة قطبية OH ومجموعة مثيل في حامض Threonine تنتج تأثيرات من نوع مجموعة محبة للماء - مجموعة محبة للماء وتأثيرات من نوع مجموعة محبة للماء - مجموعة صادة للماء لكن تأثيرات مجموعة محبة للماء - مجموعة محبة للماء هي السائدة في Threonine لذلك ستعمل على تقليل الانقباض الكهربائي وبالتالي زيادة قيم ϕ_v^* لحمض Threonine بينما نلاحظ من خلال تعويض H بمجموعة الأمين NH_2 في Lysine فان التأثيرات الموجودة هي تأثيرات مجموعة محبة للماء - مجموعة محبة للماء التي تعمل على نقصان الانقباض الكهربائي بين جزيئات الماء المحيطة أكثر من بقية الأحماض الامينية قيد الدراسة وهذا يؤدي إلى جعل قيم ϕ_v^* لحمض Lysine هي الأعلى [12] لذلك تعد هذه التأثيرات من نوع مقوي لتركيب المذيب Solvent Maker ومن جهة ثانية نلاحظ ان قيم ϕ_v^* تقل وازدياد قيم S_v^* بشكل بسيط لجميع الأحماض الامينية قيد الدراسة في محاليل 0.4 مولاري لهاليدات البوتاسيوم (KI, KBr, KCl) بزيادة درجة الحرارة التي تعمل على إبعاد الجزيئات (الأحماض الامينية + محاليل هاليدات البوتاسيوم) من خلال التغلب على القوى الناشئة بين الجزيئات المتداخلة مما يؤدي إلى نقصان التأثيرات من نوع مذاب - مذيب (نقصان ϕ_v^*) وازدياد التأثيرات من نوع مذاب - مذاب أو ايون - ايون (زيادة S_v^*) أذن في هذه الحالة تعمل ارتفاع درجة الحرارة على جعل هذه التأثيرات من النوع المهدم لتركيب المذيب Solvent Breaker [15].

ومن جهة ثالثة نلاحظ التداخلات بين الأحماض الأمينية الثلاثة قيد الدراسة كل على حدة مع هاليدات البوتاسيوم (KI, KBr, KCl) عند درجات حرارة (308.15, 303.15, 298.15) كلفن من نوع ايون . ثنائي القطب التي تكون على أوجها مع اليود ثم الكلور وذلك حسب الوزن الجزيئي للهاليدات [16].

وأيضاً من قياسات الكثافة تم حساب الحجوم المولالية الجزئية $V_{1.2}$ للأحماض الامينية [17].

$$V_{1.2} = \frac{1000 + m M_2}{\rho} \quad \text{-----} \quad 4$$

m مولالية المذاب , M_2 الوزن الجزيئي للمذاب , ρ كثافة المحلول (الأحماض الامينية + محلول 0.4 مولاري هاليدات البوتاسيوم) حيث دونت قيم $V_{1.2}$ في الجدول (5)

الجدول 5: يبين قيم الحجوم المولالية الجزئية ($V_{1.2}$) للأحماض الامينية L-Alanine, L-Lysine

Threonine, L-Alanine في محاليل 0.4 مولاري من هاليدات البوتاسيوم (KI

KBr, KCl) عند درجات حرارة (308.15, 303.15, 298.15) كلفن

$V_{1.2}(\text{cm}^3)$			
M	Alanine+KCl	Threonine+KCl	Lysine+KCl

دراسة السلوك الحجمي لبعض الأحماض الأمينية في المحاليل المائية لهاليدات البوتاسيوم عند درجات حرارة مختلفة

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(mol.l ⁻¹)	298.15	303.15	308.15	298.15	303.15	308.15	298.15	303.15	308.15
0.1	990.34	993.11	995.30	990.95	994.04	997.74	991.93	995.09	998.94
0.2	996.93	999.56	1001.65	998.22	1001.07	1005.11	1000.24	1003.45	1007.37
0.3	1003.51	1005.93	1008.49	1005.40	1008.65	1012.90	1008.70	1011.75	1015.60
0.4	1010.24	1012.57	1015.08	1013.00	1016.26	1020.50	1017.22	1020.41	1024.22
0.5	1017.15	1019.33	1021.69	1022.78	1023.39	1028.21	1026.07	1028.68	1033.11
0.6	1023.71	1026.06	1028.55	1030.37	1030.76	1035.97	1034.95	1037.64	1042.14
0.7	1030.14	1032.88	1035.29	1038.65	1038.43	1044.15	1043.68	1046.86	1051.42
0.8	1037.02	1039.68	1042.12	1046.64	1046.27	1051.97	1053.16	1056.81	1060.56
M	Alanine+KBr			Threonine+ KBr			Lysine+ KBr		
(mol.l ⁻¹)	298.15	303.15	308.15	298.15	303.15	308.15	298.15	303.15	308.15
0.1	984.35	988.12	990.03	985.14	989.00	990.85	986.13	990.03	992.00
0.2	990.59	994.37	996.38	992.64	996.22	998.12	994.34	998.22	1000.31
0.3	996.95	1000.78	1002.79	999.94	1003.87	1005.34	994.21	1006.73	1008.68
0.4	1003.53	1007.41	1009.23	1007.64	1011.64	1013.25	1011.54	1015.65	1017.20
0.5	1010.08	1014.18	1015.76	1015.47	1018.78	1020.83	1020.09	1024.38	1025.86
0.6	1016.72	1020.77	1022.51	1023.50	1026.43	1028.87	1028.84	1033.25	1034.67
0.7	1023.42	1027.50	1029.22	1031.06	1034.05	1037.13	1037.81	1042.65	1043.76
0.8	1030.06	1034.35	1036.18	1038.77	1042.10	1045.46	1046.74	1051.55	1052.63
M	Alanine+ KI			Threonine+ KI			Lysine+ KI		
(mol.l ⁻¹)	298.15	303.15	308.15	298.15	303.15	308.15	298.15	303.15	308.15
0.1	968.01	970.86	974.91	969.31	971.72	975.85	969.87	972.71	977.12
0.2	973.97	976.97	981.06	976.03	978.72	983.30	978.12	980.70	985.72
0.3	980.12	983.26	987.28	983.09	986.10	990.83	985.91	988.17	993.92
0.4	986.25	989.46	993.74	990.22	993.68	998.22	994.42	997.15	1002.27
0.5	992.55	995.80	1000.04	997.32	1000.73	1005.94	1002.77	1005.88	1010.79
0.6	998.94	1002.16	1006.51	1005.10	1008.54	1013.80	1011.55	1015.28	1020.29
0.7	1005.36	1008.68	1012.93	1012.55	1016.42	1021.58	1021.87	1023.98	1029.45
0.8	1011.98	1015.16	1019.83	1019.88	1024.08	1029.73	1027.51	1032.75	1038.41

نلاحظ من الجدول (5) ان قيم $V_{1,2}$ للأحماض الأمينية L-Alanine, L-Threonine, L-Lysine في محاليل 0.4 مولاري من هاليدات البوتاسيوم (KI, KBr, KCl) عند درجات حرارة (308.15, 303.15, 298.15) كلفن تزداد مع زيادة التركيز المولاري للحامض الأميني و زيادة درجة الحرارة وهذا يتفق مع دراسات أخرى (18) حيث تعمل الأحماض الأمينية قيد الدراسة على تكوين تراكيب متاصرة للفجوات في تركيب (الماء + هاليد البوتاسيوم) هذا من جهة ومن جهة أخرى من المعروف أن الحجم المولاري الجزئي للجليد اكبر من الحجم المولاري الجزئي للماء لذلك من المتوقع حصول زيادة في الحجم المولالية الجزئية الناتجة من اضافة الأحماض الأمينية للمحاليل المائية لهاليدات البوتاسيوم وهذا ما تؤكدده قيم $V_{1,2}$ الموجودة في الجدول (5) وهذا يؤكد على ان اضافة الحامض الأميني لتركيب الماء من النوع المقوي له [11].

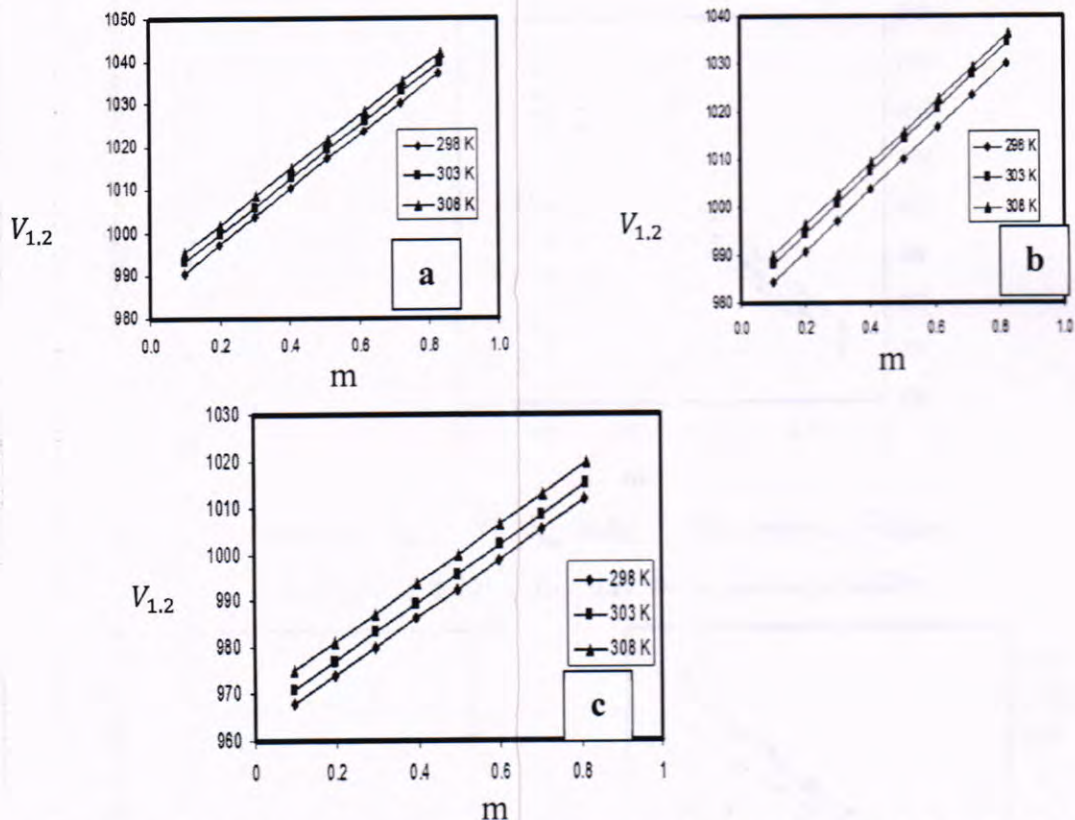
يعتمد الحجم المولالي الجزئي $V_{1,2}$ على التركيز المولالي من خلال المعادلة الآتية [19]

$$V_{1,2} = V_s^e + \overline{V}_{2,0}m + V_{2,2}m^2 + V_{2,2,2}m^3 \text{-----5}$$

ρ_s , $V_s^\circ = 1000 / \rho_s$ حيث $V_{1,2} = V_s^\circ + \bar{V}_{2,0}m$ ان الحجم المولي للمذيب والذي يساوي كثافة المذيب النقي، $\bar{V}_{2,0}$ الحجم المولي الجزئي المحدد عند التخفيف إلى ما لانهاية، $V_{2,2}$ و $V_{2,2,2}$ معاملات في حالة حدوث تجمعات (Aggregates) ثنائية الجزيئة أو ثلاثية الجزيئة لذا من الممكن إهمالها لان مساهمتها في التغير بالحجم المولي قليل وعليه تتحول المعادلة (5) إلى العلاقة البسيطة الآتية :

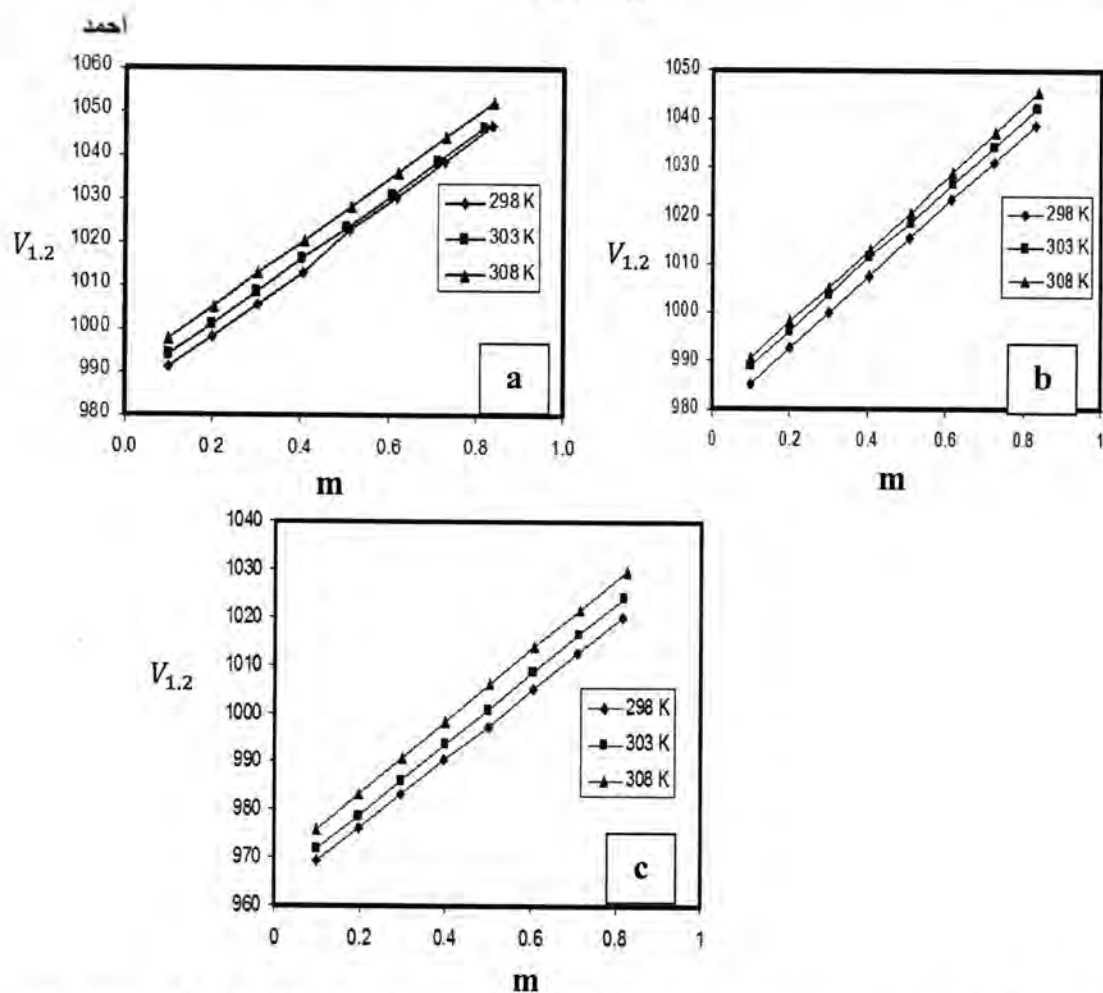
$$V_{1,2} = V_s^\circ + \bar{V}_{2,0}m \quad \text{-----6}$$

من خلال العلاقة (6) عند الرسم بين التركيز المولي و $V_{1,2}$ نحصل على قيم $\bar{V}_{2,0}$ الحجم المولي المحدد للأحماض الامينية من ميل الخطوط المستقيمة في الأشكال (6 و 7 و 8) ودونت في الجدول (6)

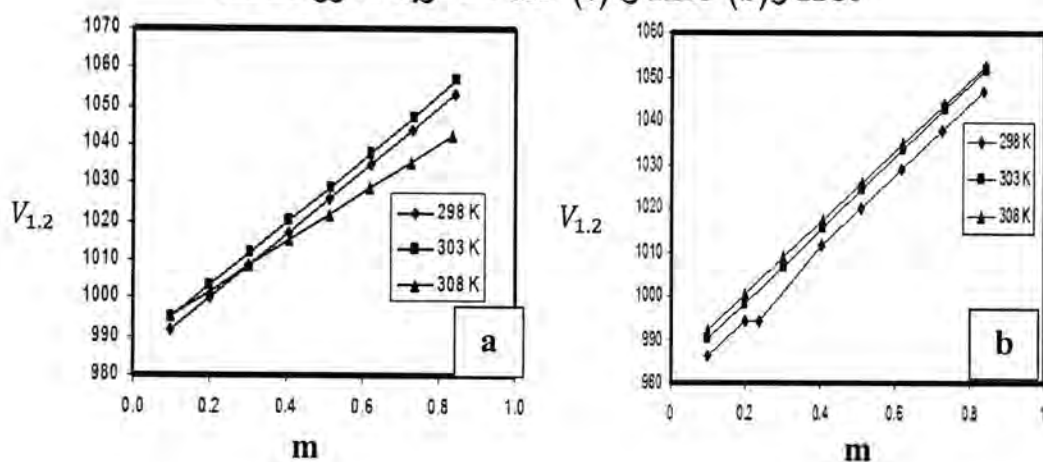


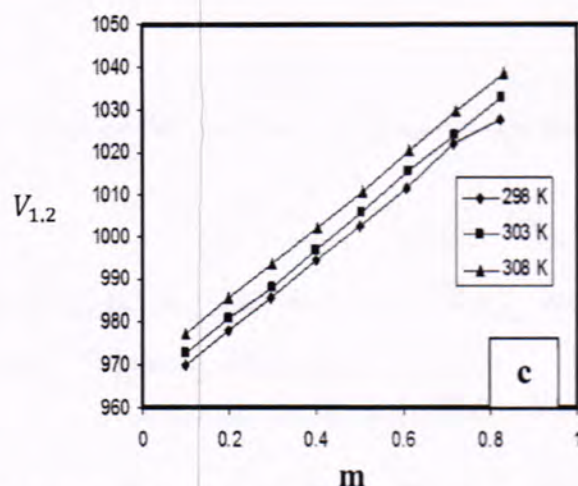
شكل 6: اعتماد الحجم المولي ($V_{1,2}$) على التركيز المولي لحامض الالنين في محاليل (a) KCl و (b) KBr و (c) KI عند درجات حرارة مختلفة

دراسة السلوك الحجمي لبعض الأحماض الامينية في المحاليل المائية لهاليدات البوتاسيوم عند درجات حرارة مختلفة



شكل 7: اعتماد الحجم المولي ($V_{1.2}$) على التركيز المولي لحامض الثريونين في محاليل KCl (a) و KBr (b) و KI (c) عند درجات حرارة مختلفة





شكل 8: اعتماد الحجم المولالي ($V_{1.2}$) على التركيز المولالي لحامض الاليسين في محاليل (a) KCl و (b) KBr و (c) KI عند درجات حرارة مختلفة

جدول 6: قيم الحجم المولالية المحددة $\bar{V}_{2.0}$ للأحماض الامينية L-Lysine, L-Threonine, L-Alanine في محاليل 0.4 مولاري من هاليدات البوتاسيوم (KI, KBr, KCl) عند درجات حرارة (308.15, 303.15, 298.15) كلفن

Amino Acid	$\bar{V}_{2.0}$ (cm ³ /mol ⁻¹)		
	KCl		
	298.15	303.15	308.15
L-Alanine	63.59	63.69	63.86
L-Threonine	71.37	72.54	73.22
L-Lysine	82.24	82.33	82.41
	KBr		
	298.15	303.15	308.15
L-Alanine	63.17	63.59	64.14
L-Threonine	72.30	73.49	74.12
L-Lysine	81.70	83.20	83.7
	KI		
	298.15	303.15	308.15
L-Alanine	61.68	61.96	62.40
L-Threonine	70.67	72.64	74.06
L-Lysine	81.22	83.08	83.61

نلاحظ من الجدول (6) أن الحجم المولالية الجزئية المحددة للأحماض الامينية L-Lysine, L-Alanine, L-Threonine تزداد بشكل قليل مع زيادة درجة الحرارة ومن جهة ثانية تزداد حسب هاليد البوتاسيوم وفق التسلسل التالي

$$KI < KBr < KCl$$

حيث تكون على أعلاها في الكلوريد مقارنة مع البروميد واليوديد وذلك لكون كهروسلبية الكلوريد تكون هي الأعلى وبالتالي تعمل على زيادة ميل كلوريد البوتاسيوم على تكوين تأثيرات من نوع ايون - زويتر ايون لجميع الأحماض الامينية قيد الدراسة وهذا يتفق مع ما سبق [20]

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أحمد

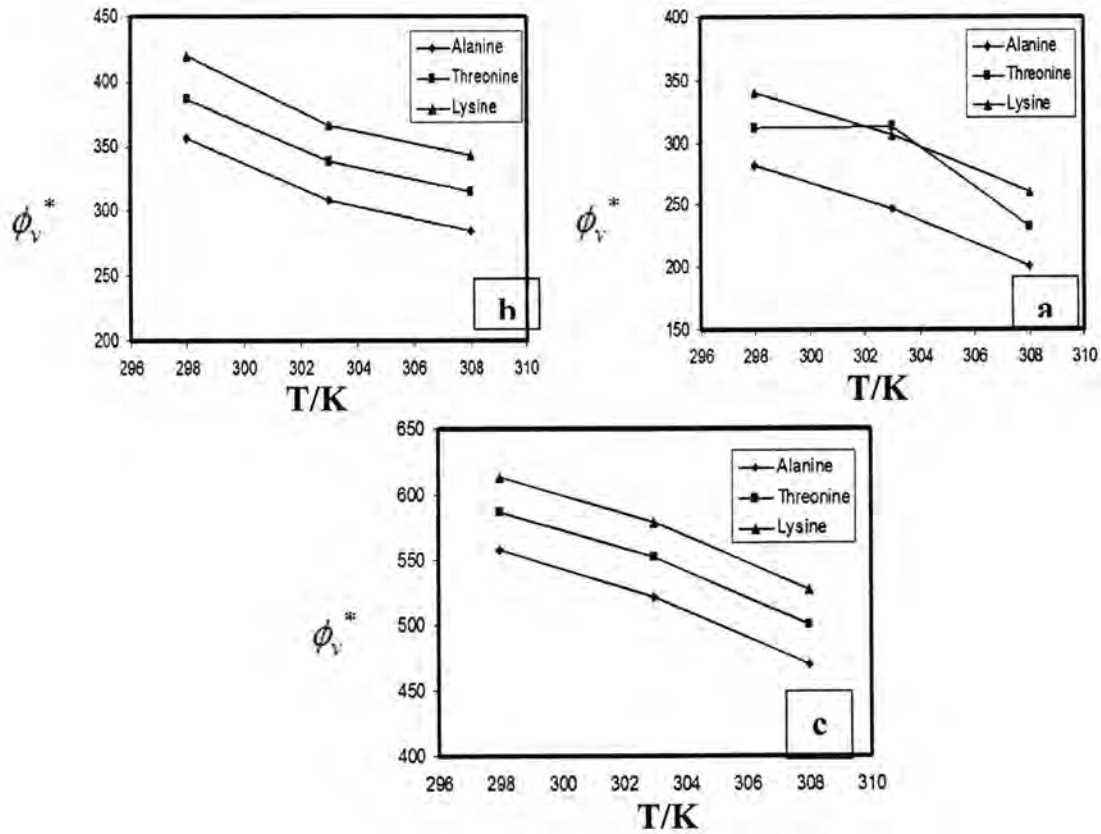
ان التغير في الحجم المولالي الظاهرية المحددة مع درجة الحرارة يمكن التعبير عنه من خلال العلاقة الآتية [21]

$$\phi_v^{\circ} = a + bT + cT^2 \quad \text{-----7}$$

حيث T درجة الحرارة بالكلفن كما يمكن أيجاد التمدد المولالي الجزئي عند التخفيف، إلى ما لا نهاية من خلال اشتقاق العلاقة (7) لتصبح بالشكل التالي

$$\phi_E^{\circ} = \left(\frac{\partial \phi_v^{\circ}}{\partial T} \right)_P = b + 2cT \quad \text{-----8}$$

حيث ϕ_E° هو التمدد المولالي الجزئي الذي تم الحصول عليه من الإشكال (9) و دونت قيمه في الجدول (7)



شكل 9: الحجم المولالي الظاهري المحدد كدالة لدرجة حرارة الأحماض الأمينية L-Alanine, L-Threonine, L-Lysine في محاليل KCl (a) و KBr (b) و KI (c)

جدول 7 : قيم التمدد المولالي الجزئي ϕ_E° للأحماض الامينية L-Lysine ,L-Threonine , في محاليل 0.4 مولاري من هاليدات البوتاسيوم (KI ,KBr ,KCl) عند درجات حرارة مختلفة

ϕ_E° (L.mol ⁻¹ .K ⁻¹)			
Amino Acid	KCl	KBr	KI
L-Alanine	-7.988	-7.742	-8.608
L-Threonine	-7.999	-7.171	-8.647
L-Lysine	-8.036	-7.114	-8.677

نلاحظ من الجدول (7) ان جميع قيم ϕ_E° للأحماض الامينية L-Lysine ,L-Threonine , Alanine في محاليل 0.4 مولاري من هاليدات البوتاسيوم (KI ,KBr ,KCl) عند درجات حرارة (308.15,303.15,298.15) كلفن سالبة يتفق مع دراسة سابقة [22] وهذا يؤكد على ان اضافة الأحماض الامينية إلى تركيب المذيب (الماء + هاليد البوتاسيوم) من النوع المقوي لتركيب المذيب ϕ_v^* عند درجة حرارة معينة لكن هذا التأثير يقل مع زيادة درجة الحرارة وهذا يتفق مع أكدت عليه كل من (21) و(22)، وعموما يمكن أجمال التأثيرات في مخاليط ثلاثية المكون (الحامض الاميني L-Lysine ,L-Threonine , L-Alanine في محاليل هاليدات البوتاسيوم (KI ,KBr ,KCl) بما يأتي :

- 1- تأثيرات ايون - ايون او مذاب - مذاب بين هاليدات البوتاسيوم (KI ,KBr ,KCl) مع النهاية المشحونة للحامض الاميني (COO^- و NH_2^+)
- 2- تأثيرات ايون - مجموعة غير محبة للماء بين هاليدات البوتاسيوم و مجموعة الميثيل (CH_3) في الالنين Alanine
- 3- تأثيرات ايون - مجموعة غير مشحونة محبة للماء بين هاليدات البوتاسيوم ومجموعة الهيدروكسيل (OH) في الثريونين Threonine
- 4- تأثيرات ايون - مجموعة مشحونة محبة للماء بين هاليدات البوتاسيوم و مجموع الأمين (NH_2) في اللايسين Lysine
- 5- تأثيرات مذاب - مذيب بين جزيئات الماء مع النهاية المشحونة للحامض الاميني (COO^- و NH_2^+).

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تحضير ودراسة تأثير الليزر على معقدات Cu^{2+} الجديدة الحاوية على مزيج من الليكندات والفعالية البيولوجية لها

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ABSTRACT

This research includes the preparation and characterization of new copper(II) with mixed ligands including dipeptide glycylalanine and semicarbazone ligands (benzoinsemicarbazone_B'SCH₂ or acetylacetonesemicarbazone_ASCH₂) using classical and microwave methods. The resulted complexes have been characterized physico-chemically. The study suggests that the above ligands form positive ionic complexes having general formula $[\text{Cu}(\text{GAH})(\text{SCH}_2)]\text{X}_2$ or $[\text{Cu}(\text{GAH})(\text{SCH}_2)\text{X}]\text{X}$ in neutral (or slightly acidic) medium, ($\text{X}=\text{CH}_3\text{CO}_2^-$ or NO_3^-). Hexacoordinated mononuclear complexes have been investigated by this study and having octahedral geometries.

Solid complexes have been irradiated by laser ray type Helium-Neon, no effect have been observed on the complexes, this means that all the complexes are stable and are not affected by this kind of radiation. The activity of all the complexes have been evaluated by agar plate diffusion techniques against five human pathogenic bacterial strains: *Staphylococcus aureus*, *Escherichia Coli*, *Pseudomonas auruginosa*, *Streptococcus Faecalis* and *Proteus mirabilis*. The complexes $[\text{Cu}(\text{B'SCH}_2)(\text{GAH})\text{Ac}]\text{Ac}$ (4) was found to have anti-bacterial activity against only *Streptococcus Faecalis* in vitro. All the complexes have been screened for antifungal activity in vitro against *Penicillium*, *Aspergillus niger*, *alternaria*, and *Rhizoctonia*. No effect have been observed. The activity of complex (4) has been evaluated on trace of periapical lesion from men and women showing significant activity against this pathogens. Two perfumers materials have been also screened for antibacterial activity, they show good activity against all the bacteria used in this study. They also screened to cure the periapical lesion they show good activity.

الخلاصة

يتضمن البحث تحضير وتشخيص معقدات جديدة للنحاس (II) مع مزيج من الليكندات التي تشمل ثنائي الببتيد كلايسيل ألانين (GAH) وليكندي السميكاربازون (بنزوين سميكاربازون B'SCH₂ أو أسيتايل أسيتون سميكاربازون ASCH₂) باستخدام الطريقة التقليدية والميكروويف.

تحضير ودراسة تأثير الليزر على مُعَقَّدَات Cu^{2+} الجديدة الحاوية على مزيج من الليكندات والفعالية البيولوجية لها
زهرة وزنا

شُخِّصَت المُعَقَّدَات الناتجة باستخدام تقنيات فيزيائية-كيميائية. أُسْتُخِجَ من هذه الدراسة أن الليكندات تُعْطِي مُعَقَّدَات أيونِيَّة (موصَّلة كهربائِيًّا) ذات صيغ $[Cu(GAH)(SCH_2)]X_2$ أو $[Cu(GAH)(SCH_2)X]X$ ($CH_3CO_2^-$ أو NO_3^-). وأُثْبِتَت الدراسة أَنَّ المُعَقَّدَات تكون سُدَاسِيَّة التَنَاسُق ذات أَشْكَال ثُمَانِيَّة السطوح أَحَادِيَّة النَوَاة.

شُعِّتَت المُعَقَّدَات الصلبة باستخدام أشعة الليزر نوع هيليوم - نيون ولم يُلاحظ أي تأثير عليها ممَّا يدل على أَنَّ المُعَقَّدَات مُسْتَقَرَّة. كذلك دُرِسَت الفعالية البيولوجية للمُعَقَّدَات على عدد من البكتريا المرضية المتضمنة *Staphylococcus aureus* و *Escherichia coli* و *Pseudomonas auruginosa* و *Streptococcus faecalis* و *Proteus mirabilis* باستخدام تقنيَّة الإِنْتِشَار على سطح الآكار بوصفها مضادات للبكتريا، لوحظ أَنَّ المُعَقَّد (4) $[Cu(B'SCH_2)(GAH)(Ac)](Ac)$ يمتلك فعالية بوصفه مضادًا لبكتريا *faecalis* *Streptococcus* أما بقيَّة المُعَقَّدَات فلوْظ أَنَّهَا لَا تَمْتَلِك فَعَالِيَّة تَجَاه جَمِيع أَنْوَاع البكتريا. دُرِسَت أيضًا الفعالية للمُعَقَّدَات على عدد من الفطريات المُتَضَمِّنَة *Pencillium* و *Aspergillus niger* و *Alternaria* و *Rhizoctonia* ولم يُلاحظ تأثير للمُعَقَّدَات على الفطريات. كذلك أُخْتَبِرَت فَعَالِيَّة المُعَقَّد (4) على مسحات خَرَّاج السن فلوْظ أَنَّهَا كَفَوَّة مُخْتَبِرِيًّا فِي عِلَاج خَرَّاج السِّن والقضاء على المرض للذكور والإناث. كما أُخْتَبِرَت فَعَالِيَّة مادَتَيْن عَطَارِيَّتَيْن A و B فلوْظ أَنَّهَا تَنْثَبُّط جَمِيع أَنْوَاع البكتريا المُسْتَحْدَمَة قِيد الدرس. فضلًا عن كونها أيضًا مُعَالِجَة لخرَّاج السن بشكل كفوء جدًّا.

المقدمة

يُعَدُّ النحاس العنصر التاسع من عناصر السلسلة الإنتقالية الأولى (3d)، ويعود إلى المجموعة الأولى ب (B 1) التي تُدْعَى حَالِيًّا بِالمجموعة الحادية عشر، وهو أحد العناصر الضرورية للعديد من الحيوانات والنباتات ويتواجد بوصفه جزءًا من المجموعة الاستبدالية للأنزيمات المؤكسدة، كما يُعَدُّ من العناصر الحيوية في جميع الكائنات الحية فهو ضروري لعمل عدد من الأنزيمات ولإدامة فعالية الخلية (1). وقد أُسْتُخِدم النحاس في العلاج منذ بدء تدوين التاريخ، فاستخدامه المصريون القدماء قبل 3000 سنة قبل الميلاد بوصفه مادة مضادة للتعفن ولعلاج الجروح ولتعقيم مياه الشرب، وفي عام 1550 قبل الميلاد استخدم لعلاج تقرح العين كما استخدم مؤخرًا لمعالجة المرضى بالإشعاع ومساعدًا في المعالجة الإشعاعية لمرضى السرطان (1). لا يُظْهَر النحاس سَمِيَّة عَالِيَّة تَجَاه الإنسان بسبب الإمتصاص الجزئي له وإفرازه بسرعة من الجسم، ومع ذلك فَإِنَّهُ فِي أَغْلَب الأحيان عند تناول بضع مليغرامات من ملحه بصورة منفردة تُسبب التقيؤ وأحيانًا الإسهال، كما إِنَّ زِيَادَة تَرْكِيزِهِ فِي أنسجة الدماغ والكبد تُسبِّب مرض ولسن وهو مرض نادر يُصِيب

الجهاز العصبي وعدم علاجه يسبب تفجر كريات الدم الحمراء ومن ثم الوفاة، ويتم علاج زيادة تركيز النحاس باستخدام عوامل كيليتية (1). يؤدي النحاس دوراً أساسياً في التفاعلات الكيميائية الحيوية وهو يشكل مع الحديد أهم العناصر الموجودة في الدم فيسمح لبروتين الترانسفيرين (Transferrin) بالنقاط الحديد ونقله إلى النخاع العظمي حيث تتشكل كريات الدم الحمراء، كما يتواجد في السيلولاريلاسين (Sedolaplasen) التي هي شرط نشاطه في التحولات الغذائية، لذا فمن إشارات نقص النحاس أيضاً التعب وفقر الدم. يعمل النحاس على حماية البشرة بمشاركته في تركيب الكولاجين والإيلاستين وهو ضروري لفيتامين C من أجل أن يؤدي وظيفته بوصفه مضاداً للأكسدة (2).

تعد السميكاربازونات من الليكندات العضوية التي لها أهمية كبيرة في تكوين العديد من المركبات التناسقية وذلك عن طريق منحها للمزدوجات الإلكترونية إلى العناصر الفلزية على نحو عام والعناصر الانتقالية على وجه خاص، إذ تتناسق من خلال ذرتي نيتروجين الأزوميثين وأوكسجين الكاربونيل (3) مكونة ترتيباً حلقياً يمنح استقراراً عالية (4) للمعقدات بسبب الحلقة الخماسية التي تعد أفضل حالات الاستقرار في التناسق فضلاً عن فعاليتها البايولوجية (5,6). ونظراً للأهمية البارزة لهذه المركبات فقد أنجزت العديد من البحوث في مختبراتنا (7,8).

يتكون ثنائي الببتيدات من حامضين أميين مرتبطين معاً بأصرة ببتيدية (peptide bond) لتكوين أبسط جزيئات الببتيد أما الأصرة الببتيدية فهي أصرة أميد متكونة من تفاعل مجموعة الكربوكسيل α للحامض الأميني الأول مع مجموعة الأمين α للحامض الأميني الثاني يُصاحبها فقدان جزيئة ماء، إن الأصرة الببتيدية (-CONH-) لها بعض خواص الأصرة المزدوجة وهذا ما يجعلها قوية وتمنع المجاميع المجاورة من الدوران بحرية (9). لقد حظيت الليكندات الببتيدية وثنائية الببتيد باهتمام الكيميائيين فحضرت معقدات عديدة لعناصر انتقالية وغير انتقالية وشخصت هذه المعقدات بتقنيات مختلفة (10,11).

ركز الباحثون جُل اهتمامهم مؤخراً في مجال كيمياء المعقدات الحاوية على مزيج من الليكندات سواء تلك التي تعود إلى أيونات العناصر الانتقالية أم غير الانتقالية، بسبب دورها البارز والمهم في العمليات الفيزيولوجية والبيولوجية بوصفها مركبات مضادة للفطريات والبكتيريا (12,13)، واستناداً إلى ذلك فإن جزءاً كبيراً من الكيمياء التناسقية المدونة مؤخراً تحتوي على مزيج الليكندات الحاوية على ذرات الكبريت والأوكسجين والنيتروجين مع العناصر الفلزية سواء كانت إنتقالية أم غير إنتقالية وبحالات تأكسدية مختلفة (14,15). ونظراً للأهمية البالغة للمعقدات الحاوية على مزيج من الليكندات فقد حضرت داود وجماعته العديد من معقدات العناصر الانتقالية وغير الانتقالية الحاوية على مزيج من الليكندات (16-18).

تحضير ودراسة تأثير الليزر على معقدات Cu^{2+} الجديدة الحاوية على مزيج من الليكندات والفعالية البيولوجية لها
زهور ورنّا

تُعدّ تقنيّة المايكروويف من أبرز التقنيّات الّتي أُستخدمت في تحضير المعقدّات الكيميائيّة بوصفها مصدراً مميّزاً للحرارة، فاستخدمت في حقل تحضيرات المركّبات العضويّة الفلزيّة وفي حقل البوليمرات والكيمياء الدوائية وكما هو معلوم فإنّ كمّيّة الناتج العالية وزمن التفاعل القصير والنقاوة العالية للمركّبات النهائيّة فضلاً عن تطبيقات التشعيع المايكرووي غير المحدودة الاستخدام في كيمياء السوائل إلّا أنّها أثبتت كفاءتها في مجالات التحضير الخالية من المذيب (الحالة الصلبة) (20,19).

لقد كان لإشعاع الليزر أثر بالغ في الاستخدامات الطبيّة مثل علاج العيون وعلاج الأسنان وعلاج الجهاز الهضمي والجراحة العامّة، وكذلك الصناعات الإلكترونيّة الدقيقة والاستخدامات العسكريّة، كما إنّ لأشعّة الليزر مخاطر على العين والجلد إذا تمّ التعرّض لها بصورة مباشرة وبطاقة عالية (21). تُعدّ تقنيّة الليزر وسيلة لإنتاج حزمة ضوئيّة تُستخدم وبكثرة علمياً وتطبيقيّاً وتتميّز حزمة الضوء هذه بسيرها بشكل موجّه وبصورة مشابهة لجميع الإشعاعات الإلكترونيّة ومغناطيسيّة، إذ يمكن أن تتميّز بتردد أعلى أو عدد موجي لكلّ ثانية، إذ يمثّل الطول الموجي المسافة بين قمتين للموجة (21).

ركّز الكيميائيّون والبيولوجيّون على دراسة البكتريا والفطريّات وابتكار عقاقير مضادّة لها، فنشرت العديد من الأبحاث في هذا المجال سواء كانت العقاقير مواداً عضويّة أم لاعضويّة (22). تحدث إصابة الفم أساساً في الأغشية المخاطيّة فتظهر بشكل بقع بيضاء ملتصقة تتكوّن بدرجة كبيرة من البسيډومايسليم (Pseudomycelium) وتقرّش الورم الظهاري مع تآكل قليل للأغشية. يُعاق نموّ الكانديدا في اللعاب بالكلوكوز وبمضادّات حيويّة و بستيرويدتيډات قشريّة (22). إنّ الخطوة الأولى لإنتاج التسوّس (النخر) تظهر بتكوّن الدمامل على سطح ميناء الأسنان الناعم والقاسي، وتتكوّن الدمامل من ترسّبات جيلاتينيّة فقط ذات وزن جزيئي عالي (كلوكسان) الّذي يلتصق فيه الحامض المُنتج للبكتريا بميناء الأسنان، إنّ بوليمرات الكاربوهيدرات (كلوكسان) تُنتج أساساً بواسطة الستريٲوكوكاي (ستريٲوكوكس ميوتان والبيٲيدستريٲوكوكس) ورٲما بالإقتران مع الفطريّات الشُعاعيّة. أمّا الخطوة الثانيّة في إنتاج التسوّس فتظهر بتكوّن كمّيّات كبيرة من الحامض ($pH < 5.0$) من الكاربوهيدرات من الستريٲوكوكاس واللاكتوباسيلس في الدمامل، فالتركيز العالية للحامض تُزيل المعادن بمحاذاة ميناء الأسنان فتُسبّب ظهور التسوّس (23). إنّ الجيوب جُنب السّن في اللثة تكون مصادر غنيّة للكائنات الّتي نادراً ما تُصادف في مكان آخر، بينما تتواجد في أمراض جُنب السّن والأنسجة المدمّرة، فجذب الانتباه إليهم عند زرعها في مكان آخر على سبيل المثال الإنتاج غير المناسب لذوات الشغاف أو تجرثم الدم في عدد من الخلايا المحييّة للمضيف كأصناف الجراثيم الملتقمة الخلايا وسلبية الغرام وإيجابيّة الغرام الّتي تتواجد في معقد الفلورا

الجرثومية في مرض جنيب السن مع تدمير بروز العظم في مرض نقصان المناعة برفض الخلايا المحببة التي يمكن أن تقود إلى آفة انتهازية في أعضاء أخرى (23). تُستخدم المضادات الحيوية كأدوية تُساعد الجسم على هروب البكتريا والفطريات إما عن طريق قتلهم وإما إيذاء الجراثيم المسببة للمرض أو إضعافهم، وعليه فإن أجهزة المناعة يمكنها التغلب عليهم وقتلهم بشكل أسهل، من أمثلة المضادات الحيوية البنسلين والإريثرومايسين والتتراسايكلين والأموكسيلين (24).

إن الغاية من هذه الدراسة هي:

- 1- تحضير معقدات جديدة النحاس (II) مع مزيج من ليكندي السميكاربازون وثنائي البيتيد بطريقة اعتيادية (مزج المواد وتصعيد حراري للمزيج المذاب). كذلك تحضير المعقدات للنحاس (II) والليكنيدات نفسها والنسب نفسها وبطريقة مايكرووية باستخدام فرن مايكروويف. وتشخيص أشكال المعقدات إستناداً إلى استخدام طرائق تحليلية وفيزيائية .
- 2- ملاحظة تأثير هذه المعقدات بتسليط أشعة ليزرية عليها.
- 3- تطبيق هذه المعقدات على عدد من أنواع البكتريا والفطريات وملاحظة تأثير هذه المركبات على هذه الأحياء المجهرية (مختبرياً) مقارنة مع تأثير المادة القياسية (الأموكسيلين والسبرومايسين والنستاتين). كذلك تطبيق هذه المواد على أشخاص فمهم مصاب بمرض (الشكل 1)، بأخذ مسحات من فمهم ومعالجتها بالمعقدات المحضرة وملاحظة تأثيرها مختبرياً .



الشكل 1 : فم مصاب بالمرض

- 4- أخذ مواد معلومة التأثير على المصابين بأمراض في الفم كالمضادات الحيوية لمعالجة أمراض الفم كالأموكسيلين والسبرومايسين، وكذلك عدد من المركبات التي يستخدمها الإنسان قديماً (مواد عطارية) ثم المقارنة بين جميع المواد المستخدمة لمعالجة هذا المرض.

المواد وطرائق العمل

المواد الكيميائية:

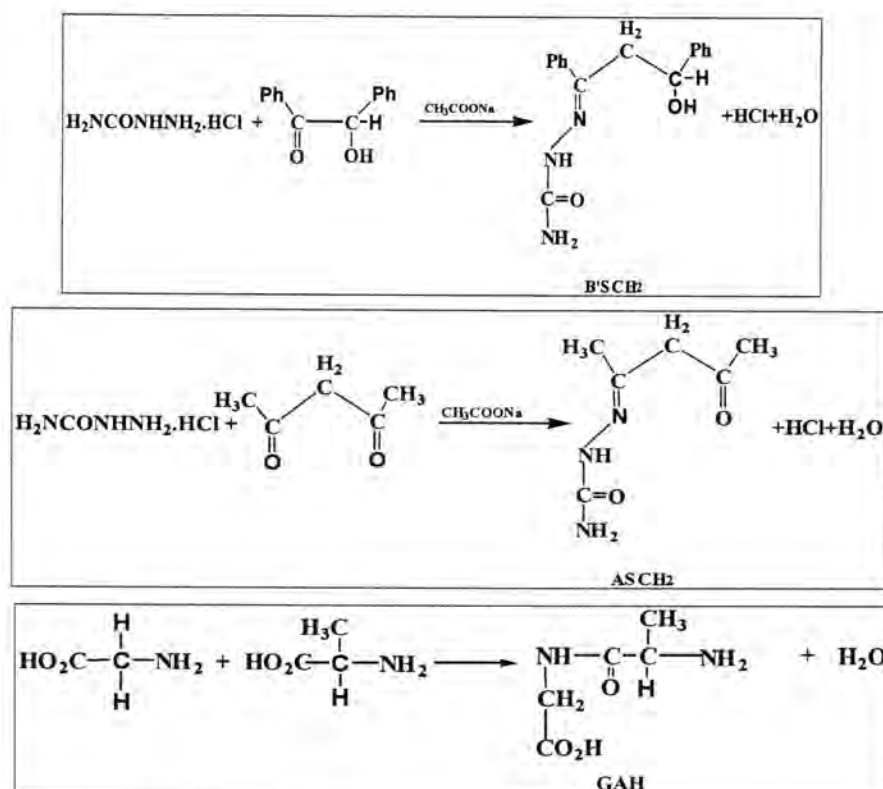
جُهزت المواد الكيميائية الأولية والمذيبات من قبل شركة Fluka و BDH و Aldrich و

Merck.

تحضير ودراسة تأثير الليزر على معقدات Cu^{2+} الجديدة الحاوية على مزيج من الليكندات والفعالية البيولوجية لها
زهرة وريتا

تحضير الليكندات

حضرت ليكندات السميكاريازون (بنزوين سميكاريازون B'SCH_2 و أسيتايل أسيتون سميكاريازون ASCH_2) باتباع طريقة من المراجع (25). وحضر ليكند ثنائي الببتيد (كلايسيل الانين) GAH باتباع طريقة من المراجع (26).



تحضير المعقدات

1- تحضير معقدات النحاس (II) في الوسط المتعادل (أو الحامضي قليلاً)

يذاب 0.5 غم (2.5×10^{-3} مول) من $\text{Cu}(\text{OCOCH}_3)_2 \cdot \text{H}_2\text{O}$ في 10 مل ماء مقطراً ويضاف إلى مزيج مكون من (2.5×10^{-3} مول) من ليكند ثنائي الببتيد كلايسيل الانين و (10^{-3} مول) من أحد الليكندين بنزوين سميكاريازون أو أسيتايل أسيتون سميكاريازون المذابين بأقل كمية من الماء المقطر (إذا كان المحلول متركباً فيضاف إليه الإيثانول ويسخن حتى يصبح رائقاً)، ويصعد حرارياً لمدة ثلاث ساعات، يُخَر المحلول إلى نصف حجمه ثم يُبرَد ويُرشح الراسب ويُغسل بثنائي أثير ويُجفف ويوزن. يتم تحضير معقد نترات النحاس (II) المائية بالطريقة نفسها (انظر الجدول (1)).

أحد أملاح النحاس (II) + كلايسيل الانين + أحد ليكندات السميكاريازون ← المعقدات ذوات الصيغة $[\text{Cu}(\text{GAH})(\text{SCH}_2)]\text{X}$ أو المعقدات ذوات الصيغة $[\text{Cu}(\text{GAH})(\text{SCH}_2)]\text{X}_2$

2- تحضير معقدات النحاس (II) بطريقة التشعيع بفرن المايكروويف

يُمزج 0.5 غم (2.5×10^{-3} مول) $\text{Cu}(\text{OCOCH}_3)_2 \cdot \text{H}_2\text{O}$ و (2.5×10^{-3} مول) من مزيج مُكوّن من ثنائي البيتيّد كلايسيل ألانين و (2.5×10^{-3} مول) من أحد الليكندين بنزوين سميكاريازون أو أسيتايل أسيتون سميكاريازون، يتم سحق المزيج جيّداً وتُضاف إليه قطرتان أو ثلاث قطرات من الماء المقطّر لغرض تجانسّه يوضع داخل فرن المايكروويف ذو قدرة (500 واط) ولمدّة زمنيّة معيّنة ولحين إكتمال التفاعل، يُجمع الراسب ويُغسل بثنائي أثيل إيثر ويجفف ويوزن. يُحضّر معقد نترات النحاس (II) المائية بالطريقة نفسها {انظر الجدول (1)}.

الجدول 1: الظروف العملية والصيغ المتوقعة للمعقدات المحضرة

ت	الصيغ الكيميائية للملح	وزن L_1 غم B'SCH_2	وزن L_2 غم ASCH_2	وزن L_3 غم GAH	الدالة الحامضية	زمن التشعيع (ثا)	نسبة الناتج %	الصيغة المتوقعة
1	$\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$	0.6745	-	0.3660	7-6	-	80.25	$[\text{Cu}(\text{B'SCH}_2)(\text{GAH})\text{AC}]\text{AC}$
2	$\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$	0.6745	-	0.3660	7-6	37	76.92	$[\text{Cu}(\text{B'SCH}_2)(\text{GAH})\text{AC}]\text{AC}$
3	$\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$	-	0.3936	0.3660	7-6	-	79.04	$[\text{Cu}(\text{ASCH}_2)(\text{GAH})\text{AC}]\text{AC}$
4	$\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$	-	0.3936	0.3660	7-6	49	78.22	$[\text{Cu}(\text{ASCH}_2)(\text{GAH})\text{AC}]\text{AC}$
5	$\text{Cu}(\text{NO}_3)_2 \cdot 1/2\text{H}_2\text{O}$	0.5789	-	0.3142	7-6	-	81.00	$[\text{Cu}(\text{B'SCH}_2)(\text{GAH})\text{NO}_3]\text{NO}_3$
6	$\text{Cu}(\text{NO}_3)_2 \cdot 1/2\text{H}_2\text{O}$	0.5789	-	0.3142	7-6	23	75.60	$[\text{Cu}(\text{B'SCH}_2)(\text{GAH})\text{NO}_3]\text{NO}_3$
7	$\text{Cu}(\text{NO}_3)_2 \cdot 1/2\text{H}_2\text{O}$	-	0.3379	0.3142	7-6	-	94.77	$[\text{Cu}(\text{ASCH}_2)(\text{GAH})]\text{NO}_3$
8	$\text{Cu}(\text{NO}_3)_2 \cdot 1/2\text{H}_2\text{O}$	-	0.3379	0.3142	7-6	20	80.55	$[\text{Cu}(\text{ASCH}_2)(\text{GAH})]\text{NO}_3$

Ac= Acetate ion, NO_3^- =Nitrate ion

القياسات التحليلية والفيزيائية:

تمّ تعيين كمّيّة النحاس باستخدام جهاز طيف الامتصاص الذري من نوع (Pye-Unicam SPG Atomic Absorption Spectrophotometer (27). تمّ قياس الوزن الجزيئي النسبي لجميع الليكندات ومعقداتها بطريقة الإنخفاض بدرجة الإنجماد (الكرايوسكوب) (28)، قيس درجات الإنصهار أو التفكك لجميع الليكندات ومعقداتها المحضرة باستخدام جهاز قياس درجة الإنصهار الكهروحراري 9300 وجهاز Rihertjung Hcizubank نوع WME. قيس التوصيلية الكهربائية للمعقدات المحضرة باستخدام جهازي التوصيل الكهربائي Multiline F/SET-2WTW 82362 و weiheim و F-42 باستخدام مذيب الماء أو ثنائي مثيل فورماميد وبتركيز 10^{-3} مولاري بدرجة حرارة 25 °م. قيس معامل الإنكسار (28) لثنائي مثيل فورماميد وكذلك المعقدات المذابة فيه بتركيز 10^{-3} مولاري باستخدام جهاز نوع Atago Illumination, Atago Co-LTD, Japan ويُستفاد من هذا القياس في معرفة خاصية الانكسار المولاري فضلاً عن حساب الوزن الجزيئي النسبي للمعقدات. تمّ قياس المغناطيسية للمعقدات (في جامعة الموصل/كلية العلوم/قسم الكيمياء) عند درجة حرارة الغرفة باستخدام طريقة فرادي بجهاز نوع (Bruker B.M6). سُجّلت الأطياف الإلكترونية لليكندات ومعقداتها وذلك باستخدام جهاز Shimadzu UV-1650 PC UV-Visible

تحضير ودراسة تأثير الليزر على معقدات Cu^{2+} الجديدة الحاوية على مزيج من الليكندات والفعالية البيولوجية لها
زهور ورنّا

Spectrophotometer وقد تمّ القياس باستخدام الماء بوصفه مذيباً وتركيز 10^{-3} مولاري وباستخدام خلايا الكوارتز ذات مسار 1 سم في المدى 200-1100 نانومتر وفي درجة حرارة 25 °م. سُجّلت قياسات طيف الأشعة تحت الحمراء لليكندات ومعقداتها (في جامعة الموصل/كلية التربية/قسم الكيمياء) إذ عملت على شكل أقراص بمادة بروميد البوتاسيوم (KBr) وبجهاز نوع FT-IR Bruker Type Tensor 27 في المنطقة المحصورة بين 4000-400 سم⁻¹.

استخدام تقنية التشعيع بالليزر

شُععت المعقدات المحضّرة الصلبة (في جامعة الموصل/كلية العلوم/قسم الفيزياء) بإشعاع ليزري من نوع ليزر الحالة الغازية (الليزر الذري) نوع هيليوم-نيون (Ne-He) قدرته 1 ملي واط أي أنّ المادة الفعالة هي خليط من هذين الغازين يعطي أشعة ليزرية في المنطقة الحمراء من الطيف بطول موجي 632.8 نانومتر بشكل موجات مستمرة، ولمدد زمنية مختلفة تتراوح ما بين ساعة إلى خمس ساعات، إذ بعد مرور كلّ ساعة من التشعيع قيست درجة الإنصهار والتوصيلية الكهربائية.

الفعالية البيولوجية

دُرست الفعالية للمعقدات على عدد من البكتريا المرضية تتضمّن (*Staphylococcus aureus* و *Escherichia coli* و *Pseudomonas aeruginosa* و *Streptococcus faecalis* و *Proteius mirabilis*) باستخدام تقنية الانتشار على سطح الآكار كمضادات للبكتريا إيجابية وسلبية الغرام (30،29). عُرّلت جميع البكتريا وشُخصت باستخدام طرائق قياسية (31،32) قبل استخدامها في قسم علوم الحياة - كلية التربية - جامعة الموصل. كذلك دُرست الفعالية للمعقدات المحضّرة على عدد من الفطريات تتضمّن (*Aspergillus niger* و *Alternaria* و *Rhizoctonia*)، إذ عُرّلت جميع الفطريات وشُخصت باستخدام طرائق قياسية (33،34) قبل استخدامها في قسم علوم الحياة - كلية التربية - جامعة الموصل.

النتائج والمناقشة

يُمكن التعبير عن تكوّن المعقدات قيد الدرس والمحضّرة بالطريقة التقليدية وبطريقة المايكروويف بالمعادلات الكيميائية الآتية في الوسط المتعادل (أو الحامضي قليلاً) :



عُيّنَت كميّة النحاس (II) باستخدام تقنية طيف الإمتصاص الذري وأُثبتت النتائج المدوّنة في

الجدول (2) بأنّ كميّة العناصر كانت متّفقة مع الصيغ المقترحة. كما أُثبتت النتائج الأخرى

المبيّنة في الجدول (2) والمعادلات المذكورة في أعلاه أنّ النسبة المولية للتفاعل 1:1:1 (فلز: ليكند

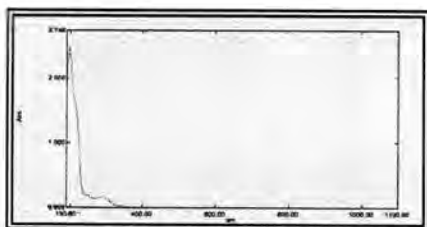
السميكاربازون: ليكند الكلايسيل (الانين). إن المعقدات الناتجة مواد صلبة وملونة ومستقرة، وتكون ذات شحنة موجبة في الوسط المتعادل (أو الحامضي قليلاً)، تذوب المعقدات الناتجة في الماء وعدد من المذيبات العضوية كإيثانول وثنائي مثيل فورماميد، في حين إنها قليلة الذوبان في ثنائي أنيل إيثر. كما وجد أن معظمها يتفكك وبعضها الآخر ينصهر. قيسست الموصلية الكهربائية للمعقدات عند تركيز 10^{-3} مولاري باستخدام الماء المزال منه الأيونات عند 25°C ، وتبين من قياسات الموصلية الكهربائية أن المعقدات المحضرة في الوسط المتعادل تكون مشحونة أي تكون موصلة إلكتروليتيّة بنسبة 1:1 أو 2:1 (35) كما مبين في الجدول (2)، كانت النتائج التي تم الحصول عليها متلائمة مع الصيغ المتوقعة للمعقدات المحضرة التي توضح تكون معقدات مشحونة (موصلة كهربائياً) $[\text{Cu}(\text{GAH})(\text{SCH}_2)\text{X}]_2\text{X}$ أو $[\text{Cu}(\text{GAH})(\text{SCH}_2)\text{X}]_2\text{X}$. وأظهرت القياسات المغناطيسية لمعقدات النحاس (II) قيماً تقترب من 1.771-2.150 مغناطون بور {الجدول (2)} مما يرجح كون ذرة النحاس سداسية التناسق ذات شكل ثماني السطوح مشوه (36).

الجدول 2: النتائج التحليلية وعدد من الخصائص الفيزيائية للمعقدات المحضرة

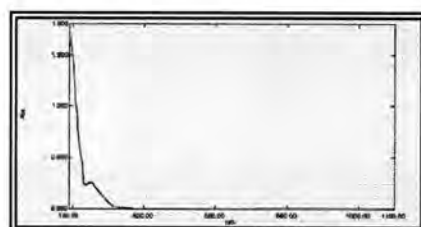
رقم المعقد	اللون	درجة الانصهار أو التفكك * (°C)	Λ_{M} اوم ⁻¹ سم ² مول ⁻¹	M% (عملياً نظرياً)	ΔT_f (°C)	M.Wt Calc.(f) في DMF	M.Wt Calc.(f) بالماء المقطر	nf x 10 ⁻⁴	μ_{eff} (B.M)
1	بنفسجي	162*	170	(10.96) 10.64	- 4.5	(579.000) 597.091	594.000	1.334005	2.150
2	بنفسجي	160*	178	(10.96) 10.64	- 4.5	(579.000) 597.091	570.000	1.334030	2.051
3	أخضر	251	167	(12.47) 13.10	- 5.5	(509.000) 484.956	476.000	1.334025	1.771
4	أخضر	248	170	(12.47) 13.16	- 5.5	(509.000) 484.956	452.000	1.334024	2.067
5	بنّي	149	205	(10.34) 10.54	- 4.0	(614.000) 603.010	641.000	1.334021	1.931
6	بنّي	153	189	(9.77) 10.54	- 3.5	(649.400) 603.010	641.000	1.334025	1.813
7	أخضر	150	234	(11.67) 12.94	- 5.0	(544.000) 490.874	523.000	1.334013	1.903
8	أخضر	147	229	(12.47) 12.94	- 5.5	(509.000) 490.874	476.000	1.334010	2.130
L ₁	أبيض	155	-	-	- 9.0	(263.000) 269.311	288.000	1.333000	
L ₂	بنّي	285	-	-	- 11.0	(123.800) 57.1756	76.300	1.335002	
L ₃	أبيض كريمي	302	-	-	- 10.5	(158.800) 46.1488	65.600	1.334010	

أظهرت الأطياف الإلكترونية لمعقدات النحاس (II) حزمة واحدة عريضة {الجدول (3)} والأشكال (2-5) في المنطقة 10060.36 - 15527.95 سم⁻¹ تعود الى تجمع انتقالين الكترونيين ${}^2\text{B}_{1g} \leftarrow {}^2\text{A}_{1g}$ و ${}^2\text{B}_{1g} \leftarrow {}^2\text{E}_g$ و ظهور هذه يدل على ان لمعقدات النحاس (II) شكل ثماني السطوح ونظراً إلى أن لحالة الاستقرار Eg قابلية عالية لتأثير يان تيلر (Jahn-Teller effect) فإن أيون النحاس في معقداته يُظهر قابلية عالية لتأثير يان تيلر ويكون ذو شكل ثماني السطوح مشوه (37).

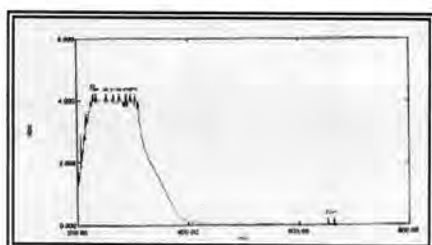
تحضير ودراسة تأثير الليزر على معقدات Cu^{2+} الجديدة الحاوية على مزيج من الليكندات والفعالية البيولوجية لها
زهرة ورنا



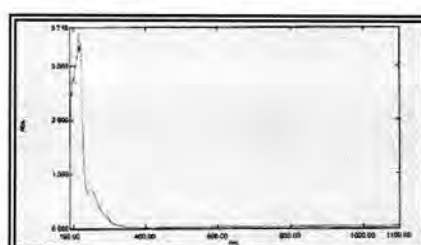
الشكل 3: الطيف الإلكتروني لليكند ASCH_2



الشكل 2: الطيف الإلكتروني لليكند B'SCH_2



الشكل 5: الطيف الإلكتروني للمعقد رقم (1)



الشكل 4: الطيف الإلكتروني لليكند GAH

الجدول 3: نتائج الطيف الإلكتروني لمعقدات النحاس (II)

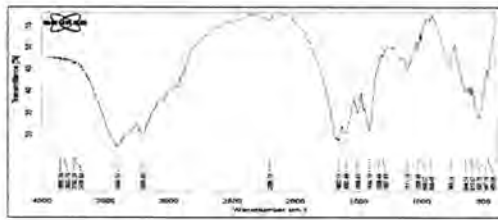
رقم المعقد	d-d سم ⁻¹	C.T سم ⁻¹	C.F.S.E	رقم المعقد	d-d سم ⁻¹	C.T سم ⁻¹	C.F.S.E
1	10989.01	40322.58	6593.406	5	14306.15	41666.66	8583.690
2	14245.01	42372.88	8547.006	6	12453.30	39215.68	7471.980
3	10060.36	42372.88	6036.216	7	15174.50	41493.77	9104.700
4	14970.05	40485.82	8982.030	8	15527.95	41152.25	9316.770

لوحظ أن التردد الامتصاصي لمجموعة $\text{C}=\text{N}$ لليكندين {جدول (4)، الأشكال (6-11)} يظهر بحدود 1603.06 - 1645.00 سم⁻¹، وعند تتاسق الليكندات مع الذرة الفلزية حدثت إزاحة نحو تردد أوطأ مما يدل على إرتباط هذه المجموعة مع الأيون الفلزي وهذه الإزاحة توضح قلة خاصية الأصرة المزدوجة في مجموعة الأزوميثين وهذا متفق مع ما نشر في البحوث (38,39). وظهرت أصرة الأمايد الناشئة من هيئة التردد الامتصاصي للكربونيل عند الموقع 1663.15 - 1685.22 سم⁻¹ في طيف الأشعة تحت الحمراء لليكندين ASCH_2 و B'SCH_2 على التوالي {جدول (4) والشكلين (6,7)} ويعزى التردد الواطي نسبياً لهذه الحزمة عن تلك الملاحظة في مركبات الأمايد (38) إلى الأصرة الهيدروجينية بين مجموعة الكيتون ومجموعة OH و NH_2 ورنين NH مع الكربونيل في الليكندات. لقد ظهرت هذه الحزمة في أطياف المعقدات المحضرة عند ترددات تتراوح بين 1623.04 - 1635.22 سم⁻¹ وذلك بسبب تتاسق ذرة الأوكسجين الكربونيلية مع الأيون الفلزي (38,39)،. لوحظ أن التردد الامتصاصي لمجموعة $\text{C}-\text{O}$ الكحولية في طيف الليكند B'SCH_2 يظهر عند 1061.76 سم⁻¹ وظهرت هذه الحزمة في أطياف المعقدات عند تردد يتراوح بين 1106.78 - 1111.72 سم⁻¹ بسبب تتاسق ذرة الأوكسجين الكحولية مع الأيون الفلزي (38).

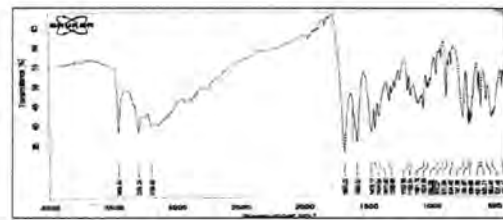
أعطى طيف الليكند $ASCH_2$ حزمة عند تردد 1663.15 سم^{-1} تعود إلى التردد الامتصاصي لمجموعة $C=O$ الأخرى ولوحظ عند التناسق أنها تبقى في محلها مما يعزز عدم ارتباطها (39,38). لوحظ أن التردد الامتصاصي لمجموعة NH في أطيف الليكندات عند 3205.00 و 3210.00 سم^{-1} وعند تكون المعقدات يصبح الحال أكثر تعقيداً بسبب العديد من العوامل (39,38)، منها تأثير الأصرة الهيدروجينية (يحدث عادة إنكسار بالأصرة الهيدروجينية عند التناسق مما يسبب إزاحة التردد الامتصاصي لمجموعة NH نحو تردد أعلى) وتأثير التناسق الذي يسبب إزاحة الحزم إلى تردد أوطأ كذلك العديد من المجاميع التي تظهر في الموقع نفسه (NH_2 و OH) ومهما يكن ففي حالة المعقدات المتكونة في الوسط المتعادل تظهر حزمة NH في الموقع نفسه تقريباً، ومن المؤكد عدم وجود تناسق بين ذرة نتروجين الأميدو مع الفلز مما يعزز الشكل الكيتوني في الليكندات. أعطى طيف الأشعة تحت الحمراء لليكندات قيد الدرس حزمة 1450.00 و 3302.24 - 3404.00 سم^{-1} تعود إلى تردد انحناء δ_{NH_2} وتردد امتطاط ν_{NH_2} على التوالي لليكندات الحرة (39,38)، ولوحظت هاتان الحزمتان في الموقع نفسه في أطيف المعقدات مما يدل على عدم تناسق هذه المجموعة مع الأيونات الفلزية. لوحظ ظهور حزمة واسعة في الموقع 3302.24 - 3456.84 سم^{-1} في طيف الأشعة تحت الحمراء لليكند $B'SCH_2$ تعود إلى التردد الإمتصاصي لمجموعة OH الكحولية ويعود المدى الواسع إلى وجود الأصرة الهيدروجينية وكذلك نظراً لوجود العديد من المجاميع الأخرى (NH_2 و NH) التي تظهر في المنطقة نفسها، ونظراً لوجود العديد من المجاميع فمن الصعوبة ملاحظة الإزاحة والتأكد من التناسق، تعود الحزمة التي ظهرت في الموقع 13330.37 سم^{-1} إلى تردد الانحناء إلى مجموعة OH الكحولية وفي المعقدات لوحظ إزاحة هذه الحزمة إلى تردد أوطأ مما يدل على إشتراك هذه المجموعة في التناسق مع الأيون الفلزي، لوحظ ظهور حزمتين عند 1297.00 سم^{-1} و 1497.00 سم^{-1} تعود إلى التردد الامتصاصي المتمائل $COO(s)$ وغير المتمائل $COO(as)$ لمجموعة الكربوكسيل على التوالي وعند التناسق تُزاح هاتان الحزمتان إلى 1310.51 - 1385.09 و 1490.51 - 1560.42 سم^{-1} على التوالي، إن الفرق بين التردد الامتصاصي لمجموعة $COO(s)$ و $COO(as)$ $(\nu_s(COO) - \nu_{as}(COO) = \Delta\nu)$ الذي يساوي 170.99 - 180.12 سم^{-1} يعطي معلومات عن أسلوب تناسق المجموعة الكربوكسيلية، أوضحت هذه القيم أن مجموعة الكربوكسيل تتناسق مع الأيون الفلزي إذ تعمل بشكل أحادية السن أي تتناسق من خلال ذرة أوكسجين واحدة (38). لوحظ ظهور حزمة عند 3445.05 سم^{-1} تعود إلى التردد الامتصاصي لمجموعة NH_2 في الليكند (38)، ولوحظ أن هذه الحزمة تُزاح إلى تردد أوطأ للمعقدات 8 مما يدل على تناسق هذه المجموعة مع الأيون الفلزي (38)، في حين بقيت هذه الحزمة في موقعها نفسه في المعقدات الأخرى مما يعزز عدم ارتباط هذه المجموعة مع الأيون الفلزي (38). أعطى طيف الأشعة تحت الحمراء لليكند ثنائي الببتيد حزمة عند 1680.00 سم^{-1} تعود إلى التردد

تحضير ودراسة تأثير الليزر على معقدات Cu^{2+} الجديدة الحاوية على مزيج من الليكندات والفعالية البيولوجية لها
زهود ورناء

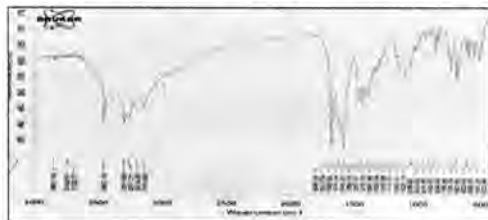
الامتصاصي لمجموعة C=O ولوحظ أن هذه الحزمة تُزاح إلى تردد أوطأ -1610.00 1649.00 سم^{-1} وذلك بسبب تناسق ذرة الأوكسجين الكربونيلية مع الأيون الفلزي (38).
لقد أظهرت المعقدات (الحاوية على أيون الخلات) نوعين من الارتباط إذ أعطت حزمة عند $1525.00-1540.00 \text{ سم}^{-1}$ تعود إلى الارتباط الأيوني لمجموعة الخلات (38)، كذلك أعطت حزمتين عند $1370.00-1370.50 \text{ سم}^{-1}$ و $1540.00-1540.50 \text{ سم}^{-1}$ تشير إلى أن مجموعة الخلات قد تناسقت مع الأيون الفلزي بشكل ليكند أحادي السن من خلال ذرة الأوكسجين، لقد أظهرت المعقدات الحاوية على مجموعة النترات ماعدا المعقدين 7 و 8 حزمتين فقط في المدى $1384.51-1384.98 \text{ سم}^{-1}$ تعود إلى الارتباط الأيوني لمجموعة النترات (38)، أما المعقدان 7 و 8 فقد أظهرتا نوعين من الارتباط إذ أعطيا حزمة عند 1385.09 سم^{-1} و 1384.27 سم^{-1} على التوالي تعود إلى الارتباط الأيوني لمجموعة النترات (38)، كذلك أعطيا ثلاث حزم أخرى تعود إلى التردد الامتصاصي لمجموعة NO في المواقع $1400.00-1449.42 \text{ سم}^{-1}$ و $1285.00-1334.00 \text{ سم}^{-1}$ و $1000.00-1003.26 \text{ سم}^{-1}$ تعود إلى الترددات المتماثلة $\text{v}_{\text{NO}_3(\text{S})}$ وغير المتماثلة $\text{v}_{\text{NO}_3(\text{as})}$ و v_{NO} وقد لوحظ أن الفرق بين الترددات (v_1 و v_5) هو $115.00-115.42 \text{ سم}^{-1}$ مما يُعزّز ارتباط مجموعة النترات بشكل أحادي السن من خلال ذرة أوكسجين واحدة أي أن هناك مجموعة من النترات ارتبطت بشكل أيوني والأخرى ارتبطت بشكل ليكند أحادي السن وهذا ما جاء مطابقاً مع النتائج التي تم الحصول عليها من قياس التوصيل الكهربائي لهذه المعقدات. لوحظت حزم عند مواقع ترددية واطئة في طيف الأشعة تحت الحمراء للمعقدات إذ ظهرت الحزم $417.00-535.00 \text{ سم}^{-1}$ و $523.07-643.45 \text{ سم}^{-1}$ تعود إلى $\text{v}_{\text{M-O}}$ و $\text{v}_{\text{M-N}}$ على التوالي، إن ظهور هذه الحزم يُعزّز تكون المعقدات قيد الدرس (38,39).



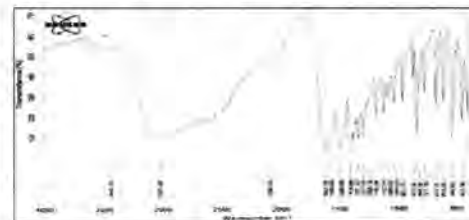
الشكل 7: طيف (IR) للليكند ASCH_2



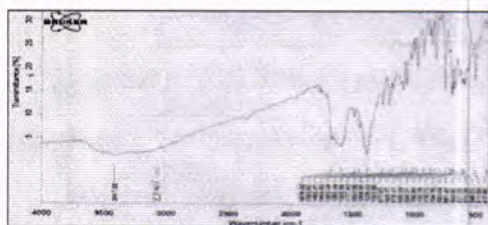
الشكل 6: طيف (IR) للليكند B'SCH_2



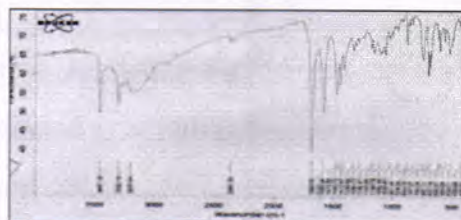
الشكل 9: طيف (IR) للمعقد 1



الشكل 8: طيف (IR) للليكند GAH



الشكل 11: طيف (IR) للمُعَقَّد 5



الشكل 10: طيف (IR) للمُعَقَّد 3

الجدول-4: عدد من الحزم المهمة في طيف الأشعة تحت الحمراء لليكنات والمُعَقَّدات (ν سم⁻¹)

رقم المركب	C=N (s)	C=O (s)	N-H (b)	C=O (s)	COO(s)	COO(as)	Δν	NH ₂ (b)	M-N (m)	M-O (m)	حزم أخرى
L ₁	1645.00	1685.22	3210.00	-	-	-	-	-	-	-	C-O(s) 3302.24 OH(b) 1061.76
L ₂	1603.06	1663.15	3205.00	-	-	-	-	-	-	-	C=O(s) 1663.15
L ₃	-	-	-	-	1297.00	1497.00	200.00	3445.05	-	-	-
1	1585.94	1630.00	3208.00	1649.00	1330.92	1507.12	176.32	3445.18	419.21	564.85	C-O(s) 1106.78 OH(b) 3201.04
2	1586.82	1623.04	3207.00	1636.25	1310.51	1490.51	180.10	3445.13	436.14	606.76	C-O(s) 1111.77 OH(b) 3204.58
3	1583.00	1628.08	3206.00	1631.00	1358.09	1536.31	172.22	3441.00	422.00	643.45	C=O(s) 1662.00 NH(b) 3204.00
4	1583.00	1627.11	3201.00	1599.00	1356.76	1536.88	180.12	3445.00	423.00	626.45	C=O(s) 1663.00 NH(b) 3209.00
5	1595.62	1635.00	3202.00	1627.00	1385.09	1560.42	175.33	3446.00	417.96	511.59	C-O(s) 1177.40 OH(b) 3246.00
6	1586.42	1623.51	3206.13	1610.00	1384.27	1557.77	173.50	3445.00	426.00	511.00	C-O(s) 1110.10 OH(b) 3240.00
7	1590.00	1635.22	3210.10	1630.00	1384.29	1560.95	176.66	3440.00	417.00	477.00	C=O(s) 1664.00 NH(b) 3209.00
8	1586.50	1633.23	3203.00	1632.00	1385.03	1556.02	170.99	3407.00	490.00	535.00	C=O(s) 1662.00 NH(b) 3205.00

S=strong; br=broad; m=medium

شعبت جميع المُعَقَّدات الصلبة بأشعة الليزر لمدد زمنية تتراوح من 1-5 ساعة ، فلو حظ أن

جميع المُعَقَّدات لم تتأثر بهذا النوع من الإشعاع فهي لا تتفكك ولا تتبلر من خلال قياسنا لدرجة

الانصهار أو التفكك وقياس التوصيلية الكهربائية للمُعَقَّدات قيد الدرس كما موضح في الجدول (5)،

مما يبين أن هذه المُعَقَّدات مستقرة.

الجدول 5 : نتائج تشييع المُعَقَّدات بأشعة الليزر

المُعَقَّدات المحضرة بطرق تقليدية				المُعَقَّدات المحضرة بطرق تقليدية				المُعَقَّدات المحضرة بطرق المايكرويف				المُعَقَّدات المحضرة بطرق المايكرويف			
رقم المعقد	زمن التشيع ساعة	درجة الانصهار °م	التوصيلية أوم ⁻¹ سم ⁻²	رقم المعقد	زمن التشيع ساعة	درجة الانصهار °م	التوصيلية أوم ⁻¹ سم ⁻²	رقم المعقد	زمن التشيع ساعة	درجة الانصهار °م	التوصيلية أوم ⁻¹ سم ⁻²	رقم المعقد	زمن التشيع ساعة	درجة الانصهار °م	التوصيلية أوم ⁻¹ سم ⁻²
1	0	162	170	1	0	251	167	3	0	160	178	3	0	248	170
1	1	162	170	1	1	251	167	3	1	160	178	3	1	248	170
2	2	162	171	2	2	251	165	3	2	161	177	3	2	248	170
3	3	165	171	3	3	250	165	3	3	161	177	3	3	248	170
4	4	165	171	4	4	250	165	3	4	161	177	3	4	248	171
5	5	165	171	5	5	250	165	3	5	163	178	3	5	246	171
5	0	149	205	5	0	150	234	7	0	153	189	7	0	147	229
1	1	149	205	1	1	150	234	7	1	153	189	7	1	147	229
2	2	145	205	2	2	155	235	7	2	150	189	7	2	147	229
3	3	145	200	3	3	155	235	7	3	150	190	7	3	147	230

تحضير ودراسة تأثير النيزر على معقدات Cu^{2+} الجديدة الحاوية على مزيج من الليكندات والفعالية البيولوجية لها
زهور ورن

230	145	4		235	155	4		190	150	4		200	145	4	
230	145	5		235	155	5		190	150	5		200	145	5	

أظهرت نتائج الفعالية البيولوجية لليكندات وللمعقدات قيد الدرس على عدد من البكتيريا المرضية (*Staphylococcus aureus* و *Escherichia coli* و *Pseudomonas auruginosa* و *Streptococcus faecalis* و *Proteus mirabilis*) أن البكتيريا تقاوم الليكندات و معظم المعقدات ماعدا المعقد 4، إذ إن المعقد المذكور يُثبِّط البكتيريا *Streptococcus faecalis* عند استخدام تراكيز منه 500 و 250 مايكروغرام /مل (29,30)، أي إن هذا المعقد الذي يُعتقد أنه يرتبط مع مجاميع SH لخلايا الأنزيم تعمل بشكل أقوى من ذرات النتروجين المانحة في الليكندات (40)، ويجب أن تمتلك أقل تركيز مثبِّط MIC والذي جاء مع ما نشر للعديد من الباحثين (41,42)، أما المركبات العطارية (A و B) فقد أظهرت فعالية جيدة ضد جميع أنواع البكتيريا وكما موضَّح في الجدولين (6 و 7) والشكل (12) .

الجدول 6: الفعالية مضادة البكتيريا لليكندات و للمعقدات

NO	<i>Staphelo. aureus</i>				<i>Strepto. faecalis</i>				<i>Escherichia coli</i>				<i>Protus mirabitoilis</i>				<i>Pseudomonas auruginosa</i>			
	500	250	125	62.5	500	250	125	62.5	500	250	125	62.5	500	250	125	62.5	500	250	125	62.5
L1	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R
L2	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R
L3	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R
1	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R
2	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R
3	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R
4	R	R	R	R	S	MS	R	R	R	R	R	R	R	R	R	R	R	R	R	R
5	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R
6	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R
7	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R
8	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R
A	S	S	MS	R	S	S	MS	MS	S	MS	R	R	S	MS	MS	R	S	S	MS	R
B	S	S	MS	MS	S	S	MS	R	MS	R	R	R	S	S	MS	MS	S	S	MS	MS
AX25	23				23				R				R				R			
CIP5	31				31				31				31				17			

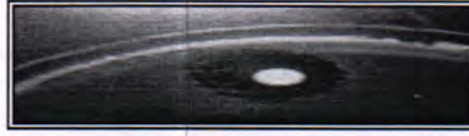
-تعني لا يوجد فعالية لهذه المعقدات ويمكن ملاحظة ذلك في الجدول (14). S = حساس ، MS

= وسط ، R = مقاومة ، R^+ و R^{++} = نمو للبكتيريا

الجدول 7: أقل تركيز تثبيطي (مايكروغرام/ مل) من المعقدات

No	<i>Staphelo. aureus</i>				<i>Strepto. faecalis</i>				<i>Escherichia coli</i>				<i>Proteus miratoilis</i>				<i>Pseudomonas auruginosa</i>			
	500	250	125	62.5	500	250	125	62.5	500	250	125	62.5	500	250	125	62.5	500	250	125	62.5
L1																				
L2																				
L3																				
1																				
2																				
3																				
4					9	6														
5																				
6																				
7																				
8																				
A	10	8	7	-	18	10	8	6	8	6	-	-	10	8	6	-	20	8	6	-
B	15	10	8	6	10	8	6	-	8	-	-	-	12	9	6	6	10	7	6	6
AX25	23				23				R				R				R			
CIP5	31				31				31				31				17			

AX25 = أموكسيلين ، CIP5 = سبرومايسين

الشكل 12: الفعالية مضادة البكتريا *Streptococcus faecalis* (المعقد 4)

أظهرت نتائج الفعالية البايولوجية للكنيدات وللمعقدات جدول (8) على عدد من الفطريات (*Penicillium* و *Aspergillus niger* و *Alternaria* و *Rhizoctonia*) أن الفطريات تقاوم جميع المعقدات قيد الدرس.

الجدول 8 : الفعالية مضادة الفطريات للمعقدات

NO	<i>Alternaria</i>				<i>Rhizoctonia</i>				<i>Penicillium roqueforti</i>				<i>Aspergillus niger</i>			
	500	250	125	62.5	500	250	125	62.5	500	250	125	62.5	500	250	125	62.5
L1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
L2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
L3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
4	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
6	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
7	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Nyst	15				15				15				R			

Nyst = نستاتين

كذلك اختبرت فعالية المعقد 42 مختبرياً على مسحات أخذت من مرض خراج السن (Periapical lesion) من مجموعة من الذكور والإناث كما موضح في الجداول (9 و 10 و 11 و 12) والأشكال (13 و 14 و 15) اتضح أن هذا المعقد يمكنه معالجة الذكور والإناث فوق سن الـ (19) إذ بينت النتائج الإحصائية أن نسبة المعالجة للمعقد 4 تتراوح بين 26%-65%، مما يوضح إمكانية المعالجة بهذه المواد والقضاء على المرض بشكل جيد، أما الذكور والإناث دون سن الثامنة عشر فقد لوحظ أن نسبة المعالجة 30%-78% . كما لوحظ أن مسحات الذكور والإناث دون سن الثامنة عشر أقل استجابة من الذكور والإناث فوق سن التاسعة عشر ويوضح هذا أن المرض يكون في البالغين أكثر انتشاراً ممن هم دون التاسعة عشر سنة، كذلك أظهرت المادة العطارية A فعالية متميزة إذ استطاعت أن تعالج المرض بنسبة 100% بإستخدام تركيز 500 مايكروغرام/مل، في حين استطاعت المادة B أن تعالج المرض بنسبة 52.43% يتضح أن المادة A هي أفضل في المعالجة من المادة B (الجدول 13).

تحضير ودراسة تأثير النيزر على معقدات Cu^{2+} الجديدة الحاوية على مزيج من الليكندات والفعالية البيولوجية لها
زهور ورفنا

الجدول 9: مسحات الفم للذكور فوق سن (19) سنة

4			العمر 50-19	رقم العينة	4			العمر 50-19	رقم العينة
125 $\mu\text{g/ml}$	250 $\mu\text{g/ml}$	500 $\mu\text{g/ml}$			125 $\mu\text{g/ml}$	250 $\mu\text{g/ml}$	500 $\mu\text{g/ml}$		
-	-	%30	45	17	-	-	-	24	1
-	-	-	43	18	-	-	-	40	2
-	-	-	28	19	-	-	-	28	3
-	-	-	27	20	-	%43	%65	23	4
-	-	-	38	21	-	-	%30	36	5
-	-	-	39	22	-	%26	%26	30	6
-	-	-	26	23	%26	%39	%65	43	7
-	-	-	22	24	-	%39	%52	34	8
-	-	%26	36	25	-	-	%26	37	9
-	-	-	26	26	-	-	-	28	10
-	-	%26	36	27	-	-	-	32	11
%26	%43	%60	40	28	-	-	-	43	12
-	-	-	24	29	-	-	-	26	13
-	-	-	48	30	-	-	%34	32	14
-	-	%26	39	31	-	-	-	22	15
-	-	-	28	32	-	-	-	35	16

الجدول 10: مسحات الفم للذكور دون سن (19) سنة

4			العمر دون 19	رقم العينة
125 $\mu\text{g/ml}$	250 $\mu\text{g/ml}$	500 $\mu\text{g/ml}$		
-	-	-	14	1
-	-	-	15	2
-	-	-	18	3
-	-	-	16	4
-	-	%30	17	5

الجدول 11: مسحات الفم للإناث فوق سن (19) سنة

4			العمر 50-19	رقم العينة	4			العمر 50-19	رقم العينة
125 $\mu\text{g/ml}$	250 $\mu\text{g/ml}$	500 $\mu\text{g/ml}$			125 $\mu\text{g/ml}$	250 $\mu\text{g/ml}$	500 $\mu\text{g/ml}$		
-	-	%26	40	26	-	%43	%65	29	14
-	-	%30	26	27	-	-	-	33	15
-	-	-	36	28	-	-	%30	40	16
-	-	%26	50	29	-	-	-	20	17
-	-	-	36	30	-	-	-	22	18
-	-	-	42	31	-	-	%26	34	19
-	-	%26	32	32	%26	%39	%60	33	20
-	-	-	27	33	-	-	-	24	21
-	-	-	37	34	-	-	%43	31	22

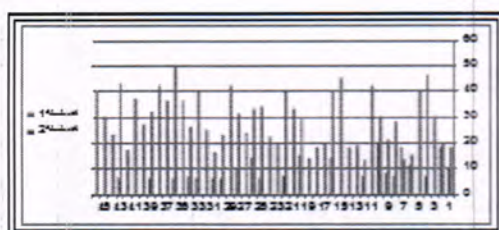
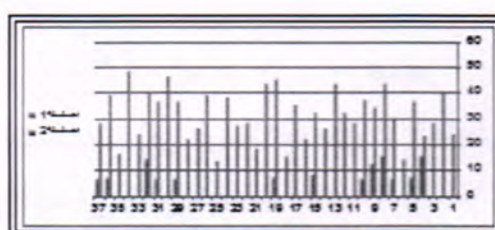
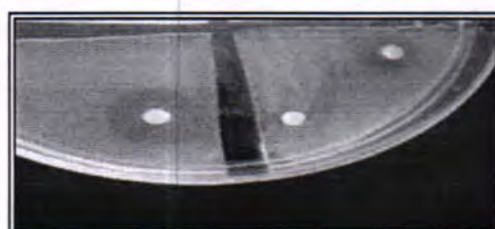
-	-	%26	43	35	-	-	-	42	23	-	-	-	45	10
-	-	-	23	36	-	-	%26	23	24	%26	%39	%60	40	11
-	-	-	30	37	-	-	-	25	25	-	-	-	20	12
											-	-	40	13

الجدول 12: مسحات الفم للإلانات دون سن (19) سنة

4			المعديون 19	رقم العينة	4			المعديون 19	رقم العينة
125 µg/ml	250 µg/ml	500 µg/ml			125 µg/ml	250 µg/ml	500 µg/ml		
-	-	-	18	6	-	%26	%43	18	1
-	-	-	14	7	-	-	%47	15	2
-	-	%26	16	8	-	%30	%78	13	3
-	-	-	17	9	-	-	-	13	4
					-	-	-	18	5

الجدول 13: مسحات الفم للإلانات للمادتين (A و B)

B			A			المعديون	رقم العينة
125 µg/ml	250 µg/ml	500 µg/ml	125 µg/ml	250 µg/ml	500 µg/ml		
%34	%43	%52	%43	%65	%100	26	1
-	%34	%43	%43	%78	%100	17	2

الشكل 14: مخطط يوضح استجابة المسحات
للمعقد (4) للإلاناتالشكل 13: مخطط يوضح استجابة المسحات
للمعقد (4) للذكور

الشكل 15: المسحات المعالجة بالمعقدات للذكور (4)

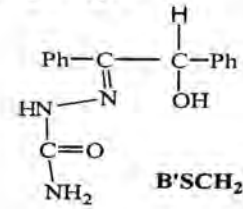
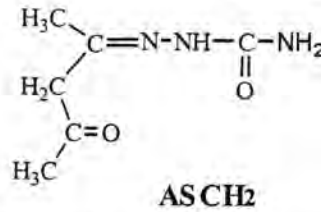
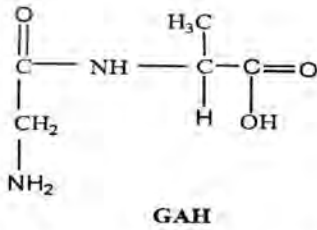
استناداً إلى الإعتبارات السابقة ومن الدراسات التحليلية والطيفية والخصائص الفيزيائية والكيميائية ودراسة تأثير أشعة الليزر ودراسة الفعالية ضد عدد من أنواع من البكتيريا والفطريات فضلاً عن التطبيق الطبي للمعقدات يمكن استنتاج ما يأتي:

تحضير ودراسة تأثير الليزر على معقدات Cu^{2+} الجديدة الحاوية على مزيج من الليكندات والفعالية البيولوجية لها
زهرة وريتا

1. يتناسق الليكند B'SCH_2 مع الأيونات الفلزية قيد الدرس من خلال ذرة نيتروجين الأزوميثين وذرة الأوكسجين الكاربونيلية وذرة الأوكسجين الكحولية إذ يعمل الليكند بشكل ثلاثي السن كيليتي متعادل الشحنة.

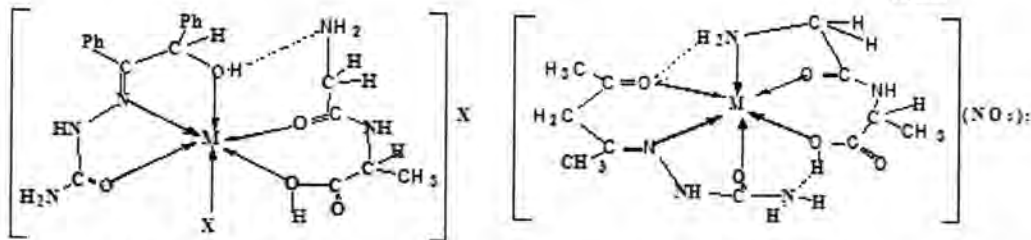
2. يتناسق الليكند ASCH_2 مع الأيونات الفلزية قيد الدرس من خلال ذرة نيتروجين الأزوميثين وذرتي الأوكسجين الكاربونيلية، إذ يعمل الليكند بشكل ليكند ثلاثي السن كيليتي متعادل الشحنة.

3. يتناسق الليكند GAH مع الأيونات الفلزية قيد الدرس من خلال ذرة الأوكسجين الكاربوكسيلية وذرة الأوكسجين الكاربونيلية أو من خلال ذرة الأوكسجين الكاربوكسيلية وذرة الأوكسجين الكاربونيلية وذرة نيتروجين الأمين، إذ يعمل بشكل ليكند ثنائي السن كيليتي أو ثلاثي السن كيليتي على التوالي متعادل الشحنة.



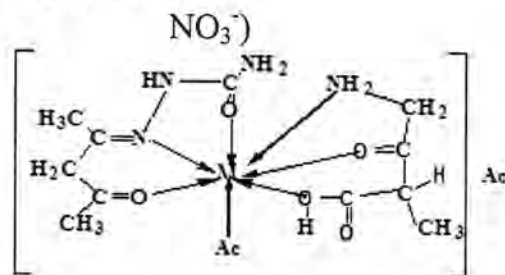
4. يكون الأيون الفلزي في جميع المعقدات الناتجة (في الوسط المتعادل أو الحامضي قليلاً) سداسي التناسق إذ يأخذ شكل ثماني السطوح وتنتج معقدات أحادية النواة كما مبين في

أدناه:



(X = CH_3COO^- or المعقد 1 و 2 و 5 و 6)

المعقد 7 و 8



المعقد 3 و 4

5. استناداً إلى النتائج التي تم الحصول عليها من درجة الإنصهار أو التفكك والتوصيلية الكهربائية بعد تشيع المعقدات بأشعة الليزر لوحظ أن المعقدات الصلبة لم تتأثر.
6. أظهرت نتائج الفعالية مضادة البكتريا أن معقد 4 فقط يكون فعالاً ضد بكتريا *Streptococcus faecalis* أما البكتريا الأخرى (*Escherichia coli* و *Pseudomonas auruginosa* و *Staphylococcus aureus* و *Proteus mirabilis*) فتمتلك مقاومة ضد جميع المعقدات، أي إن المعقدات لا تمتلك فعالية مضادة البكتريا إنجاهها. كما لوحظ أن التركيز المثبط من المعقد في أعلاه مضادة بكتريا *Streptococcus faecalis* يكون 500 مايكروغرام/مل.
7. أظهرت نتائج الفعالية المضادة للفطريات أن جميع المعقدات لا تؤثر على الفطريات المستخدمة قيد الدرس أي بعبارة أخرى أن الفطريات تمتلك مقاومة تجاه هذا النوع من المعقدات.
8. أظهر المعقد (4) فعالية على مسحات أخذت من خراج السن، ف لوحظ أن الذكور فوق سن 19 يكونون أكثر عرضة للإصابة بهذا المرض من الذكور دون سن 19. كما لوحظ أن استجابة المسحات مختبرياً للمعقد يكون أعلى بالنسبة للذكور فوق سن 19 من الذكور دون سن 19. كما إن أعلى نسبة استجابة لعلاج المسحات مختبرياً للذكور فوق سن 19 قد وصلت 65% باستخدام تركيز 500 مايكروغرام/مل في حين للذكور دون سن 19 فأعلى استجابة كانت 30% باستخدام تركيز 500 مايكروغرام/مل ، ولوحظ أن النساء فوق سن 19 أكثر عرضة للإصابة بخراج السن من النساء دون سن 19، وقد وجد أن أعلى نسبة استجابة كانت 86% بتركيز 500 مايكروغرام/مل ، أما النساء دون سن 19 فبلغت أعلى نسبة استجابة 78% بتركيز 500 مايكروغرام/مل.
9. أظهرت المواد العطارية A و B المستخدمة أيضاً فعالية جيدة تجاه جميع أنواع البكتريا فقد بلغت أعلى نسبة تثبيط لبكتريا *Staphylococcus aureus* 43% باستخدام A و 65% باستخدام B، في حين بلغت النسبة 78% باستخدام A و 43% باستخدام B ضد بكتريا *Streptococcus Faecalis*، كما بلغت النسبة 34% باستخدام A أو B ضد بكتريا *Escherichia coli*، كما بلغت النسبة 43% باستخدام A و 52% باستخدام B ضد بكتريا *Pseudomonas auruginosa*، في حين بلغت 86% باستخدام A و 43% باستخدام B ضد بكتريا *Proteus mirabilis* إذ كان التركيز الكفوء في تثبيط البكتريا هو 500 مايكروغرام/مل. أظهرت المواد العطارية A و B فعالية جيدة إذ لوحظ أنها تعالج خراج السن مختبرياً بشكل كفوء جداً. كذلك أظهرت المواد العطارية ولاسيما A فعالية متميزة

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عن B فضلاً عن جميع المعقدات قيد الدرس لذا نرجح استخدام المادّة العطاريّة A لعلاج
المرض بكفاءة عالية جداً وبفترات زمنيّة قليلة بأخذ جرعة مناسبة.

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تحضير معقد القصدير - السستائين ودراسة العوامل المؤثرة على ناتج تعليمه بنظير التكنشيوم - 99م

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ABSTRACT

Cysteine complex preparation can be labeled with technetium – 99m of a high labeling yield ($\geq 95\%$). Results obtained proved that the best amount of the preparation reactants (5 mg cysteine and and 250 μg tin chloride) at optimal pH (pH = 8.0) with the best labeling yield using paper chromatographic technique. Results cleared that the reaction medium at alkaline pH (pH = 8.0) showed its optimum pH among other values studied depending on the high percentage of the labeling yield ($\geq 95\%$). Both, the amounts of chelating agent and reducing agent have been shown no effect on the percentage of the labeling yield. The persistence of high labeling yield for 4 hours with a fast formation rate of the labeled complex is a good indication to its stability and efficiency of labeled preparation. These chemical specifications led to its suitability for radiodiagnosis examination in nuclear medicine centers.

الخلاصة

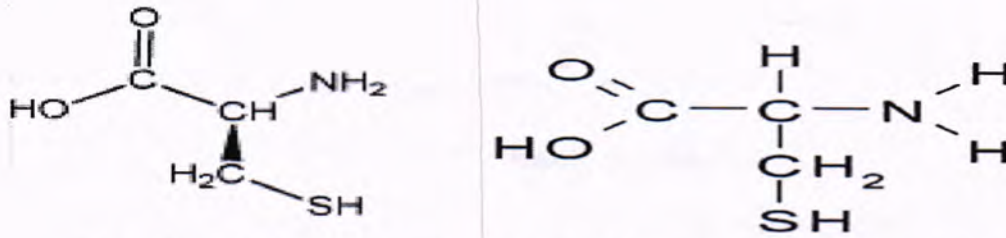
تم تحضير مستحضر صيدلاني من معقد السستائين يمكن تعليمه بنظير التكنشيوم -99 م وبنسبة مئوية عالية ($\leq 95\%$) . اثبتت النتائج بأن أفضل مكونات المستحضر المتفاعلة (5 ملغم سستائين و 250 مايكروغرام كلوريد القصديروز المائي) وبدالة أسيه مناسبة (pH = 8.0) قد أعطت أفضل نتائج لتعليم المعقد باستخدام تقنية الفصل الورقي. أظهرت نتائج تأثير قيمة الدالة الأسيه في محيط قاعدي (pH = 8.0) أفضليتها عن بقية القيم المستخدمة في الدراسة مع إمكانية الحصول على نسبة مئوية عالية لتعليم المعقد ($\leq 95\%$) . كما لوحظ ومن خلال النتائج بأنه ليس هنالك تأثير واضح لكمية العامل المخليبي والعامل المختزل (ضمن حدود الدراسة) على النسبة المئوية لتعليم المعقد. بينت النتائج بقاء النسبة المئوية العالية للمعقد المعلم ولفترة تزيد على 4 ساعات مع سرعة تكونه دليل على ثباتية وكفاءة المستحضر المعلم وإمكانية استخدامه لأجراء الفحوصات الخاصة بالتشخيص الطبي لدى مراكز الطب النووي .

المقدمة

أصبحت النظائر المشعة ومنها نظير التكنيشيوم -99 م من النظائر الرئيسية في الكثير من التطبيقات الطبية في مجال الطب النووي ، اذ يشغل التكنيشيوم -99م النسبة الأكبر من مجمل تطبيقات النظائر المشعة في هذا المجال ، ثم يليه اليود ولاسيما اليود -131 الذي يستخدم لأغراض العلاج الطبي . وقد قام العديد من الباحثين بتعليم عدد كبير من المعقدات بنظير التكنيشيوم - 99م (Tc^{99m}) لغرض تشخيص الأورام السرطانية والعديد من الحالات المرضية الأخرى .

ونظرا للتوسع في التشخيص والتصوير الأيضي ، فإن تعليم الأحماض الأمينية بالنظائر المشعة قد اكتسبت اهتمام سريري واسع، وقام العديد من الباحثين المهتمين في الصيدلة الإشعاعية باستخدام الأحماض الأمينية ومشتقاتها للكشف عن الخلايا السرطانية مثل تعليم الميثيل تايروسين باليود - 123 لتشخيص الأورام السرطانية (1). وفيما يخص تعليم الحامض الأميني السستائين (شكل رقم 1) (1) ، الذي يعتبر من الأحماض الأمينية غير الأساسية (أي من الأحماض الأمينية التي تصنع داخل الجسم) (2) ، فقد قام العديد من الباحثين بتعليم هذا الحامض الأميني بنظير التكنيشيوم - 99م من أجل تحضير مستحضرات صيدلانية معلمة تستخدم في التشخيص الطبي . ففي عام 1997 قام العالم Wang A. بأجراء مقارنة في التوزيع البايولوجي بين مركب السستائين المعلم بنظير التكنيشيوم - 99م و I^{131} - Hippuran (3). وقام الباحث Moran JK. وجماعته عام 1999 باستخدام مركب السستائين المعلم بنظير التكنيشيوم - 99م في تشخيص وظيفة الكليتين (4). كما أجريت دراسة على الفئران من قبل الباحث Mangera K. وجماعته عام 2000 الذي لاحظ تجمع مركب السستائين المعلم بنظير التكنيشيوم - 99م في الكليتين بنسبة 57 % بعد مرور 30 دقيقة من الزرق (5). وقام الباحث Wang A. عام 2002 بتعليم الحامض الأميني السستائين بنظير التكنيشيوم 99م لغرض استخدامه في تشخيص الخلل في النبيبات الكلوية وعملية الطرح (6) . وفي عام 2004 تم تعليم هذا الحامض الأميني من قبل الباحث Taylor A. وجماعته لغرض استخدامه في تشخيص وظيفة الكليتين (7). وأشار الباحث Y.P. Quinan وجماعته عام 2006 ان تعليم الحامض الأميني السستائين بخطوات بسيطة من الممكن استخدامه في تشخيص الأورام السرطانية ومنها سرطان الثدي (2).

أن جميع الدراسات اعلاه التي أجريت كانت تعتمد بالدرجة الأساس على تعليم مركب السستائين في وسط حامضي . أما الهدف من هذه الدراسة فهو تحضير مستحضر السستائين المعلم بنظير التكنيشيوم - 99م في ظروف مناسبة وفي دالة أسية قاعدية لغرض استخدامه في تشخيص سرطان الثدي .



شكل 1: يمثل مركب السستائين 2-Amino-3-Mercaptopropionic acid

المواد وطرائق العمل

طريقة تحضير المستحضر:

تم تحضير مستحضر السستائين بطريقة مبسطة وسريعة وذلك بأذابة كمية مناسبة من الحامض الأميني السستائين في حجم معين من محلول بيكاربونات الصوديوم من أجل تهيئة وسط قاعدي مناسب وبدالة أسية قاعدية. بعدها يضاف حجم مناسب من العامل المختزل كلوريد القصديروز الثنائي. ويتم امرار مزيج المواد المتفاعلة عبر اغشية فائقة المسامية (0.2 مايكرون) ، ويتم تعليم هذا المعقد بأخذ حجم معين من المستحضر النهائي وتضاف له كمية مناسبة من النشاط الإشعاعي من مستحلب التكنيشيوم - 99م ويترك المعقد المعلم لفترة زمنية معينة ، بعدها تجرى عليه طرائق التحليل الراديوكيميائية لأيجاد النقاوة الراديوكيميائية للمعقد المعلم باتباع تقنية الفصل الورقي.

طرائق التحليل الراديوكيميائية :

تم استخدام ورق واتمان من نوع 3mm (Whatman 3mm chromatography) كطور ثابت والأسيتون كطور متحرك . وهذه الطريقة مستخدمة لفصل نظير التكنيشيوم - 99م غير المتفاعل عن مركب السستائين المعلم بنظير التكنيشيوم - 99م . يقطع الطور الثابت الى شرائح عرضها (20 ملم) وطولها (280 ملم) ، ثم تعين نقطة البداية للنموذج المراد فحصه على أحد طرفي الشريحة وبعدها يتم وضع أصغر حجم من النموذج على الشريحة وفي نقطة البداية ، وتوضع الشريحة في محلول الأسيتون وبصورة عمودية ويستمر الفصل حتى وصول الطور المتحرك الى نقطة النهاية، حيث أن التكنيشيوم غير المتفاعل يتحرك مع الأسيتون بينما يبقى التكنيشيوم المختزل المرتبط بالمعقد في البداية. ولتحديد نسبة التكنيشيوم المختزل غير المرتبط بالمعقد يتم استخدام محلول ملح الطعام الفسيولوجي (0.9% NaCl sol.) كطور متحرك ، حيث يبقى التكنيشيوم المختزل غير المرتبط بالمعقد في البداية بينما يتحرك التكنيشيوم المرتبط بالمعقد الى نقطة النهاية ، عند الانتهاء من عملية الفصل يتم تجفيف وتقطيع الشرائح وثم قياس النشاط

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النتائج والمناقشة

تم تحضير مستحضر صيدلاني مكون من 5 ملغم من الحامض الأميني السستائين و 250 مايكروغرام من كلوريد القصدير المائي وفي وسط قاعدي ($pH = 8.0$) ، وقد أظهرت هذه الصيغة الجديدة النتائج التالية:-

جدول 1: تأثير قيمة الدالة الأسية (pH) على النسبة المئوية لناتج تعليم مركب السستائين المعلم بنظير التكنيشيوم - 99م بعد مرور 30 دقيقة من التعليم باستخدام تقنية الفصل الورقي

قيمة الدالة الاسية	النسب المئوية للنشاط الإشعاعي للأجزاء المختلفة		
	تكنيشيوم مختزل	تكنيشيوم غير مختزل	تكنيشيوم مرتبط مع السستائين
6.0	31.5	2.2	66.3
7.0	10.6	1.9	87.5
7.5	4.1	1.9	94.0
8.0	1.8	1.7	96.5
8.5	7.2	5.4	87.4

جدول 2: تأثير كمية العامل المختزل على النسبة المئوية لناتج تعليم مركب السستائين المعلم بنظير التكنيشيوم - 99م بعد مرور 30 دقيقة من التعليم باستخدام تقنية الفصل الورقي

كمية العامل المختزل (كلوريد القصدير / مايكروغرام)	النسب المئوية للنشاط الإشعاعي للأجزاء المختلفة		
	تكنيشيوم مختزل	تكنيشيوم غير مختزل	تكنيشيوم مرتبط مع السستائين
100	2.0	2.4	95.6
200	1.9	2.2	95.9
250	1.8	1.7	96.5
350	1.9	1.7	96.4

جدول 3: تأثير كمية العامل المخليبي (السستائين) على النسبة المئوية لناتج تعليم مركب السستائين المعلم بنظير التكنيشيوم - 99م بعد مرور 30 دقيقة من التعليم باستخدام تقنية الفصل الورقي

كمية العامل المخليبي (السستائين / ملغم)	النسب المئوية للنشاط الإشعاعي للأجزاء المختلفة		
	تكنيشيوم مختزل	تكنيشيوم غير مختزل	تكنيشيوم مرتبط مع السستائين
2.5	2.0	2.2	95.8
5.0	1.8	1.7	96.5
7.5	2.0	2.3	95.7
10.0	2.1	2.4	95.5

جدول 4 : سرعة تكوين مركب السستائين المعلم بنظير التكنيشيوم - 99م بفترات زمنية مختلفة باستخدام تقنية الفصل الورقي

النسب المئوية للنشاط الإشعاعي للأجزاء المختلفة			الوقت بعد التعليم / دقيقة
تكنيشيوم مرتبط مع السستائين	تكنيشيوم غير مختزل	تكنيشيوم مختزل	
88.1	6.6	5.3	15
96.5	1.7	1.8	30
96.7	1.6	1.7	60
96.8	1.6	1.6	240
82.4	6.2	11.4	1440

تم استخدام طريقة الفصل الورقي على ورق ترشيح وإتمان نوع 3mm كطور ثابت والأسيتون ومحلول ملح الطعام 0.9 % كطور متحرك لحساب النسب المئوية للمتغيرات الخاصة لتحضير مستحضر السستائين المعلم بنظير التكنيشيوم - 99 م . كانت النتائج التي تم الحصول عليها والمبينة في الجدول رقم 1 تشير الى ان النسبة المئوية للمركب المعلم تزداد مع زيادة قيمة الدالة الأسية وصولاً الى الأفضل (المثلى) وهي الدالة الأسية 8 ($pH = 8$) بدليل انخفاض النسبة المئوية للمركب المعلم في الدالة الأسية 8.5 وهذا يدل على ان الدالة الأسية مؤثرة ضمن حدود معينة كما تشير الى ان افضل نسبة مئوية للمعقد المعلم تصل الى 96.5 % عند الدالة الأسية 8.0، وان نسبة التكنيشيوم الغير مختزل أقل من 2 % عند استعمال كمية ثابتة من العامل المخليبي (5 ملغم) والعامل المختزل (250 مايكروغرام) ، اما الجدول رقم 2 يوضح تأثير كمية العامل المختزل على النسبة المئوية للمعقد المعلم بعد تثبيت الدالة الأسية ($pH = 8$)، حيث تشير النتائج الى انه لا يوجد تأثير واضح لكمية العامل المختزل على النسبة المئوية للمعقد و بالامكان استخدام مدى واسع (100 - 350 مايكروغرام) الذي يمكن ان يعطي ناتج تعليم عالي ، ويوضح جدول رقم 3 تأثير كمية العامل المخليبي على النسبة المئوية للمعقد المعلم بعد تثبيت الدالة الاسية ($pH = 8.0$) والعامل المختزل (250 مايكروغرام) ، حيث انه يمكن استخدام كميات مختلفة من العامل المخليبي (2.5 - 10.0 ملغم) مع بقاء النسبة المئوية العالية لناتج التعليم للمعقد المعلم .

اما نتائج استقرارية المعقد المعلم فانها موضحة في جدول رقم 4 ، حيث تظهر النتائج بأن النسبة المئوية للمعقد المعلم عالية (96.5 %) بعد اكثر من 4 ساعات وهذا دليل على استقرارية المعقد المعلم وكفاءته في امكانية اجراء فحوصات التشخيص الطبي في مراكز الطب النووي .

ان اهم الاستنتاجات التي يمكن الاشارة اليها من خلال نتائج الدراسات الراديوكيميائية امكانية استعمال الدالة الأسية القاعدية من 7.5 الى 8.0 مع امكانية استعمال كميات مختلفة من العامل المختزل والعامل المخليبي للحصول على مستحضر معلم ذو ناتج تعليم واستقرارية عاليين . وكذلك بينت نتائج البحث بقاء النسبة المئوية للمعقد المعلم ثابتة لفترة اربع ساعات وهي فترة مناسبة جدا

لأجراء فحوصات التشخيص الطبي في مراكز الطب النووي .توصي الدراسة الى ضرورة إجراء تجارب التوزيع البايولوجي على الحيوانات المختبرية، ومن ثم إجراء جميع فحوصات السيطرة النوعية الدسورية، ليتسنى بعد ذلك إجراء التقييم السريري للمستحضر على المرضى في مراكز الطب النووي.

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دراسة تأثير بعض مشتقات حامض النيكوتيك على فعالية انزيم ALP في امصال النساء الاصحاء و المصابات بداء الفشل الكلوي المزمن

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ABSTRACT

The aim of this research is studying the effect of new synthesized nicotinic acid derivatives on alkaline Phosphatase activity (ALP) The compound included: hydrazide, and 5 Schiff base and 4 oxadiazole obtained from ring closed of Schiff bases by acetic anhydride. ALP activity was measured in sera of 17 women with chronic Renal Failure & 75 healthy women as control group. The activity of enzyme was inhibited when incubated the derivatives with the enzyme in the sera of patients depending upon the type of the compound under study (29-65)% the percent of inhibition increased (34.7-69.9)% with increasing inhibitory concentration. Also, the type of inhibition & inhibition constant k_i and V_{max} in the presence of inhibitor was determined. The effect of Enz, Sub conc., pH, temperature and incubation time were studied on the rate of enzyme reaction in the presence inhibitor under study in both sera of normal & Patient. Kinetic parameter (K_{abs} , K_{+1} , K_a & K_d) were determined in the inhibitor R2 in both sera of normal & patient also studied the thermodynamic parameters of std. state (ΔG° , ΔS° , ΔH°) and transition state (ΔG^* , ΔS^* , ΔH^*).

الخلاصة

هدف هذا البحث دراسة تأثير بعض المشتقات المحضرة حديثاً لحامض نيكوتيك على انزيم الفوسفاتيز القاعدي ALP التي تضمنت الهيدرازيد وخمسة قواعد شيف واربعة اوكسادايازول ناتجة من الغلق الحلقي لقواعد شيف بواسطة حامض الخليك اللامائي ، تم قياس فعالية ALP في امصال 17 من النساء المصابات بالفشل الكلوي المزمن و 75 امرأة من الاصحاء كمجموعة سيطرة. لوحظ وجود انخفاض فعالية الانزيم عندما حضن معه المركبات اعلاه بمقدار 29% - 65%. اعتماداً على نوع المركب و لوحظ زيادة النسبة المئوية للتثبيط 34.7% - 69.9% مع زيادة تركيز المثبط. تم قياس وتحديد نوع التثبيط، ثابت التثبيط K_i و السرعة العظمى للمثبط V_{max} . مع دراسة تأثير تركيز الانزيم ، تركيز المادة الاساس، الدالة الحامضية ، درجة الحرارة ، زمن التفاعل على سرعة التفاعل الانزيمي بوجود المثبطات قيد الدراسة في كل من امصال المرضى

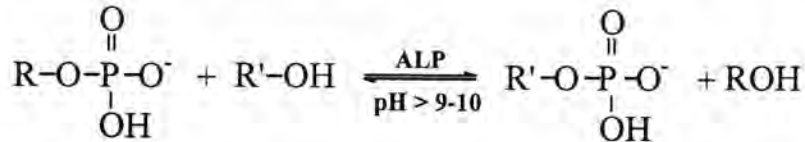
دراسة تأثير بعض مشتقات حامض النيكوتك على فعالية انزيم ALP في امصال النساء الاصحاء و المصابات بداء الفشل الكلوي المزمن

رضا وفاتن ورولا

والاصحاء. اجريت دراسة حركية وحساب المعاملات الحركية (K_{abs} , K_{+1} , K_a & K_d) بوجود المثبط R_2 في امصال المرضى والاصحاء وكذلك درست المعاملات الترموداينميكية للحالة القياسية (ΔG° , ΔS° , ΔH°) والحالة الانتقالية (ΔG^* , ΔS^* , ΔH^*).

المقدمة

يعتبر الفوسفاتيز القاعدي Ortho-phosphoric monoester phosphhydrolase أنزيم غير متخصص وذلك لانه ينتمي إلى مجموعة الأنزيمات المحللة للعديد من استرات الاورثوفوسفات عند pH=9-10.5 يقوم بنقل مجموعة الفوسفات من جزيئة إلى أخرى (1) مخلفاً الكحول ومركبات الفوسفات الثانوية حسب المعادلة الكيميائية التالية (2):



ثبت ان الانزيم موجود في مصل الدم وفي جميع أنسجة الجسم لاسيما خلايا الأغشية البلازمية، ونسبته عالية في الغشاء المبطن للأمعاء (3) واقنية الكلية (4)، والعظم (الخلايا العظمية) (5)، والكبد (6)، والمشيمة، وغدد الثدي المنتجة للحليب (7)، وفي الأنسجة النباتية مثل السبانخ، والتغناغ البستاني والطماطم والشاي، والبطاطا، وفي جذور النباتات مثل الذرة، وبعض أنواع الأزهار (8). يمتلك الانزيم أربعة مماثلات انزيمية تنشأ من أربعة جينات منفصلة وهي:

المشيمة Placental، الأمعاء Intestinal، الكبد Liver، الكلية Kidney، العظم Bone إن (6). الفوسفاتيز القاعدي ذو المنشأ الكلوي لا يظهر في أمصال دم الأصحاء إلا انه يظهر في أمصال الأشخاص المصابين بأمراض كلوية

إن زيادة فعالية أنزيم الفوسفاتيز القاعدي في مصل الدم قد يعزى إلى حالات مرضية كثيرة وهناك سببان رئيسيان يفسران ازدياد الفعالية إضافة إلى أسباب ثانوية أخرى اضطرابات وامراض العظام وامراض الكبد، والاورام الخبيثة.

ان من أهم الخصائص الحركية التي تم دراستها للانزيم هي حساب قيم ثابت ميكالس - منتن (8) (K_m Michals-Menth'on) ان حجم ومكونات سوائل الجسم تنظم من قبل الكلتيان وبالتالي تحافظان على الضغط والتوازن مابين السوائل والالكتروليات في الجسم وينتج العجز الكلوي من عدة امراض أهمها التهاب الأنابيب الكلوية، حصى الكلى، داء السكري، التهاب الكلتيان الوراثي

(9) يعد حامض النيكوتيك (النياسين) من المركبات الضرورية للجسم والتي لا يستطيع الجسم ان يصنعها ولمشتقات استخدامات طبية ودوائية متعددة كمخدر موضعي ، واثبتت ان لمشتقات الهيدرازيد المغلفة حلقيا فعاله ضد الجراثيم و بكتريا السل(10)
إن الهدف من البحث هو :

- دراسة تأثير بعض مشتقات حامض النيكوتيك على فعالية أنزيم الفوسفاتيز القاعدي في امصال دم النساء الأصحاء والمصابات بداء الفشل الكلوي، وداسة نوع التنشيط و الظروف المثلى لارتباط الأنزيم مع المادة الأساس بوجود هذه المركبات.
- دراسة حركيات ارتباط الأنزيم مع المادة الأساس بوجود مشتق الهيدرازيد لحامض النيكوتيك وتحديد مرتبة التفاعل، وحساب المعاملات الثرموديناميكية للحالة القياسية والانتقالية على التوالي $(\Delta H^0, \Delta G^0, \Delta S^0)$, $(\Delta E_a^*, \Delta H^*, \Delta G^*, \Delta S^*)$

المواد وطرائق العمل

أجريت الدراسة على مجموعتين من النساء، المجموعة الأولى 75 امرأة من الأصحاء (Control) حيث تم الحصول على عينات الدم من طالبات الجامعة المستنصرية تراوحت مدى اعمارهن (18-45) سنة. أما المجموعة الثانية 17 امرأة مصابات بداء الفشل الكلوي، وقد تم الحصول على عينات الدم من مستشفى الجراحات التخصصية في مدينة الطب لنساء تتراوح أعمارهن (22-50) سنة وذلك بعد إجراء الفحوصات المختبرية والتشخيص السريري من قبل الأطباء الاختصاص. وحضرت أمصال الدم كالاتي: تم سحب (5ml) من دم الوريد من الذراع وتركبت العينة لمدة (15) دقيقة بدرجة حرارة الغرفة ليتم التخرثر، توضع الأنبوبة في جهاز الطرد المركزي بسرعة (3000) دورة في الدقيقة لمدة (15) دقيقة، ومن ثم تم سحب مصل الدم وأجريت عليه التجارب المختلفة في يوم السحب نفسه.

تعيين مستوى فعالية أنزيم الفوسفاتيز القاعدي

تم تعيين فعالية أنزيم الفوسفاتيز القاعدي في مصل الدم بطريقة King & Armstrong للنساء الاصحاء والمصابات بداء الفشل الكلوي بوجود وغياب المركبات المحضرة
تعيين النسبة المئوية للتنشيط والاسترجاعية

تم حساب النسبة المئوية للتنشيط والاسترجاعية لكل مثبت من القوانين التالية :

$$\text{التنشيط \%} = \frac{\text{الفعالية الانزيمية بوجود المثبط}}{\text{الفعالية الانزيمية بغياب المثبط}} \times 100$$

$$\text{الاسترجاعية \%} = 100 - \text{نسبة التنشيط \%}$$

ويقصد بالاسترجاعية النسبة المئوية لما تبقى من الفعالية الانزيمية الحقيقية للأنزيم بوجود المثبط

دراسة تأثير بعض مشتقات حامض النيكوتيك على فعالية انزيم ALP في امصال النساء الاصحاء و المصابات بداء الفشل الكلوي المزمن

رضا وفاتن ورولا

تعيين نوع التثبيط

تمت دراسة التأثير التثبيطي للمركبات المشتقة من حامض النيكوتيك باستخدام تركيزين مختلفين لكل منهما $[10^{-8}, 10^{-5}]$ M مع سبعة تراكيز مختلفة من المادة الأساس. تم تحديد نوع التثبيط اعتماداً على طريقة (Lineweaver-Burk) بين $(1/v)$ و $(1/[S])$ (11).

تم تحديد ودراسة تأثير الظروف المثلى لارتباط الأنزيم مع المادة الأساس بوجود المثبطات قيد الدراسة ($R_{18}-R_{15}, R_8-R_4, R_2$) في مصل الدم وشملت الظروف التالية:
(تأثير تركيز المادة الأساس الأمثل وحجم الانزيم الأمثل والاس الهيدروجيني الأمثل وزمن الحضان الأمثل ودرجة الحرارة المثلى).

تم تحديد مرتبة التفاعل الأنزيمي من خلال متابعة التفاعل الأنزيمي في درجات حرارية مختلفة (37,25,15,10) °م وباستخدام التركيز الأمثل من المادة الأساس $[7 \times 10^{-3} M]$ ، والحجم الأمثل للأنزيم $\mu l (62,59)$ لكل من مصل دم النساء الأصحاء والمصابات بداء الفشل الكلوي على التوالي، والأس الهيدروجيني الأمثل (10.4)، وقد طبقت المعادلات العامة لمرتبة التفاعل وكذلك المعادلات ذات العلاقة بالأنزيم مباشرة.

تم قياس الفعالية الأنزيمية لأنزيم ALP مع المادة الأساس في مصل دم النساء الأصحاء والمصابات بداء الفشل الكلوي بوجود المثبط (R_2) نيكوتيك هيدرازين بتركيز $[10^{-5} M]$ واستخدام الظروف المثلى وفي أزمان مختلفة (45,40,35,30,25,20,15,10) دقيقة، أعيدت التجربة باستخدام درجات حرارية مختلفة (55,45,37,25,15,10) °م لحساب أفضل ارتباط للأنزيم مع المادة الأساس عند كل درجة حرارة لكل من الأزمان المختلفة.

أجريت الدراسات الترموديناميكية للأنزيم بوجود المثبط (R_2) بتركيز $[10^{-5} M]$ في درجات حرارية مختلفة (5,15,25,37) °م تم الاستعانة بمعادلة فانت-هوف (Vant-Hoff plot) وأرينيوس في إيجاد قيم المعاملات الترموديناميكية للحالة المستقرة والحالة الانتقالية للأنزيم.

الحسابات (12)

1- تم حساب الثوابت الترموديناميكية للحالة القياسية باستخدام معادلة فانت-هوف، حيث ترسم

العلاقة بين لوغاريتم ثابت التوازن ($\ln K_a$) الذي تم حسابه في درجات حرارية مختلفة

(37,25,15,5) °م ضد معكوس درجة الحرارة بالكلفن ($1/T$) حسب المعادلة التالية:

$$\ln K_a = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT}$$

حيث: ΔS^o = التغير في الانتروبي في الحالة القياسية.

ΔH° = التغير في الإنثالبي في الحالة القياسية.

R = الثابت العام للغازات (8.314 جول/مطلقة.مول=1.987 سعرة/مول.مطلقة=0.082 لتر.جو/مول.مطلقة).

2- تم حساب الثوابت الترموديناميكية للحالة الانتقالية باستخدام معادلة أرينيوس، حيث ترسم العلاقة بين ثابت السرعة $(\ln k_{+1})$ ضد معكوس درجة الحرارة، حيث نحصل على علاقة خطية وفق معادلة أرينيوس التالية:

$$\ln K_{+1} = \ln A - \frac{E_a}{RT}$$

حيث: A = ثابت أرينيوس.

E_a = طاقة التنشيط لتفاعل الارتباط ونحصل عليه من ميل الخط المستقيم.

النتائج والمناقشة

تم قياس مستويات الفوسفاتيز القاعدي في مصل الدم حسب طريقة King & Armstrong الجدول (1) يوضح ارتفاع معدل قيم الفعالية الانزيمية للنساء المصابات بداء الفشل الكلوي 38.39 K.A.U/100ml نسبة الى معدل قيم الفعالية الانزيمية للنساء الأصحاء وكانت 9.06 K.A.U/100ml

جدول 1: الفعالية الأنزيمية للفوسفاتيز القاعدي في مصل النساء الأصحاء و المصابات بداء الفشل الكلوي باستخدام طريقة التحليل الطيفي

المجموعة	العدد	مدى العمر/سنة	فعالية الفوسفاتيز القاعدي (K.A.U./100ml) والمدى		القيم الطبيعية (K.A.U./100ml)
			المعدل		
نساء اصحاء	75	18-45	9.06	5.8-13.0	3-13
نساء مصابات بداء الفشل الكلوي	17	22-50	38.93	26.8-65.7	3-13

تم أخذ عدد من قواعد شيف المشتقة من حامض النيكوتيك (R_4-R_8) كما تم أخذ عدد من المشتقات ($R_{15}-R_{18}$) إضافة إلى مشتق الهيدرازيد (R_2) بسلسلة من التراكيز (10^{-8} , 10^{-7} , 10^{-6} , 10^{-5}) باستخدام DMSO كمذيب ولغرض التخفيف، بعد أن تم قياس تأثير DMSO التثبيطي والذي بلغ $(2.36 \pm 0.8\%)$. الجدولان 2,3 يبين انخفاض فعالية الانزيم عند حضنه مع كل مركب وعليه اعتبرت المركبات مثبطات جيدة حيث بلغ مدى النسبة المئوية للتثبيط $(29-65\%)$ عند استخدام التراكيز الأعلى للمثبطات (10^{-5} M) في مصل دم النساء الأصحاء، أما في مصل دم النساء المصابات بداء الفشل الكلوي فقد بلغ مدى النسبة المئوية للتثبيط $(34.7-69.6\%)$. وجد إن التأثير التثبيطي للمركبات يزداد بزيادة تركيز المثبطات في كل من مصل الدم للأصحاء

دراسة تأثير بعض مشتقات حامض النيكوتيك على فعالية أنزيم ALP في امصال النساء الاصحاء و المصابات
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رضا وفاتن ورولا

والمصابات بداء الفشل الكلوي كما أن التأثير التثبيطي للمركبات (المثبطات) يظهر بصورة أعلى في مصل النساء المصابات بداء الفشل الكلوي مما هو عليه في النساء الأصحاء. ان اختلاف التأثير التثبيطي المتغير للمركبات قيد الدراسة على فعالية أنزيم الفوسفاتيز القاعدي يمكن أن يعزى إلى أن الأنزيم يتكون من عدد من الأنزيمات المماثلة (Isoenzymes) التي تختلف في معدل تأثرها بالمثبطات، كذلك فإن هذا التغير قد يعزى أيضاً إلى فعالية المجاميع المؤثرة في هذه المثبطات على المركز الفعال للأنزيم، وكما أن الأنزيم قد يتعرض إلى تغير في تركيبه الفراغي (Stereostructure) خلال مراحل تطور المرض مما يؤدي إلى سهولة ارتباط المثبطات بالأنزيم وبالتالي تعطي تثبيط أعلى (13)

كما يلاحظ أن الفعالية التثبيطية لمركب (R_2) لأنزيم الفوسفاتيز القاعدي تكون عالية، وقد يعود ذلك إلى وجود الزوج الإلكتروني الموجود على ذرة نتروجين مجموعة الأمين ($-NH_2$) الذي يكون ذا حرية عالية، وبالتالي سهولة ارتباط المركب (R_2) مع المواقع الفعالة في الأنزيم، ذلك أن الموقع الفعال للأنزيم يحمل شحنة موجبة. أما بالنسبة لمشتقات حامض النيكوتيك والمتمثلة بقواعد شيف فإن المركبات (R_5, R_4) تحتوي على مجاميع ساحبة (أيون الكلوريد ومجموعة النترو على التوالي) والتي لها القابلية على سحب المزدوجات الإلكترونية على ذرة النتروجين ($-NHN=C-$) وتحويلها إلى شحنات سالبة موجودة على هذه المجاميع الساحبة، وبما أن الشحنات السالبة هي أكثر فعالية للارتباط مع الأنزيم أكثر من المزدوجات الإلكترونية الحرة، لذا فإن المركبات (R_5, R_4) تعطي فعالية تثبيطية عالية مقارنةً بالمركبات (R_8, R_7, R_6) التي تحتوي على مجاميع دافعة للإلكترونات (مجاميع البايروولدين والهيدروكسيل على التوالي)، حيث سيكون تأثيرها التثبيطي أقل من تأثير المجاميع الساحبة، ويعود ذلك إلى عدم قدرتها على توليد الشحنات السالبة والتي تكون ذات فعالية أكبر للارتباط مع الأنزيم من المزدوجات الإلكترونية لأن الزوج الإلكتروني عادةً يشارك في تكوين أواصر الرزونانس أي أنها أقل حرية في الحركة والتأثير⁽¹⁾. أما مركبات الغلق الحلقي لقواعد شيف والتي تشمل ($R_{18}, R_{17}, R_{16}, R_{15}$) فقد أظهرت فعالية تثبيطية أقل من مركبات قواعد شيف والهيدرازيد الأصلي، وقد يعود السبب في ذلك إلى الإعاقة الفراغية التي يعاني منها الزوج الإلكتروني الموجود على ذرة النتروجين ($C=N$) مما يعيق ارتباطه مع الموقع الفعال للأنزيم ذلك أن تهجين ذرة النتروجين أصبح (sp^2) مما يجعل شكل الجزيئة مستوي وتصبح جميع المجاميع بنفس المستوي وبالتالي يعاني من إعاقة فراغية تعيق ارتباط هذه المركبات بالأنزيم بحرية مما يؤدي إلى تثبيط أقل، أي أن عملية تطويق هذه المركبات من قبل المجاميع الفعالة ($C=N, C=O$) يكون ضعيف بسبب الإعاقة الفراغية (14)

تم تعيين قيمة كل من V_{max} , K_i وذلك من خلال قياس فعالية الأنزيم بطريقة كينك و بيلفيلد (King and Belfield)، بوجود المثبطات وغيابها، وذلك باستخدام تراكيز مختلفة من المادة الأساس تحت الظروف المثلى للتفاعل الأنزيمي وباستخدام معادلة لينوفير-برك، وكما موضح في الجدول (3,4) الذي يبين ثبوت قيم K_m بوجود وغياب المثبطات أما V_{max} فقد انخفضت مع زيادة تركيز المثبط، نستدل من ذلك ان نوع التثبيط للمركبات (R_{18} - R_{15} , R_8 - R_4 , R_2) هو تثبيط من نوع اللاتنافسي (non-competitive). إن المثبط اللاتنافسي يرتبط مع الأنزيم بصورة مستقلة وعكوسة بموقع ما على سطح الأنزيم وعليه لا يمكن زحزحة المثبط من موقعه بزيادة تركيز المادة الأساس (15)

جدول 2: يبين نوع التثبيط بوجود (10^{-8} - 10^{-5}) M من المركبات لأنزيم الفوسفاتيز القاعدي في مصل دم النساء الأصحاء

نوع التثبيط	Km بوجود المثبط $\times 10^{-3}$	بوجود المثبط (I)				بغيا ب المثبط		اسم المركب	رمز المركب
		$[I]=10^{-8}$ M	$[I]=10^{-7}$ M	$[I]=10^{-6}$ M	$[I]=10^{-5}$ M	V_{max}	Km (M) $\times 10^{-3}$		
		V_{maxi}	V_{maxi}	V_{maxi}	V_{maxi}				
لاتنافسي	2.564	13.30	12.50	11.76	10.80	15.38	2.564	Nicotinoyl hydrazide	<u>R₂</u>
لاتنافسي	2.702	13.30	10.25	9.09	6.45	16.6	2.702	7-Chloro isatindine nicotinoyl hydrazide	R ₄
لاتنافسي	3.448	10.52	8.33	6.89	6.06	18.18	3.448	p-Nitro benzididene nicotinoyl hydrazide	R ₅
لاتنافسي	3.170	14.28	12.50	11.11	10.00	18.18	3.170	2-Pyrolidine nicotinoyl hydrazide	R ₆
لاتنافسي	2.564	12.50	11.11	10.00	9.09	15.38	2.564	p-Amin benzididene nicotinoyl hydrazide	R ₇
لاتنافسي	2.857	12.50	11.42	10.52	9.09	16.6	2.857	p-Hydroxy benzididene nicotinoyl hydrazide	R ₈
لاتنافسي	2.506	13.30	12.50	11.11	9.52	16.6	2.506	N-Acetyl-2-(7-chloro isatiny-5-pyridal-3-yl)-1,3,4-oxadiazole	R ₁₅
لاتنافسي	2.409	14.28	13.33	12.50	11.10	16.6	2.409	N-Acetyl-2-(p-nitro phenyl-5-pyridal-3-yl)-1,3,4-oxadiazole	R ₁₆
لاتنافسي	2.649	14.28	12.85	12.50	11.76	16.6	2.649	N-Acetyl-2-(2-pyrol-5-pyridal-3-yl)-1,3,4-oxadiazole	R ₁₇
لاتنافسي	2.380	14.30	13.79	12.50	11.80	16.6	2.380	N-Acetyl-2-(p-hydroxy phenyl-5-pyridal-3-yl)-1,3,4-oxadiazole	R ₁₈

دراسة تأثير بعض مشتقات حامض النيكوتيك على فعالية انزيم ALP في امصال النساء الاصحاء و المصابات بداء الفشل الكلوي المزمن

رضا وفاتن ورولا

جدول 3: يبين نوع التنشيط بوجود (10^{-8} , 10^{-5}) M من المركبات لانزيم الفوسفاتيز القاعدي في

مصل دم النساء المصابات بداء الفشل الكلوي

نوع التنشيط	Km بوجود المثبط $\times 10^{-3}$	بوجود المثبط (I)		بغياض المثبط		اسم المركب	رمز المركب
		$[I]=10^{-8}$ M	$[I]=10^{-5}$ M	V_{max}	Km (M) $\times 10^{-3}$		
		V_{maxi}	V_{maxi}	V_{max}			
لاتنافسي	2.875	33.00	25.00	50	2.875	Nicotinoyl hydrazide	R ₂
لاتنافسي	3.030	28.50	18.18	50	3.030	7-Chloro isatindine nicotinoyl hydrazide	R ₄
لاتنافسي	3.840	28.57	16.60	54	3.840	p-Nitro benzididene nicotinoyl hydrazide	R ₅
لاتنافسي	2.94	33.30	22.20	50	2.94	2-Pyrolidine nicotinoyl hydrazide	R ₆
لاتنافسي	2.702	35.08	28.50	50	2.702	p-Amin benzididene nicotinoyl hydrazide	R ₇
لاتنافسي	2.770	30.00	22.20	50	2.770	p-Hydroxy benzididene nicotinoyl hydrazide	R ₈
لاتنافسي	2.500	33.30	25.00	47.6	2.500	N-Acetyl-2-(7-chloro isatiny-5-pyridal-3-yl)-1,3,4-oxadiazole	R ₁₅
لاتنافسي	2.380	33.30	25.60	50	2.380	N-Acetyl-2-(p-nitro phenyl-5-pyridal-3-yl)-1,3,4-oxadiazole	R ₁₆
لاتنافسي	2.270	35.70	28.50	50	2.270	N-Acetyl-2-(2-pyrol-5-pyridal-3-yl)-1,3,4-oxadiazole	R ₁₇
لاتنافسي	2.380	40.00	33.30	50	2.380	N-Acetyl-2-(p-hydroxy phenyl-5-pyridal-3-yl)-1,3,4-oxadiazole	R ₁₈

وجد أن قيم (V_{maxi}) قد انخفضت بمقدار $[1+I/K_i]$ وذلك بزيادة تركيز كل مثبط (10^{-8} - 10^{-5}) M

يبين الجدول (4) ان ظروف ارتباط الانزيم مع المادة الاساس بوجود المثبط في مصل دم النساء الاصحاء والمصابات بداء الفشل الكلوي متشابهه باستثناء ان الفترة الزمنية لحصول اعلى ارتباط قد ازداد من 45, 40 دقيقة على التوالي بدلا من 35 دقيقة والذي يمثل اعظم ارتباط للانزيم والمادة الاساس بوجود المثبط.

جدول 4:- يبين الظروف المثلى لتعيين الفعالية الانزيمية بوجود المثبطات بتركيز 10^{-5} M في

امصال دم النساء الاصحاء والمصابات بالفشل الكلوي

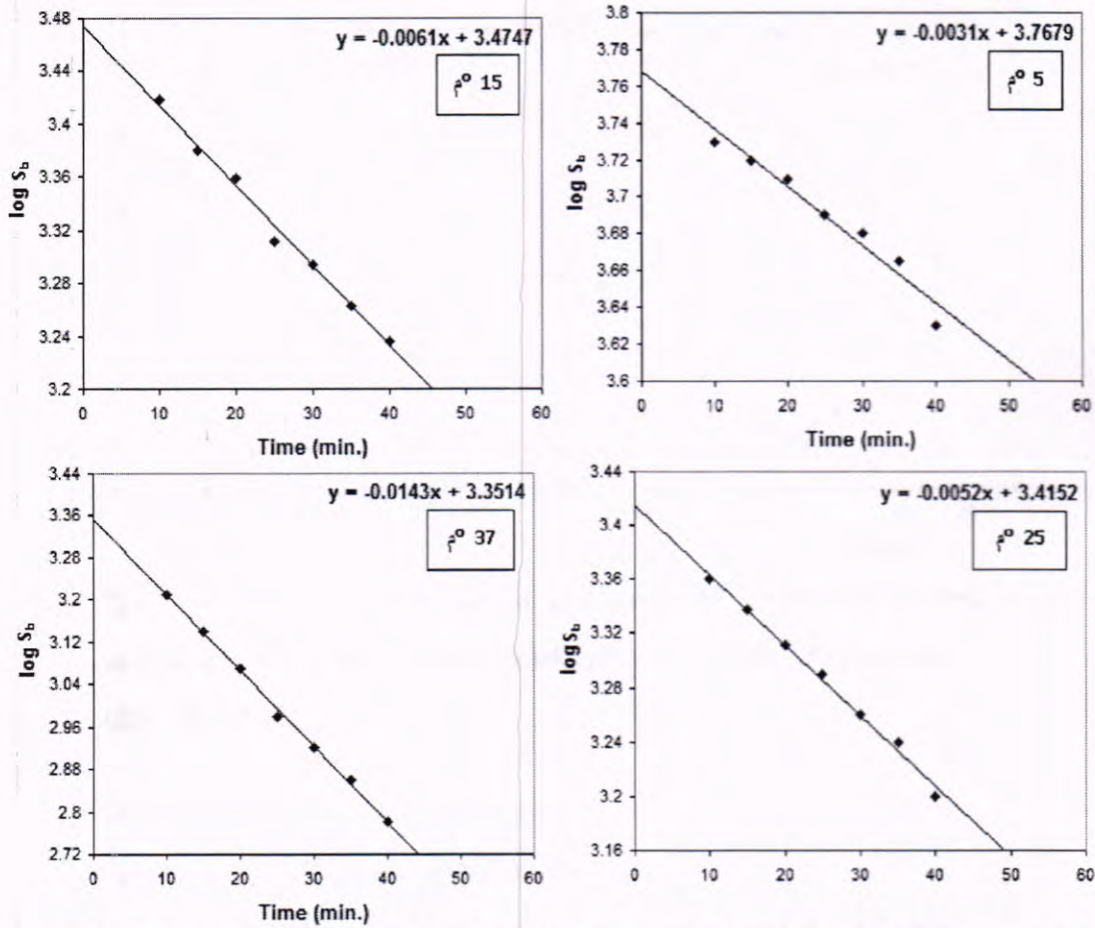
النساء المصابات بداء الفشل الكلوي			النساء الاصحاء			
R15-R18	R4-R8	R2	R15-R18	R4-R8	R2	Inhr
0.007	0.007	0.007	0.007	0.007	0.007	[S] Molar
59	59	59	59	59	59	[E] μ L
10.4	10.4	10.4	10.4	10.4	10.4	Ph
37	37	37	37	37	37	Tc
40	40	45	35	35	40	Time Min

دراسة حركيات مرتبة التفاعل لأنزيم الفوسفاتيز القاعدي

تعتمد سرعة تفاعل المرتبة الأولى في أي درجة حرارية على تركيز مادة المتفاعلة الواحدة ، ويعبر عن سرعة تفاعل المرتبة الأولى بالمعادلة التالية:

$$\log S = \frac{-k}{2.303} t + \log S_0 \dots \dots \dots (1)$$

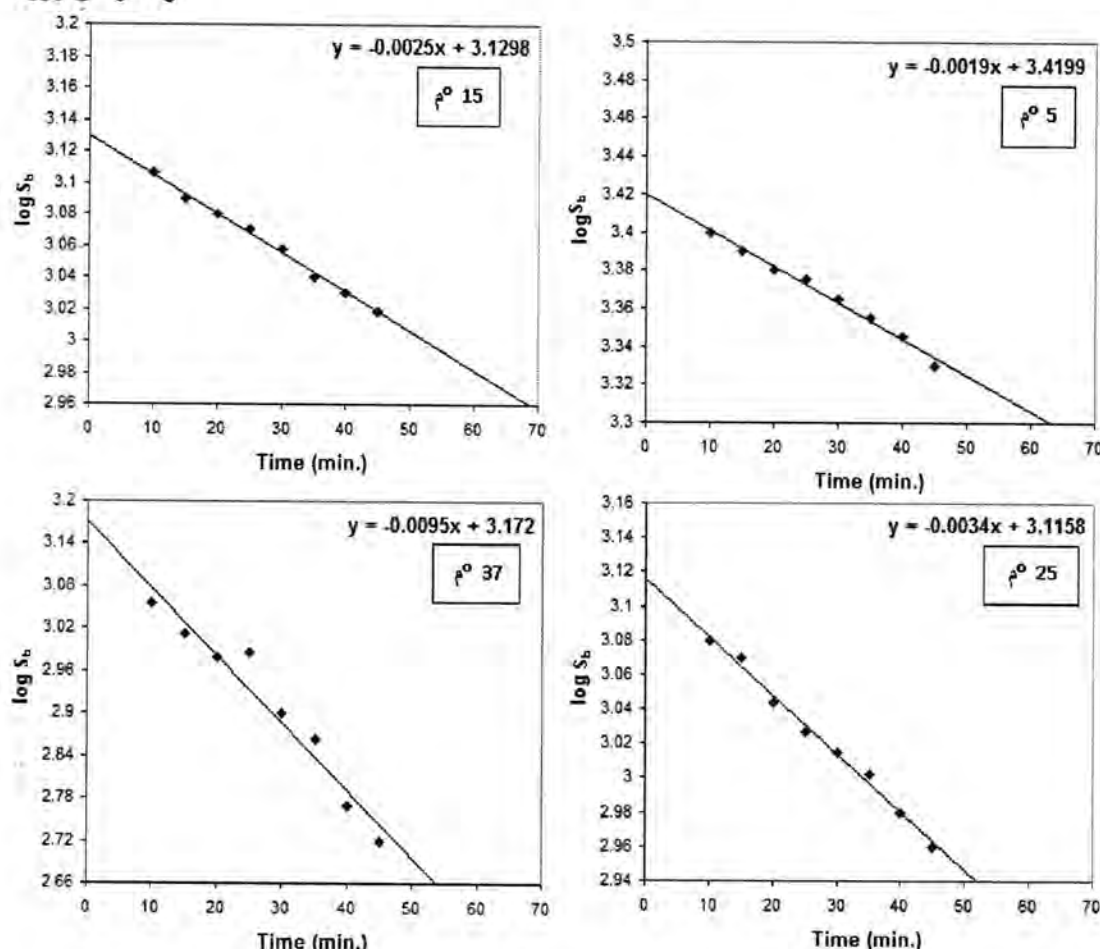
إذ تم الحصول على خط مستقيم من رسم العلاقة بين $(\log S)$ والزمن (t) بميل مساوي إلى $(-k/2.303)$. يوضح الشكلان (1) و (2) تطبيقاً للمعادلة (1) لأنزيم الفوسفاتيز القاعدي، حيث تم الحصول على خط مستقيم ويتبين من الشكلين أن التفاعل لأنزيم الفوسفاتيز القاعدي هو من المرتبة الأولى.



شكل 1: رسم معادلة السرعة للمرتبة الأولى لأنزيم الفوسفاتيز القاعدي في مصل دم النساء الأصحاء بوجود المثبط (R_2) بتركيز $(10^{-5} M)$ وباستخدام درجات حرارة مختلفة (5, 15, 25, 37) °م

دراسة تأثير بعض مشتقات حامض النيكوتيك على فعالية إنزيم ALP في امصال النساء الاصحاء و المصابات بداء الفشل الكلوي المزمن

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شكل 2: رسم معادلة السرعة للمرتبة الأولى لأنزيم الفوسفاتيز القاعدي في مصل دم النساء المصابات بداء الفشل الكلوي بوجود المثبط (R_2) بتركيز ($10^{-5} M$) وباستخدام درجات حرارية مختلفة (37, 25, 15, 5) °م

ويمكن استعمال معادلات أكثر شمولية لإيجاد مرتبة التفاعل وهي

المعروفة باسم معادلة سكجارد Scatchard:

$$[S]_b / [S]_f = -1 / K_d [S]_b + n [E]_t / K_d \dots\dots\dots(2)$$

يوضح الجدولان 5 و 6 قيم المعاملات الحركية لأنزيم الفوسفاتيز القاعدي في مصل دم النساء الأصحاء والمصابات بداء الفشل الكلوي بوجود المثبط (R_2) وبتراكيز ($10^{-5} M$) وباستخدام درجات حرارية مختلفة.

جدول 5: قيم المعاملات الحركية لأنزيم الفوسفاتيز القاعدي في مصل دم النساء الأصحاء بوجود المثبط (R₂) بتركيز (10⁻⁵ M) وباستخدام درجات حرارية مختلفة (5, 15, 25, 37) °م

درجة الحرارة °م	التركيز الكلي للمادة الأساس المرتبطة بأنزيم ALP 10 ⁻³ × β _{max} (mg/ml)	K _{obs} × 10 ⁻³ (min)	k ₊₁ (mg ⁻¹ .m/min)	k ₋₁ × 10 ⁻¹ (min ⁻¹)	K _a = k ₋₁ / k ₊₁ (mg ⁻¹ .ml)	K _d = k ₋₁ / k ₊₁ × 10 ⁻² (mg.ml ⁻¹)
5	3.6	50.3	13.90	8.80	15.7	6.360
15	3.7	65.9	22.50	10.30	21.8	4.580
25	4.6	70.7	23.92	9.70	24.5	4.080
37	6.0	83.7	37.90	6.51	58.2	1.718

جدول 6: قيم المعاملات الحركية لأنزيم الفوسفاتيز القاعدي في مصل دم النساء المصابات بداء الفشل الكلوي بوجود المثبط (R₂) بتركيز (10⁻⁵ M) وباستخدام درجات حرارية مختلفة (5, 15, 25, 37) °م

درجة الحرارة °م	التركيز الكلي للمادة الأساس المرتبطة بأنزيم ALP 10 ⁻³ × β _{max} (mg/ml)	K _{obs} × 10 ⁻³ (min)	k ₊₁ (mg ⁻¹ .m/min)	k ₋₁ × 10 ⁻¹ (min ⁻¹)	K _a = k ₋₁ / k ₊₁ (mg ⁻¹ .ml)	K _d = k ₋₁ / k ₊₁ × 10 ⁻² (mg.ml ⁻¹)
5	6.20	51.8	17.20	7.10	24.1	4.14
15	6.03	67.6	23.30	6.75	34.5	2.89
25	7.20	77.9	26.39	6.16	42.8	2.33
37	9.4	84.3	40.46	6.54	61.8	1.61

يوضح الجدولان (7 و 8) المعاملات الترموديناميكية للحالة القياسية، حيث يلاحظ أن قيم ΔH^0 ، لكل من التفاعل الأنزيمي للفوسفاتيز القاعدي بوجود المثبط (R₂) وفي كلا مجموعتي النساء الأصحاء والمصابات بداء الفشل الكلوي، هي قيم موجبة (17.836, 15.395) كيلوجول/ مول على التوالي، هذا يدل على أن التفاعل هو تفاعل ماص للحرارة، في حين تدل قيم ΔG^0 السالبة على أن التفاعل تلقائي، أي أن التفاعل مجهز بطاقة ملائمة باتجاه تكوين المعقد، كما تدل القيم الموجبة للتغير في الانتروبي على أن التفاعل يميل إلى السير تلقائياً في اتجاه تكوين المعقد الأنزيمي، وأن القيمة الموجبة للتغير في الانثالبي القياسي ΔH^0 من الممكن أن تعود إلى التفاعلات بين المجاميع ضمن المادة الأساس ثنائي صوديوم فنييل فوسفيت (disodium phenyl phosphate) وأنزيم الفوسفاتيز القاعدي بوجود المثبط (R₂)، حيث تتضمن الروابط غير التساهمية حيث تكون الكتروستاتيكية في طبيعتها كروابط شحنة-شحنة، شحنة-قطبية، قطبية-قطبية وأواصر هيدروجينية. حيث تساعد هذه الروابط في استقرارية تركيب المعقد الأنزيمي بوجود المثبط (R₂) في كلا المجموعتين في مصل دم النساء الأصحاء والمصابات بداء الفشل الكلوي، وهذا يتوافق مع القيمة الموجبة للتغير في الانتروبي القياسي (16).

دراسة تأثير بعض مشتقات حامض النيكوتيك على فعالية أنزيم ALP في امصال النساء الاصحاء و المصابات بداء الفشل الكلوي المزمن

رضا وفاتن ورولا

جدول 7: قيم المعاملات الترموديناميكية للحالة القياسية لأنزيم الفوسفاتيز القاعدي في مصل دم النساء الأصحاء بوجود المثبط (R_2)

درجة الحرارة °م	ΔH° كيلو جول/مول	ΔG° كيلو جول/مول	ΔS° كيلو جول/مول
5	15.345	-6.364	+78.78
15	15.345	-7.379	+78.88
25	15.345	-7.980	+78.75
37	15.345	-10.475	+78.71

جدول 8: قيم المعاملات الترموديناميكية للحالة القياسية لأنزيم الفوسفاتيز القاعدي في مصل دم النساء المصابات بداء الفشل الكلوي بوجود المثبط (R_2)

درجة الحرارة °م	ΔH° كيلو جول/مول	ΔG° كيلو جول/مول	ΔS° كيلو جول/مول
5	17.836	-7.3550	+91.180
15	17.836	-8.4785	+91.200
25	17.836	-9.5057	+91.175
37	17.836	-10.7287	+91.160

والجدولان (9 و 10) يوضحان قيم المعاملات الترموديناميكية للحالة الانتقالية لارتباط المادة الأساس مع أنزيم الفوسفاتيز القاعدي بوجود المثبط (R_2) بتركيز ($10^{-5} M$). في مصل دم النساء الاصحاء والمصابات بداء الفشل الكلوي على التوالي .

جدول 9: قيم المعاملات الترموديناميكية للحالة الانتقالية لارتباط المادة الأساس مع أنزيم الفوسفاتيز القاعدي بوجود المثبط (R_2) في مصل دم النساء الأصحاء

درجة الحرارة °م	ΔH^* كيلو جول/مول	ΔG^* كيلو جول/مول	ΔS^* كيلو جول/مول	E_a كيلو جول/مول
5	14.648	61.84565	-169.77	16.96
15	14.565	63.00560	-168.19	16.96
25	14.482	65.129213	-169.95	16.96
37	14.382	67.131963	-170.16	16.96

جدول 10: قيم المعاملات الترموديناميكية للحالة الانتقالية لارتباط المادة الأساس مع أنزيم الفوسفاتيز القاعدي بوجود المثبط (R_2) في مصل دم النساء المصابات بداء الفشل الكلوي

درجة الحرارة °م	ΔH^* كيلو جول/مول	ΔG^* كيلو جول/مول	ΔS^* كيلو جول/مول	E_a كيلو جول/مول
5	16.003	61.36028	-163.15	18.315
15	15.920	62.91400	-163.17	18.315
25	15.836	64.88140	-164.58	18.315
37	15.737	66.88760	-165.00	18.315

يلاحظ من الجدولين 9 و 10 أن قيمة (ΔH^*) لكل من الحالتين في مصل دم النساء الأصحاء والمصابات بداء الفشل الكلوي هي قيمة موجبة وهذا يدل على أن تكوين المعقد الأنزيمي (الأنزيم-المادة الأساس بوجود المثبط R_2) هو تفاعل ماص للحرارة، بينما تدل القيمة الموجبة لـ (ΔG^*) لكل من الحالتين على أن ظهور المعقد النشط ليس تلقائياً ويحتاج إلى كمية من الطاقة للوصول إلى الحالة الانتقالية التي تؤدي إلى تكوين الناتج النهائي. وتدل القيمة السالبة لـ (ΔS^*) لكل من الحالتين على أن التركيب البنائي للمعقد النشط هو أكثر ترتباً من التركيب البنائي للمتفاعلات. حيث تفترض أن ظهور المعقد الأنزيمي يتكون بخطوتين، الخطوة الأولى هي استقرارية المعقد بالروابط غير المحبة للماء، والخطوة الثانية هي استقرارية المعقد بالروابط القصيرة كالروابط الالكتروستاتيكية والأواصر الهيدروجينية وقوى فاندرفالز. وتسهم الروابط غير المحبة للماء في استقرارية المعقد من خلال التغير الموجب في الانتروبي، بينما تسهم الروابط الالكتروستاتيكية والأواصر الهيدروجينية وقوى فاندرفالز في استقرارية المعقد الأنزيمي من خلال التغيرات الانثالبية السالبة (17).

مما تقدم اعلاه نستنتج ان مشتقات حامض النيكوتك تثبط ارتباط الانزيم ALP مع المادة الاساس بشكل لا تنافسي اي دون ان يؤثر زيادة تركيز المادة الاساس وان هذا الانخفاض في فعالية الانزيم يزداد في دم النساء المصابات بداء الفشل الكلوي عن النساء الاصحاء مما يفتح الافق للصناعات الدوائية في ادراج مشتقات الهيدرازيد لحامض النيكوتك والاكسادايازول كعقار مستقبلي لمرضى الفشل الكلوي لخفض فعالية انزيم ALP.

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بداء الفشل الكلوي المزمن

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قياس انزيم الادنوسين دي امينيز باستخدام جهاز ال (HPLC) في مصل مرضى سرطان الثدي وعلاقته بجرع العلاج الكيميائي

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وزارة العلوم والتكنولوجيا

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ABSTRACT

The main goal of this work is to measure the activity of ADA enzyme in blood of patient with breast cancer this enzyme is an indicator of cancer stages and it is used to evaluate the chemotherapy and detecting the response of patients to chemical drugs if we used one or more than one drug in the treatment. Blood samples where collect from different areas all over the country, from north, middle and south of Iraq and then stored in cool place and their used HPLC for measurement of ADA level as a new sensitive method for measurement.

الخلاصة

الهدف الرئيسي من هذا العمل هو قياس انزيم الادنوسين دي امينيز في دم مرضى سرطان الثدي ويعتبر هذا الانزيم كمؤشر لمراحل المرض ويمكن استخدامه لتقدير كفاءة العلاج الكيميائي وتحديد استجابة المرضى للعلاج الكيميائي سواء استخدمنا عقار كيميائي واحد او مجموعة ادوية في العلاج. نماذج الدم تم جمعها من مناطق مختلفة من القطر من المحافظات الشمالية والوسطى والجنوبية وبعد ذلك يتم حفظها في مكان مبرد وتم استخدام جهاز ال HPLC لقياس مستويات انزيم الادنوسين دي امينيز كطريقة حديثة وتمتاز بالحساسية والدقة في القياس.

المقدمة

سرطان الثدي هو شكل من أشكال الاورام التي تصيب أنسجة الثدي وعادة ما يظهر في قنوات (الأنابيب التي تحمل الحليب إلى الحلمة) وغدد الحليب ، ويصيب النساء والرجال على السواء ولكن الإصابة لدى الذكور نادرة الحدوث فمقابل كل 200 إصابة للنساء يوجد إصابة واحدة للرجال (1).

السرطان بشكل عام نوع من الأمراض الذي يجعل الخلايا تنمو وتتغير وتتضاعف بصورة خارجة عن نطاق السيطرة. فسرطان الثدي يعني عدم انتظام نمو وانتشار الخلايا التي تنشأ من أنسجة الثدي ومجموعة الخلايا التي تنقسم وتتضاعف بسرعة. ويمكن أن تشكل قطعة أو كتلة من الأنسجة

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الإضافية وهذه الكتل النسيجية تدعى الأورام ، والأورام إما أن تكون سرطانية (خبيثة) أو سرطانية (حميدة) والأورام الخبيثة تتكاثر وتدمر أنسجة الجسم السليمة ويمكن لبعض الخلايا ضمن الأورام أن تتفصل وتنتشر بعيداً إلى أجزاء أخرى من الجسم وهذا الانتشار من منطقة إلى (3,2) أخرى يسمى انبثاث بصورة عامة الثدي يتألف من نوعين رئيسيين من الانسجة :انسجة غدية و انسجة داعمة .:

وهناك اضطرابات قد تكون حميدة (benign) أو غير حميدة (malignant) ، فالاضطرابات الحميدة تشمل ؛ ألم الثديين ،حويصلات الثديين ،تليف أنسجة الثديين ، والتهاب الثديين وتشمل الاضطرابات غير الحميدة الأعراض التالية :

كتل أو تجمعات وكثافة المنطقة المحيطة بالثدي وتحت الجلد ، تغيرات في شكل وحجم حلمة الثدي، حصول تغيرات في جلد الثدي ليصبح مثل قشرة البرتقال ، تورم وسخونة جلد الثدي ويكون لونه أحمر ، إفرازات دموية من الثدي (4).

و تهدف الدراسة الى ايجاد طريقة جديدة لقياس انزيم الادنوسين دي امينيز في امصال المرضى المصابين بسرطان الثدي تمتاز بالحساسية والدقة العالية مقارنة بالطريقة اللونية الاكثر شيوعا والمستخدم بكثرة لقياس هذا الانزيم .

أنزيم الادينوسين دي أمينيز (ADA)

وهو من الأنزيمات الفعالة والضرورية ووظيفته توضح صورة ومدى فعالية الجهاز المناعي ويلعب دور مهم وفعال في التطور الطبيعي للجهاز المناعي الذي بدوره يعتبر المحرك الأساس لتطور خلايا (T&B) (5).

في اللبائن خلايا B هي المسؤولة عن إنتاج الأجسام المضادة المتخصصة والنوعية ، أما الخلايا T فتعتبر خلايا قاتلة وذاكرة للإصابات المرضية السابقة (killer& memory cells) (6) .

وهذا الأنزيم موجود في أنسجة اللبائن الحاوية على الأعضاء الليمفاوية ، وفعاليته تعتبر مؤشر للاستجابة المناعية (Immune response) ، حيث يوجد ارتباط بين العوز المناعي (Immuno-deficiency) والوظيفة المناعية الطبيعية .

وتتواجد معدلات عالية للأنزيم في الخلايا غير الناضجة وبالتحديد في الطبقة القشرية (Cortex layer) للغدة الزعترية(Thymus gland) مقارنة مع اللب (Medulla) وفي سايتوبلازم الخلية وبمقدار محدد في النواة .ولوحظ انخفاض بفعالية الأنزيم مع تطور مراحل نضج خلايا B (7) 0 بالإضافة إلى ذلك تمت تنقية الأنزيم من صفار بيض الدجاج باستخدام تقنية الفصل بالعمود (Column chromatography)، ومن سلالات معينة من الفطريات الشعاعية

(actinomycetes). وبصورة عامة فإن أعلى مستوى للأنزيم يمكن الحصول عليه من أنسجة الجهاز الهضمي والغدة الزعترية (8).

وبما أن هذا الأنزيم من الأنزيمات المناعية الأساسية، فهو يعطي صورة لاستقرارية الجهاز المناعي، وأن نقص أنزيم ADA في أمصال المرضى يوضح تأثير المرض نفسه وكذلك تأثير الأدوية المستخدمة لعلاج سرطان الثدي.

أظهرت الدراسات الحديثة وجود اختلافات في تركيز الأنزيم باختلاف أنواع اللبائن، حيث تم إجراء التجارب على (6) أنواع مختلفة من اللبائن وكانت تلك الاختلافات نتيجة التباين في : درجة الحمضية pH، الألفة الكهربائية و خصوصية المادة الركيزة للأنزيم (9,10) فيما بين تلك الأنواع من اللبائن.

المواد وطرائق العمل

أولاً : تحضير محلول دارئ الفوسفات (Phosphate buffer)

يوزن 4.73 غم من (hydrated sodium dihydrogen phosphate) و 5.62 غم من (hydrated disodium hydrogen phosphate) ويذاب في لتر واحد من الماء اللآيوني وتنظم الحمضية (pH) إلى 6.5 بواسطة حامض الفوسفوريك .

ثانياً : تحضير المحلول القياسي المنظم للأنزيم (Standard)

يضاف 15 مل من دارئ الفوسفات إلى 140 غم من الاديونسين ويسخن في حمام مائي لمدة 10 دقائق ويبرد تحت الماء وتنظم الحمضية إلى 6.5 بواسطة حامض الفوسفوريك ويكمل الحجم إلى 25 مل .

ثالثاً : تنظيم عمل جهاز (HPLC) من خلال غسله يوميا" بالايثانول (الطور المتحرك) لتهيئته لتمرير نماذج المصل من المصابات بسرطان الثدي.

رابعاً : جمع النماذج من مناطق مختلفة من القطر وحسب الجداول المبينة .

خامساً : تهيئة النماذج من خلال فصل الدم بجهاز الطرد المركزي المبرد (4 درجة مئوية) ولمدة 15 دقيقة وبسرعة (3000 دورة / دقيقة) للحصول على مصل الدم .

سادساً : تنقية الامصال من خلال إجراء المعاملات والتخافيف اللازمة لغرض حقنها في جهاز HPLC والغرض من هذه المعاملات هو التخلص من الدهون والشوائب الموجودة في المصل والتي قد تتداخل مع محتويات عمود الفصل الخاص بالجهاز وتكون معقدات تؤدي لانسداده وبالتالي فشل أظهار النتائج النهائية.

يتم تمرير المحلول القياسي المحضر أعلاه (فقرة ثانياً) في جهاز HPLC وتمكنا من قراءة النتيجة بعد مرور زمن قدره (2.9 دقيقة) ويعتبر هذا الزمن هو الأمثل لظهور القمة (Peak) في جميع

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النماذج التي تم تمريرها. وهذا يدل على أن الوقت (2.90 دقيقة) هو الأمثل والفعلي لقراءة تركيز الإنزيم لجميع النماذج .

سابعاً : يتم قراءة النماذج في جهاز HPLC لحساب تركيز الإنزيم في كل نموذج ومقارنة بالإنزيم القياسي ولحساب تركيز المحلول القياسي لإنزيم الادينوسين اعتمدنا الطرق الكيميائية لحساب المولارية حيث كانت قيمته (2.45) .

أما بالنسبة لحساب تركيز العينة تم اتباع المعادلة التالية :

$$\text{تركيز العينة} = \frac{\text{تركيز الإنزيم القياسي}}{\text{قيمة المنحني القياسي للإنزيم}} = \frac{\text{التركيز المطلوب للعينة}}{\text{قيمة المنحني القياسي للعينة}}$$

(جهاز HPLC) (جهاز HPLC)

ثامناً : الجداول اللاحقة توضح قيم التركيز المطلوب للعينات من خلال المعادلة أعلاه.

النتائج والمناقشة

جدول 1: يبين تركيز الادينوسين دي أمينيز للعينات المدروسة للمنطقة الشمالية

رقم العينة	أسم المحافظة والاقضية والنواحي	عدد الجرعات	تركيز الانزيم	عمر المريضة
1	أربيل	6 جرع كيمياوي	2.2	45
2	أطراف اربيل	6 جرع كيمياوي	2.1	56
3	بادوة	12 جرع كيمياوي	1.2	43
4	دهوك	8 جرع كيمياوي	1.45	44
5	بعشيقه	6 جرع كيمياوي	1.45	27
6	عقره	6 جرع كيمياوي	1.95	37
7	أربيل	7 جرع كيمياوي	2.125	45
8	أربيل	لم تأخذ أي جرع	2.7	60
9	الموصل	6 جرع كيمياوي	2.27	57
10	كويسنجق	4 جرع كيمياوي	3.05	49
11	أربيل	6 جرع كيمياوي	2.21	41
12	تلكيف	6 جرع كيمياوي	2.47	42
13	كركوك	6 جرع كيمياوي	2.43	49
14	أربيل	6 جرع كيمياوي	1.09	40

15	دهوك	6 جرعة كيميائي	2.42	48
16	كركوك	12 جرعة كيميائي	0.956	57
17	سنجار	8 جرعة كيميائي	1.98	40
18	أربيل	قبل أول جرعة كيميائي	2.98	65

جدول 2: يبين تركيز الاديносين دي أمينيز للعينات المدروسة للمنطقة الوسطى

رقم العينة	اسم المحافظة	عدد الجرعات	تركيز الانزيم	عمر المريضة
1	ديالى	6 جرعات كيميائي	2.24	40
2	بابل	5 جرعات كيميائي	2.6	46
3	صلاح الدين	6 جرعات كيميائي	2.6	60
4	بغداد	6 جرعات كيميائي	2.41	45
5	صلاح الدين	6 جرعات كيميائي	2.38	44
6	ديالى	6 جرعات كيميائي	2.22	42
7	بغداد	6 جرعات كيميائي	2.37	40
8	بغداد	6 جرعات كيميائي	2.39	41
9	بغداد	فحص مبكر	2.73	39
10	بغداد	قبل أول جرعة كيميائي	2.86	49
11	بغداد	فحص مبكر	2.84	40

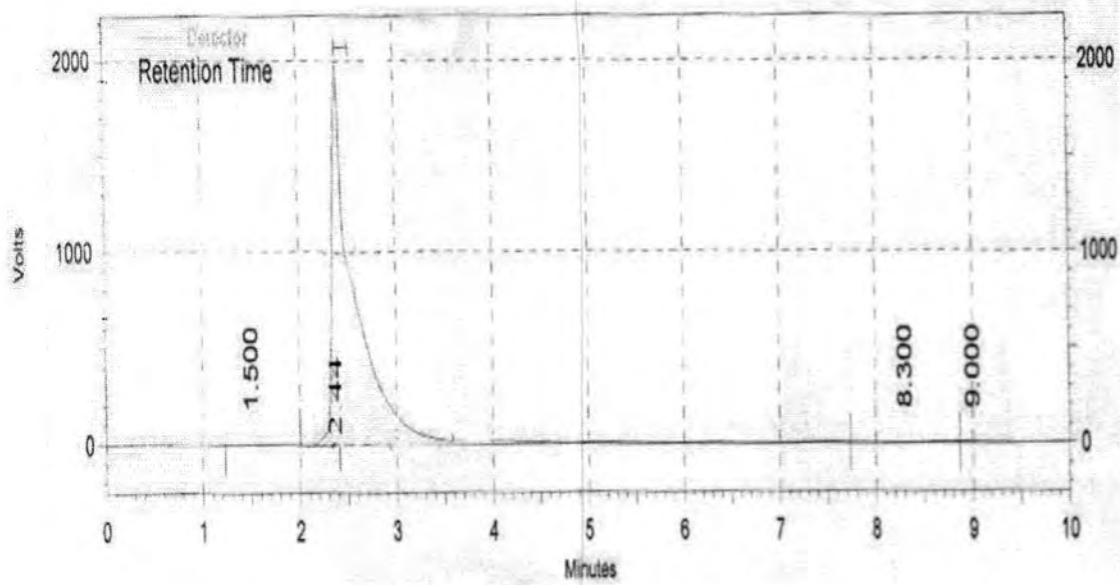
جدول 3: يبين تركيز الاديносين دي أمينيز للعينات المدروسة لمنطقة الفرات الاوسط

رقم العينة	اسم المحافظة	عدد الجرعات	تركيز الانزيم	عمر المريضة
1	كربلاء	فحص مبكر	2.45	30
2	كربلاء	فحص مبكر	2.45	14
3	كربلاء	فحص مبكر	2.67	39
4	كربلاء	أصابة غير مشخصة	2.49	28
5	كربلاء	فحص مبكر	2.72	37
6	كربلاء	فحص مبكر	2.82	17
7	كربلاء	قبل أول جرعة كيميائي	2.95	39
8	كربلاء	6 جرعات كيميائي	2.46	57
9	كربلاء	قبل أول جرعة كيميائي	2.8	43

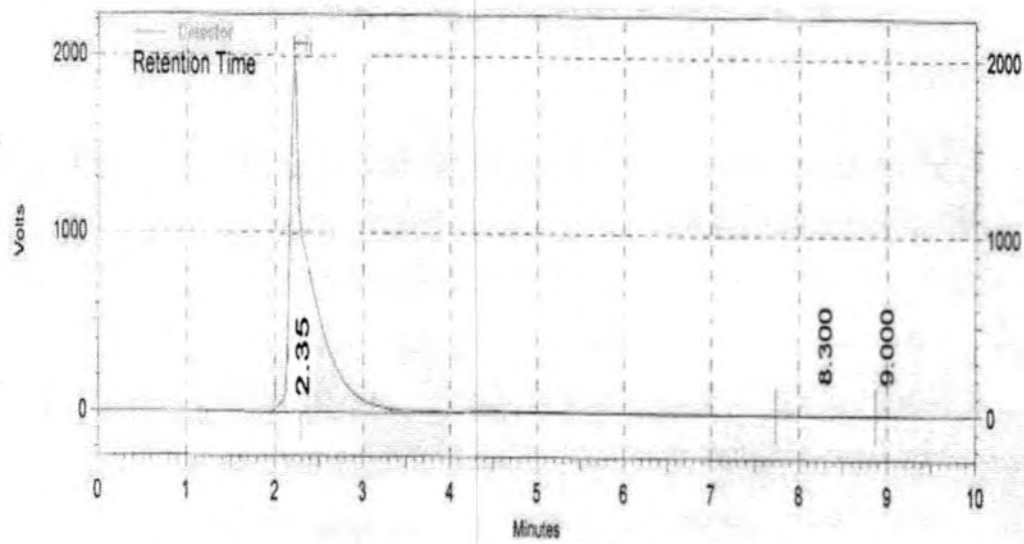
قياس انزيم الادنوسين دي امينيز باستخدام جهاز ال (HPLC) في مصل مرضى سرطان الثدي وعلاقته بجرع العلاج الكيميائي

قيس وعلي وإيمان وشذى ووسام وبشرى

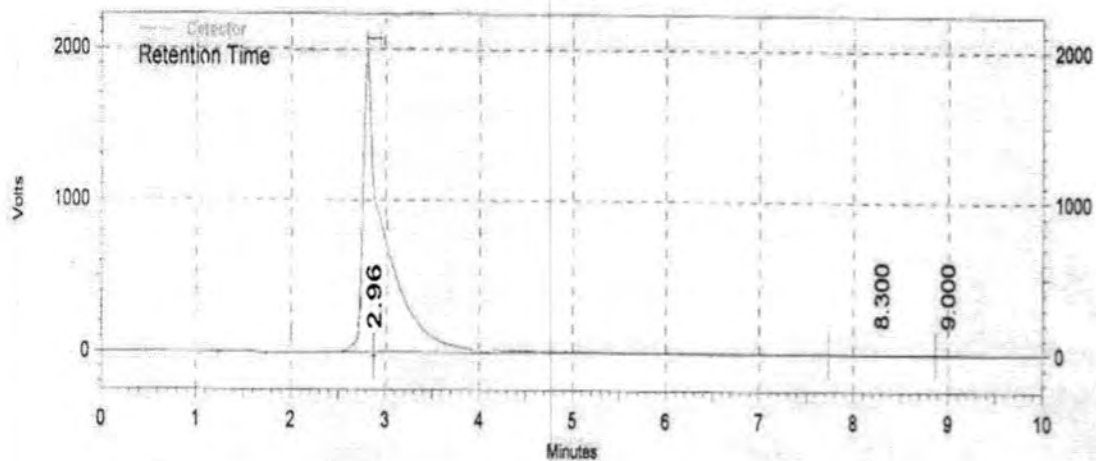
47	1.19	6 جرعات كيميائي واشعاع	كربلاء	10
38	2.73	فحص مبكر	كربلاء	11
32	2.96	فحص مبكر	كربلاء	12
28	2.49	فحص مبكر	كربلاء	13
40	2.83	فحص مبكر	النجف	14
24	2.89	فحص مبكر	النجف	15
25	2.73	فحص مبكر	النجف	16
45	2.95	فحص مبكر	النجف	17
32	2.93	فحص مبكر	النجف	18
28	2.89	فحص مبكر	النجف	19
28	2.9	فحص مبكر	النجف	20
50	2.2	3 جرعات كيميائي وجرعة أشعاع	النجف	21
25	2.76	فحص مبكر	النجف	22
45	2.46	فحص مبكر	النجف	23
27	2.8	فحص مبكر	النجف	24
20	2.42	6 جرعات كيميائي	النجف	25
18	2.73	فحص مبكر	النجف	26
45	2.62	فحص مبكر	النجف	27
40	2.81	فحص مبكر	النجف	28
24	2.51	فحص مبكر	النجف	29
55	2.72	فحص مبكر	النجف	30



شكل 1: قيمة الأنزيم القياسي



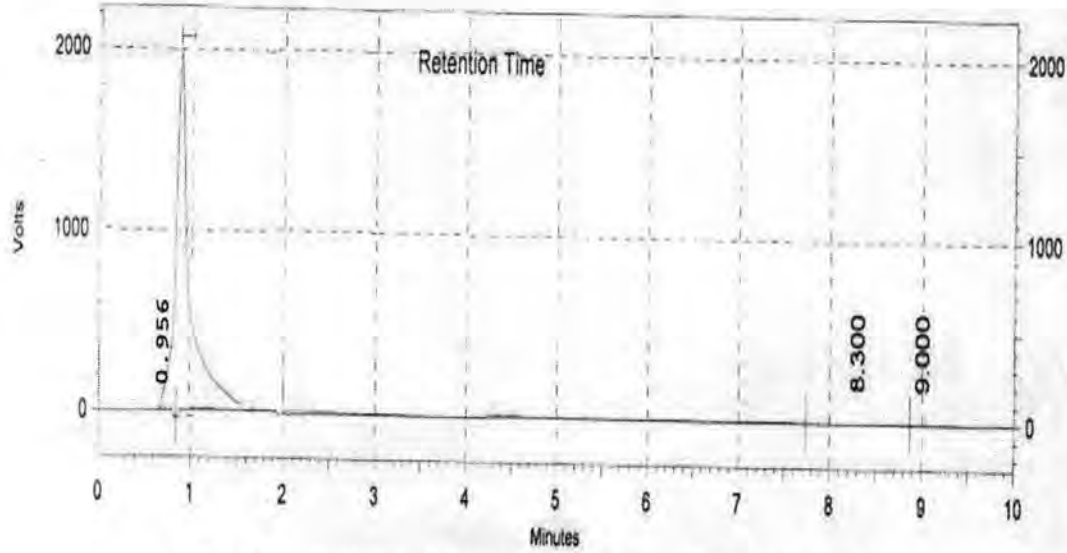
شكل 2: قيمة الأنزيم لعينة من النساء السليمات



شكل 3: قيمة الانزيم لعينة من النساء من مجموعة الفحص المبكر

قياس الأنزيم الادنوسين دي امينيز باستخدام جهاز ال (HPLC) في مصل مرضى سرطان الثدي وعلاقته بجرع العلاج الكيميائي

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شكل 4: قيمة الأنزيم لعينة من النساء المصابات بعد الجرعة 12

النتائج والمناقشة

يوضح هذا البحث تأثير تركيز الأنزيم في امصال مرضى سرطان الثدي مع الجرعة الكيميائية المعطاة للمريضات بعد ظهور المرض ومقارنتها بالأنزيم القياسي ويعتبر سرطان الثدي المسبب الثاني للوفاة بعد سرطان الرئة وفقا لإحصائيات منظمة الصحة العالمية .

حيث تم أولا قياس تركيز الأنزيم القياسي فكانت قيمته 2.44 مولاري وثبتت المنحنى القياسي له لغرض مقارنته مع نتائج الأنزيم للعينات المختلفة حيث يجب تثبيت المنحنى القياسي لكل مادة ثم فحصها باستخدام جهاز HPLC وقد تم الحصول على الأنزيم القياسي من كلية طب النهرين على شكل باور تم أذابته حسب الطريقة المذكورة في طرق العمل لتحضير المحلول القياسي ومن خلالها تمت مقارنة النتائج بهذا الأنزيم القياسي فكانت قيمها موضحة بالجدول (1 و 2 و 3).

إن تركيز الأنزيم يبدأ بالاستقرار ويقارب تركيز الأنزيم القياسي بعد الجرعة السادسة على أساس أنها الجرعة الأخيرة والمقررة من قبل الطبيب في اغلب الحالات فكانت قيم الأنزيم عند إعطاء الجرعة السادسة تتراوح ما بين (1.09-2.46) وبمعدل 2.25 مقارنة بالأنزيم القياسي الذي هو 2.45 وتعتبر هذه النتيجة مقاربه لتركيز الأنزيم القياسي وهذا يدل على ان المريضة بدأت تتماثل للشفاء إلى حد ما.

تم إعطاء بعض المريضات أكثر من 6 جرعات كيميائي وهذا يدل على انتشار الخلايا السرطانية في أماكن أخرى وإن الجرعة السادسة المقررة لم تفي بالغرض فتم رفعها من قبل الطبيب المعالج إلى (8 أو 12 جرعة)، و لوحظ هبوط في مستوى تركيز الأنزيم إي انخفضت الكفاءة المناعية

فكانت قيمة تركيز الإنزيم تتراوح ما بين (1.2-1.98-2.125-0.956) إي اقل من قيمة الإنزيم القياسي.

تبين إن تركيز الإنزيم للمصابات قبل اخذ أول جرعة من العلاج الكيميائي بعد ثبوت الإصابة بالسرطان واستئصال الورم يكون عالي لتحفيز الجهاز المناعي فكانت قيم تركيز الإنزيم (2.95-2.98).

إما بالنسبة للفحص المبكر للنساء قد تكون قيمة الإنزيم ضمن الحد الطبيعي في حالة عدم وجود إي إصابة أو قد تكون اعلي من الحد الطبيعي وقد تم اعتمادها كنتيجة للنساء السليمات غير المصابات واعتبرت كمجموعة سيطرة موجبة وهذه هي الحالة المرضية قد يكون السرطان حميد أو خبيث وحسب تشخيص الطبيب (9).

وفي هذا البحث تم اعتماد قياس إنزيم الادنوسين دي امينيز كمؤشر لمدى تأثر الجهاز المناعي بالأدوية العلاجية (العلاجات الكيميائية) وباستخدام طريقة حديثة تمتاز بالدقة والحساسية العالية وهي طريقة كروموتوغرافيا السائل ذات الأداء العالي وباستخدام جهاز HPLC والذي من خلال استخدام إنزيم قياسي يمكن اعتمادها كنموذج لمقارنة التراكيز المختلفة لأي إنزيم والموجودة في العينات المطلوبة ومقارنته بشكل منحنيات يتم استخراج قيم التراكيز المقاسة من خلالها لذا تعتبر هذه الطريقة منحنى جديد في طرق القياس والتشخيص ومتابعة مستويات الإنزيمات وتمتاز بالدقة والكفاءة العالية، ويبين الشكل (1) المنحنى القياسي للإنزيم القياسي كما تم قياسه باستخدام جهاز HPLC إما الشكل (2) يبين قيمة الإنزيم لعينة من النساء السليمات والشكل (3) يبين قيمة الإنزيم لعينة من النساء من مجموعة الفحص المبكر والشكل (4) يبين قيمة الإنزيم لعينة من المصابات بعد الجرعة 12.

وفيما يخص العلاقة ما بين الرضاعة الطبيعية والإصابة بسرطان الثدي وحسب المسح الوطني والعينات التي تم الحصول عليها علما إن أكثر المصابات يرضعن أطفالهن رضاعة طبيعية، وإن كل مصابة قد أرضعت ما بين (2-5) أطفال عدا حالات قليلة جداً كانت الرضاعة صناعية (10). نستنتج ان الرضاعة الطبيعية لا تقي من الإصابة بسرطان الثدي إذا ما كان العامل المؤهب predisposing factor (11) للإصابة بالسرطان قوي على الرغم من عدم وجود إصابات سابقة بالعائلة ومن الدرجة الأولى إلا حالات قليلة وعلى مختلف مناطق القطر .

تبين من البحث ان السبب الرئيسي للإصابة بسرطان الثدي هو التلوث البيئي الذي نجم عن مخلفات الحروب السابقة التي عانى منها القطر لسنوات طويلة والتي استخدمت فيها الكثير من الأسلحة المتنوعة هذا بالدرجة الأساس إضافة إلى عوامل بيئية أخرى أدت إلى ظهور إصابات كثيرة بسرطان الثدي وبأعمار مختلفة تتراوح بين (15-50) وبمناطق مختلفة من القطر وينسب مرتفعة فاقت الحد الطبيعي.

قياس انزيم الادنوسين دي امينيز باستخدام جهاز ال (HPLC) في مصل مرضى سرطان الثدي وعلاقته بجرع العلاج الكيميائي

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وتم اعتماد صيغة الاستبيان المرفقة حيث اخذت المعلومات فيها كاملة لكل مريضة لاكمال مستلزمات البحث.

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تأثير التشعيع النيوتروني ودرجة الحرارة على الخواص الكهربائية لمطاط النتريل-بيوتاديين (NBR) النقي والمطعم بالرصاص

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ABSTRACT

The study deals with the effect of temperature and neutron radiation on electrical properties of NBR as pure and doped with lead percentage 10, 40, and 50% in direct electrical field, by using voltage-current (1-V) technique. Firstly, the (1-V) characteristics has been done at temperature (20°C, 40°C, 60°C, 80°C, and 100°C) respectively. Secondly, the effect of neutron radiating on (1-V) characteristics at different radiated time (1, 2, 3, 4 and 5 days) respectively has been done at 20°C. The results have showed in case of pure NBR, the value of the leaking current increased with the increase of applied voltage and temperature. While, in the case of NBR doped with lead, the results showed that the value of leaking current has been increased more than in the case of pure NBR. However, the results have showed that the value of leaking current has increased with the increase of radiating time for pure NBR and more for doped NBR. It has been observed the two separate regions with two different slopes in (1-V) characteristic for pure and doped NBR which proved that the mechanism of conductivity is space charge limited current (SCLC) is dominant. The activation energy of pure and doped NBR has been calculated and it was found that the appearance of change in the values as lead percentage increase.

الخلاصة

تم في هذا البحث دراسة تأثير درجة الحرارة والتشعيع النيوتروني على الخواص الكهربائية للمطاط NBR النقي والمطعم بالرصاص بنسب (10% ، 40% و 50%) في المجالات الكهربائية المستمرة، وذلك باستخدام تقنية فرق الجهد-التيار (I-V). فلقد تم دراسة أولاً: خواص (I-V) عند درجات حرارة (20°C، 40°C، 60°C، 80°C، 100°C) على التعاقب. وثانياً: تم دراسة تأثير التشعيع النيوتروني على الخواص (I-V) للمطاط NBR النقي والمطعم عند درجات حرارة 20°C وبأزمنة تشعيع (1، 2، 3، 4، 5 يوم) على التعاقب. أظهرت النتائج في حالة المطاط النقي إن قيمة التيار المتسرب تزداد بزيادة الفولتية ودرجة الحرارة. أما في حالة المطاط NBR المطعم بالرصاص، فلقد بينت النتائج انه كلما ازدادت درجة الحرارة ازداد التيار المتسرب بشكل أكثر مما هو عليه في

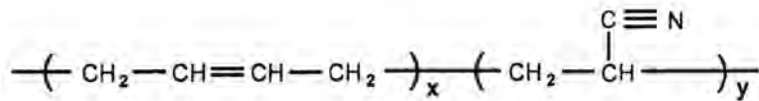
تأثير التشعيع النيوتروني ودرجة الحرارة على الخواص الكهربائية لمطاط النتريل - بيوتاديين (NBR) النقي والمطعم بالرصاص

يحيى والياس

المطاط النقي. أما بالنسبة للمطاط NBR النقي والمطعم المشع، فلقد لوحظ أن للتشعيع النيوتروني دور في زيادة ملحوظة في التيار المتسرب عما هو عليه في المطاط النقي والمطعم غير المشع. لوحظ ظهور منطقتين في خواص (I-V) في المطاط النقي والمطعم وفي حالتي المطاط NBR النقي والمطعم بالرصاص يمتلكان ميلين مختلفين، وهذا يثبت على أن آلية التوصيل المتغلبة هي آلية التيار المحدد بالشحنة الفراغية SCLC. تم حساب طاقة التنشيط للمطاط NBR النقي والمطعم بالرصاص من خلال التوصيلية، فوجد ان هنالك تغيرا ملحوظا في قيم طاقة التنشيط كلما ازدادت نسب التطعيم.

المقدمة

على الرغم من ان انتشار استخدام المطاط وتطوره قد حدث في القرن العشرين، إلا أن المطاط الطبيعي قد عرف منذ القرن السادس عشر. ولقد استطاع الباحثون التوصل الى الصيغة الكيميائية له وهي الايزوبرين (C₅ H₈) [1]. وعلى ضوء ذلك استطاع العلماء تحضير عدة انواع من المطاط الصناعي ومنها مطاط النتريل- بيوتاديين NBR، والذي تم الحصول عليه من بلمرة الاكريلونتريل مع البيوتاديين بنسب معينة وان صيغته الكيميائية على النحو التالي [2]



يطلق على هذا النوع من المطاط، لما له من مقاومة عالية تجاه الزيوت والمذيبات العضوية وكذلك قوة عزله الكهربائي، بالمطاط ذات الاستخدامات الخاصة. إن تلك الخواص الفيزيائية جعلت منه مادة أساسية في صناعة إطارات الطائرات والسيارات وفي صناعة مستودعات الوقود ذاتية الالتحام المستخدمة في الطائرات وفي صناعة الأنابيب الناقلة للنفط وغيرها من الاستخدامات العسكرية الأخرى. فضلاً عن ذلك يستخدم في المعدات الكهربائية وذلك لما يمتلكه من عزل جيد [3].

ان التطور الحاصل في المفهوم النظري لتقنيات التوصيل الكهربائي في البوليمرات وخاصة في المواد المطاطية العازلة أصبح الآن أكثر وضوحاً مما كان عليه سابقاً، وان العمل على زيادة التوصيلية في المواد البوليمرية يحظى بنشاط الباحثين [4-7]، لقد قام العلماء بإجراء دراسات مستفيضة للتعرف على تأثير التطعيم والتشعيع على التوصيل الكهربائي للمواد البوليمرية وكذلك

دراسة تأثير تفاعل تلك المواد مع الإشعاعات المؤينة وغير المؤينة على التوصيل الكهربائي وبقية الخواص الفيزيائية [8-10].

إن الهدف الأساسي من هذا البحث هو دراسة تأثير درجة الحرارة والتشعيع النيوتروني على التيار - الفولتية (I-V) للمطاط NBR النقي والمطعم بالرصاص في المجالات الكهربائية المستمرة وكذلك التعرف على آلية التوصيل وطاقة التشيط.

المواد وطرائق العمل

تم تحضير العينات التي استخدمت في هذه الدراسة من المطاط NBR النقي والمطعم بنسب وزنية 10%، 40%، 50% من الرصاص في منشأة جابر بن حيان.

لغرض إجراء القياسات الكهربائية للعينات قيد الدراسة عند درجات حرارة مختلفة، فلقد تم تصميم وتصنيع خلية للقياس موضحة في المصدر [11]، تم الحصول على التيار والفولتية باستخدام دائرة قياس (التيار - الفولتية) حيث زودت العينات بالتيار المستمر D.C من مجهز القدرة عالي الكفاءة من نوع LEYBOLDE 52237 يعطي تياراً مستمراً تبلغ أقصى قيمة له 2.5mA وجهداً مستقرًا ذات مدى (0-6 KV). ولمعرفة قيمة التيار المتسرب في العينة استخدم مقياس للتيار نوع Digital multimeters ذو مدى (10^{-6} A). أما لقياس فرق الجهد المسلط على العينة فلقد استخدم فولتميتر ذو حساسية عالية.

أما المصدر النيوتروني المستخدم في تشعيع العينات بالنيوترونات هو Radium-Beryllium sources من شركة Leybold-Heraeu، إن المصدر النيوتروني هذا يحتوي على سبعة قنوات للتشعيع، ويختلف الفيض النيوتروني لكل قناة عن الأخرى وذلك حسب المسافة الفاصلة بين القناة وبين منبع النيوترونات بحيث يكون الفيض النيوتروني للقنوات القريبة أكبر من الفيض النيوتروني للقنوات البعيدة، وقد استخدمت القناة رقم (2) ذات الفيض النيوتروني بحدود $100 \text{ n/cm}^2/\text{sec}$ ، إذ تم تشعيع العينات في هذه القناة ولفترات زمنية مختلفة وغير تراكمية.

النتائج والمناقشة

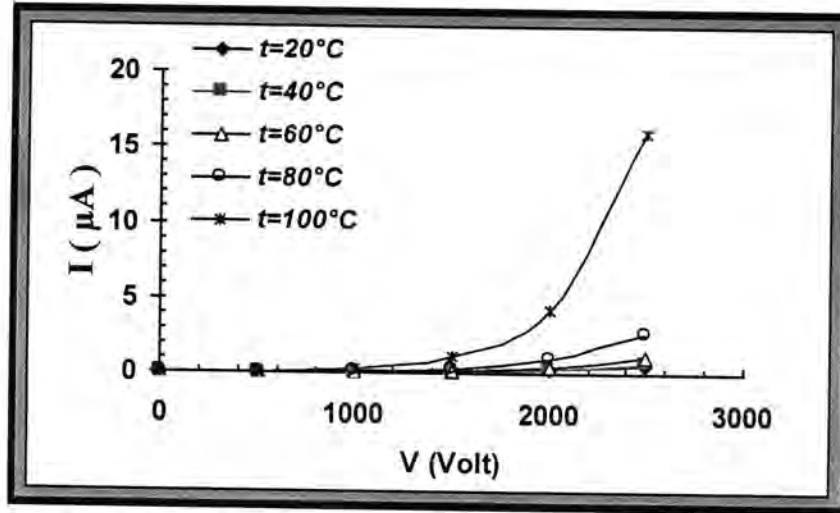
تم في هذا البند عرض ومناقشة نتائج تأثير درجة الحرارة والتشعيع النيوتروني على الخواص (I-V) للعينات التي تم الحصول عليها من المطاط NBR النقي والمطعم بالرصاص وكذلك عرض نوع آلية التوصيل وطاقة التشيط.

أولاً: تأثير درجة الحرارة على الخواص (I-V) للمطاط NBR النقي و المطعم :

تأثير التشعيع النيوتروني ودرجة الحرارة على الخواص الكهربائية لمطاط النتريل - بيوتاديين (NBR) النقي والمطعم بالرصاص

يحيى والياس

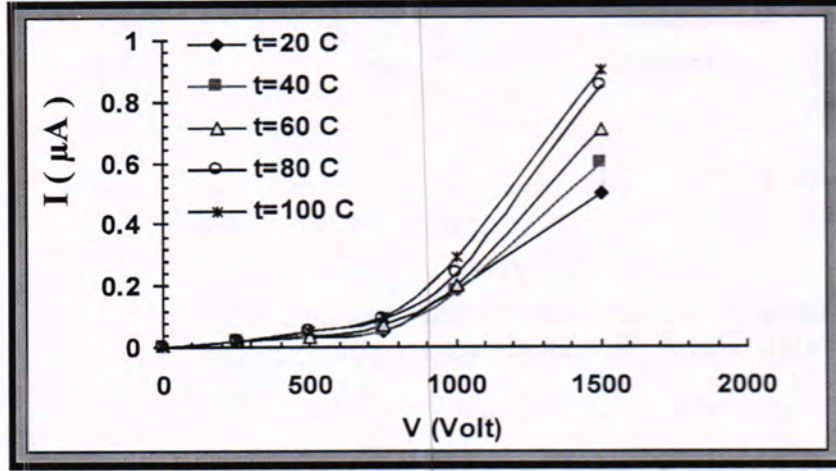
يبين الشكل (1) العلاقة بين التيار المتسرب والجهد المسلط على عينة من المطاط NBR النقي ذات سمك 1.4mm وقطر 1.4cm وعند درجات حرارة 20°C ، 40°C ، 60°C ، 80°C ، 100°C ، على التعاقب.



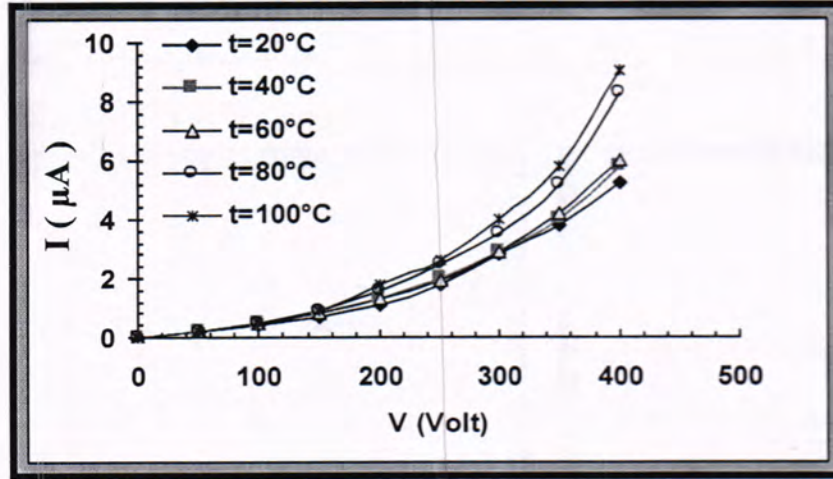
شكل 1: العلاقة بين التيار والفولتية المسلطة على المطاط NBR النقي عند درجات حرارة مختلفة

ونلاحظ من الشكل (1) أنه كلما ازدادت الفولتية المسلطة ازداد التيار المتسرب. وكذلك نلاحظ ظهور زيادة في التيار المتسرب كلما ازدادت درجة الحرارة ونلاحظ ان هناك منطقتان، وقد تعزى إلى آلية التوصيل بالشحنة الفراغية أي التيار المحدد بالشحنة الفراغية (SCLC). ويمكن تفسير الزيادة في التيار المتسرب نتيجة زيادة درجة الحرارة إلى اكتساب الذرات أو الجزيئات طاقة إضافية تعمل على زيادة اهتزازها حول مواقع استقرارها، وبهذا تزداد احتمالية قفزها وتسلقها حواجز الجهد المتكونة نتيجة لترتيب السلاسل البوليمرية المطاطية، وبذلك تكتسب البوليمرات المطاطية طاقة حرارية بتأثير درجة الحرارة إذ تعاني السلاسل الجانبية للبوليمرات عملية اهتزاز حول مواقع ثابتة وعند رفع درجة الحرارة أكثر فأن الحركة الاهتزازية سوف تصبح أكثر شمولاً لتشمل السلسلة الرئيسية والمجموعات الجانبية التي تعمل بدورها على زيادة حركة حواجز الجهد وتقليلها أو قد تختفي أحياناً، ومن ثم تزداد حركية حاملات الشحنة التي تؤثر بدورها على زيادة التوصيلية الكهربائية للبوليمرات المطاطية. كما أن زيادة درجة الحرارة تؤدي إلى حدوث تكسر في سلاسل البوليمرات المطاطية مما يؤدي إلى تحرر جذور حرة وهذه الجذور عندما تحصل على طاقة كافية ترتبط مع بعضها البعض مكونه روابط (أواصر) جديدة (سلاسل بوليمرية جديدة) قد تؤدي إلى زيادة في تسرب التيار [12].

توضح الاشكال (2)،(3)،(4) التيار المتسرب من عينات من المطاط NBR المطعم بنسب 50% ، 40%، 10% من الرصاص وذلك عند تغير الفولتية المسلطة وعند درجات حرارة 20°C ، 40°C ، 60°C ، 80°C ، 100°C ، على التعاقب.



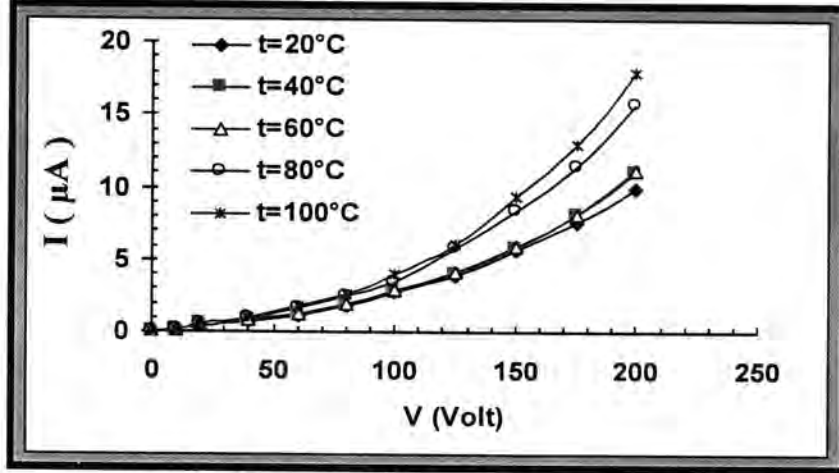
شكل 2: العلاقة بين التيار والفولتية المسلطة على المطاط NBR المطعم بالرصاص عند درجات حرارة مختلفة Pb=10%



شكل 3: العلاقة بين التيار والفولتية المسلطة على المطاط NBR المطعم بالرصاص عند درجات حرارة مختلفة Pb=40%

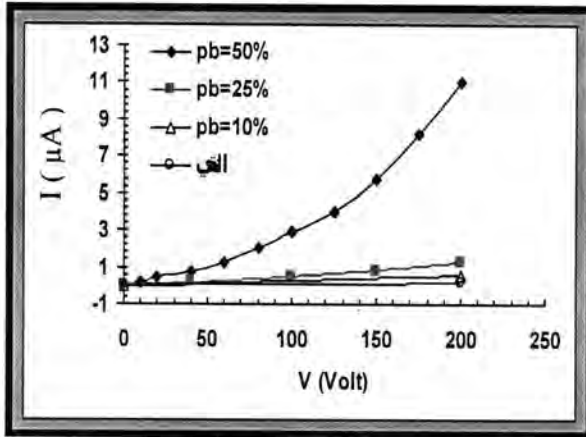
تأثير التشعيع النيوتروني ودرجة الحرارة على الخواص الكهربائية لمطاط النتريل - بيوتاديين (NBR) النقي والمطعم بالرصاص

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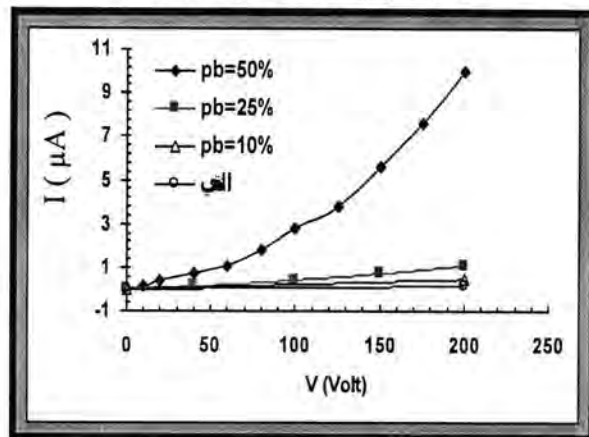


شكل 4: العلاقة بين التيار والفولتية المسطوة على المطاط NBR المطعم بالرصاص عند درجات حرارة مختلفة Pb=50%

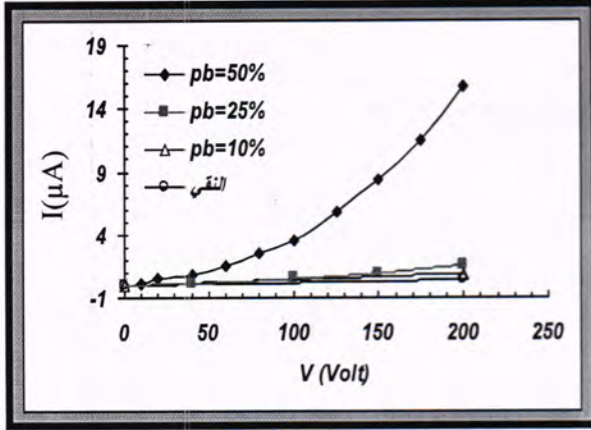
ويلاحظ من الأشكال (2) و (3) و (4) أنه كلما ازدادت درجات الحرارة وازداد تركيز الرصاص ازداد أيضا التيار المتسرب . ولإيضاح تأثير التطعيم بالرصاص على التيار المتسرب فلقد اخترنا درجة الحرارة 20°C ، 40°C ، 60°C ، 80°C ، 100°C وتم رسم العلاقة بين التيار والفولتية I- (V) المسطوة على المطاط المطعم بتركيز مختلفة 10% و 40% و 50% وكما هو مبين في الأشكال (5) و (6) و (7) و (8) و (9).



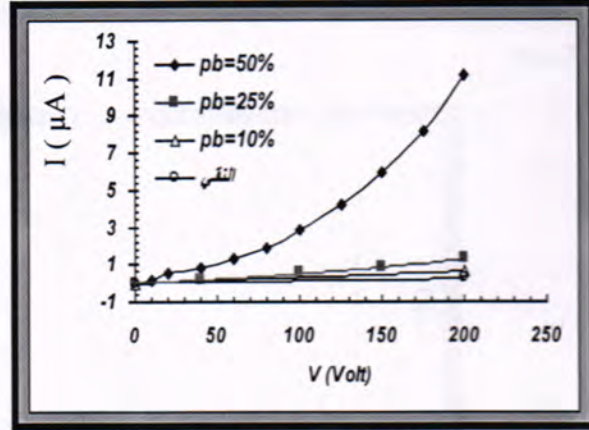
شكل 6: العلاقة بين التيار والفولتية المسطوة على المطاط NBR النقي والمطعم بتركيز مختلفة من الرصاص عند درجة الحرارة t=40 °C.



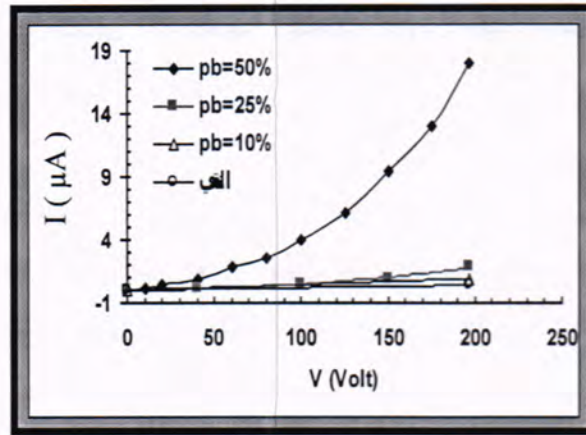
شكل 5: العلاقة بين التيار والفولتية المسطوة على المطاط NBR النقي والمطعم بتركيز مختلفة من الرصاص عند درجة الحرارة t=20 °C.



شكل 8: العلاقة بين التيار والفولتية المسلطة على المطاط NBR النقي والمطعم بتركيز مختلفة من الرصاص عند درجة الحرارة $t=80^{\circ}\text{C}$.



شكل 7: العلاقة بين التيار والفولتية المسلطة على المطاط NBR النقي والمطعم بتركيز مختلفة من الرصاص عند درجة الحرارة $t=60^{\circ}\text{C}$.



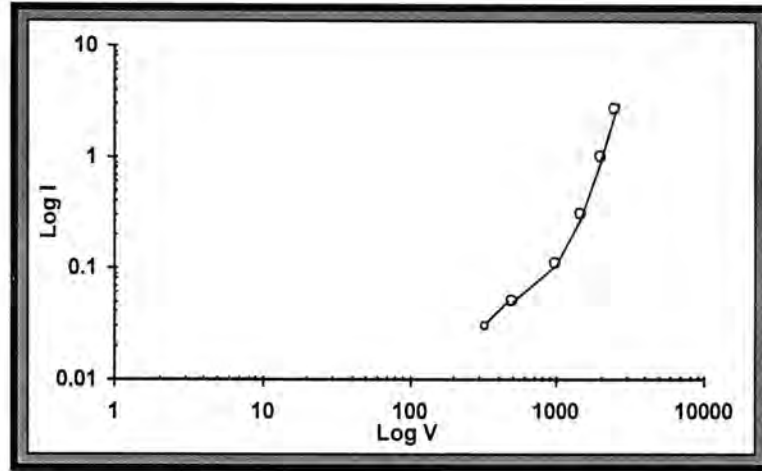
شكل 9: العلاقة بين التيار والفولتية المسلطة على المطاط NBR النقي والمطعم بتركيز مختلفة من الرصاص عند درجة الحرارة $t=100^{\circ}\text{C}$.

ويمكن الملاحظة من الأشكال أنه كلما ازدادت نسبة التطعيم بالرصاص، كلما ازداد التيار المتسرب مع البقاء على آلية التوصيل التيار المحدد بالشحنة الفراغية (SCLC) ويعزى ذلك إلى زيادة ناقلات الشحنة الكهربائية، إذ أن الرصاص ذو توصيلية كهربائية أكبر من توصيلية المطاط NBR ومن ثم فإن تطعيم المطاط NBR بالرصاص يؤدي إلى زيادة في التوصيل الكهربائي للمطاط.

من أجل التعرف على آلية التوصيل من النتائج التي حصلنا عليها، فلقد قمنا برسم العلاقة بين $\log I$ و $\log V$ وكما هو مبين في الشكل (10).

تأثير التشعيع النيوتروني ودرجة الحرارة على الخواص الكهربائية لمطاط النتريل - بيوتاديين (NBR) النقي والمطعم بالرصاص

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شكل 10: العلاقة بين التيار والفولتية المسلطة على المطاط NBR النقي

نلاحظ من الشكل (10) ظهور منطقتين ذاوتي ميلين مختلفين، ويمكن التعبير عن ذلك رياضيا من خلال المعادلة الآتية:

$$I \propto V^m \dots\dots\dots(1)$$

إذ إن m عدد حقيقي يمثل درجة الاعتماد .

ويمكن تفسير هذه الظاهرة إلى آلية التوصيل التيار المحدد بالشحنة الفراغية (SCLC) [14-13]

1. المنطقة الأولى : يمكن عدها منطقة أومية إذ وجدت ($m \sim 1.15$) أي أن التيار المار يتناسب طرديا مع الفولتية المسلطة أي أنها تخضع لقانون أوم . ويمكن تفسير هذا على النحو الآتي :

عندما تكون كثافة الحاملات المحقونة (n_i) أقل بكثير من كثافة الحاملات الحرة (n_0) ($n_i < n_0$) ومن ثم فإن كثافة التيار في هذه المنطقة تتناسب طرديا مع الفولتية المسلطة ($J \propto V$) وحسب العلاقة

$$J = nq\mu \frac{V}{d} \dots\dots\dots(2)$$

2. المنطقة الثانية : يتبين من هذه المنطقة أن التيار يتناسب طرديا مع مربع الفولتية المسلطة، إذ وجدت قيمة (m) بحدود ($m \sim 2.2$). ويمكن تفسير ذلك من حيث أن التيار المحدد بالشحنة الفراغية (SCLC) يكون متغلبا في هذه المنطقة، أي أن كثافة التيار في هذه المنطقة تتناسب طرديا مع مربع الفولتية المسلطة [15].

لقد جاءت نتائجنا مطابقة تقريبا لنتائج الباحث [16] الذي وجد أن آلية التوصيل الأكثر شمولاً هي آلية التيار المحدد بالشحنة الفراغية (SCLC) وأن قيمة m في المنطقة الأولى ($m \sim 1$) وقيمتها في المنطقة الثانية ($m \sim 2.5$)

تعد طاقة التنشيط مقياساً للتمييز بين التوصيل الأيوني والتوصيل الإلكتروني. فقد تمكن [17] عند دراسته للخصائص الكهربائية أن يفصل بين التوصيل الأيوني والتوصيل الإلكتروني، إذ بين أن طاقة تنشيط الإلكترونات (E_a) تكون بحدود (0.2eV) أما طاقة تنشيط الأيونات فتكون بحدود (0.6-0.8 eV).

إن قيمة طاقة تنشيط المطاط NBR النقي التي تم الحصول عليها كانت بحدود 0.64eV. وجاءت هذا النتيجة مقارنة تقريباً لقيمة طاقة تنشيط الأيونات، وهذا ما يؤكد أن توصيلية مطاط NBR أيونية.

ويلاحظ من النتائج أن طاقة تنشيط مطاط NBR النقي تقل عندما تطعم بالرصاص. إذ إن طاقة تنشيط مطاط NBR المطعم بنسبة 10% من الرصاص هي $E_a = 0.58\text{eV}$ في حين كانت طاقة تنشيط مطاط NBR النقي $E_a = 0.64\text{eV}$ هذا يعني أن الطاقة اللازمة لنقل حاملات الشحنة في مطاط NBR المطعم بالرصاص أقل من الطاقة اللازمة لنقل حاملات الشحنة في مطاط NBR النقي، وعند زيادة نسبة الرصاص إلى 40% فإن طاقة التنشيط تقل أيضاً إلى $E_a = 0.48\text{eV}$ ، وعند زيادة نسبة الرصاص إلى 50% فإن طاقة التنشيط تقل أيضاً إلى $E_a = 0.45\text{eV}$. ويمكن أن يعزى سبب انخفاض طاقة تنشيط مطاط NBR المطعم بالرصاص إلى انخفاض حواجز الجهد نتيجة تغير شكل السلاسل البوليمرية المطاطية لجزيئات مطاط NBR عند إضافة الرصاص إليه، مما يؤدي إلى زيادة المسافة الفاصلة بين بئري جهد متتاليين، ومن ثم تزداد احتمالية تغلب الأيونات لحواجز الجهد بطاقة تنشيط قليلة ولذلك سوف تزداد الحركية الانتقالية للأيونات.

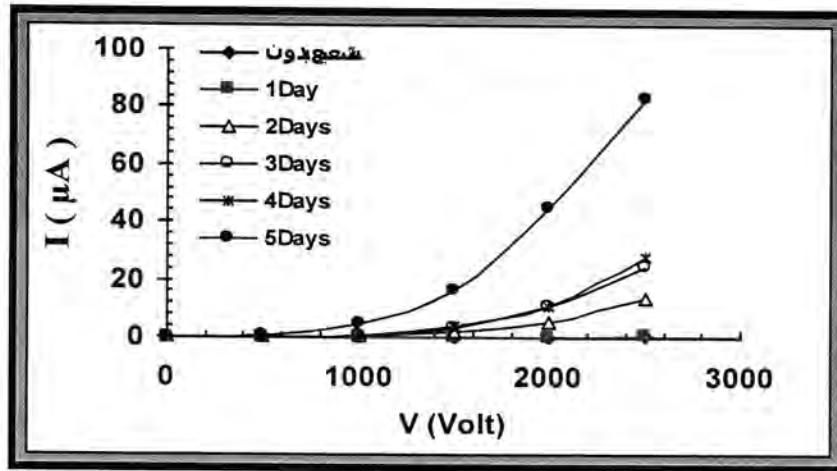
ثانياً: تأثير التشعيع النيوتروني على الخواص (I-V) للمطاط NBR النقي والمطعم:

تم تسليط فيض نيوتروني ($100\text{n/cm}^2/\text{sec}$) ولمدة (1Day, 2Days, 3Days, 4Days, 5Days) على عينات من المطاط NBR النقي والمطعم وبسمك 1.4mm ثم تم قياس خواص (I-V) عند درجة حرارة $t = 20^\circ\text{C}$ باستخدام خلية القياس [11].

يبين الشكل (11) خواص (I-V) للمطاط NBR النقي المشع بالنيوترونات بفيض نيوتروني ($100\text{n/cm}^2/\text{sec}$) وسمك 1.4mm وبأزمنة تشعيع (1Day, 2Days, 3Days, 4Days, 5Days) على التعاقب.

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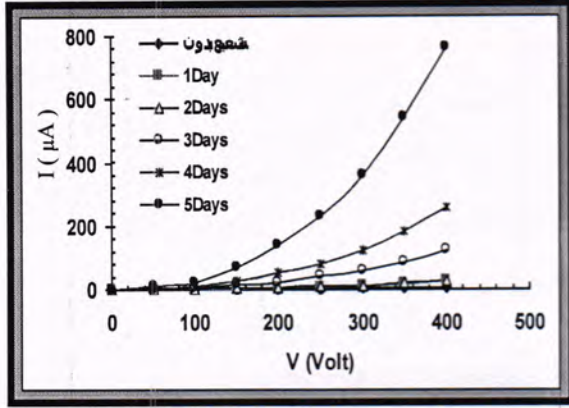
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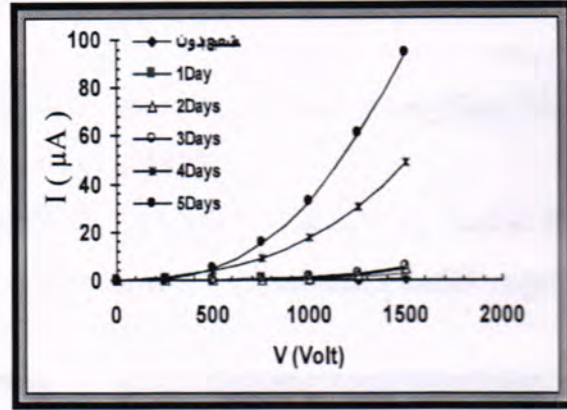
شكل 11: العلاقة بين التيار والفولتية المسطوة على المطاط NBR النقي عند درجة الحرارة $t=20^{\circ}\text{C}$ مشععة بالنيوترونات وبأزمنة تشعيع مختلفة

ونلاحظ من الشكل (11) انه كلما ازدادت الفولتية المسطوة ازداد التيار المتسرب وكذلك تحصل زيادة في التيار المتسرب كلما ازدادت زمن التشعيع وكذلك نلاحظ ظهور منطقتين مما يدل على أن آلية التوصيل هي لازالت من نوع التيار المحدد بالشحنة الفراغية (SCLC) . وهو يشبه التصرف الذي يسلكه مطاط NBR عند التسخين الاعتيادي . يمكن تفسير الزيادة في التيار المتسرب إلى الزيادة في ناقلات الشحنة ، فيمكن القول أنها ناتجة عن التكسير الجزيئي نتيجة التشعيع النيوتروني، وهذا قد يؤدي الى زيادة ناقلات التيار (الجذور الحرة في السلسلة البوليمرية) وكذلك اكتسابها طاقة اضافية مما يجعلها ذات قدرة عالية على اصال التيار الكهربائي المتسرب تحت تأثير المجال الكهربائي .

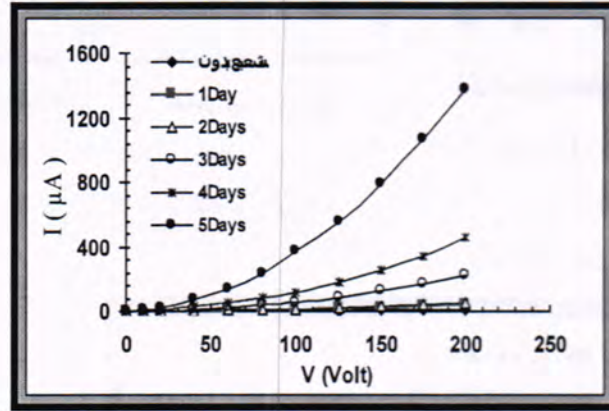
تبين الأشكال (12) و(13) و(14) العلاقة بين التيار والفولتية المسطوة على المطاط NBR المطعم بنسب مختلفة من الرصاص 10% و 40% و 50% وللسمك 1.4mm وقطر 1.4cm والمشععة بالنيوترونات وبأزمنة تشعيع مختلفة 1Day، 2Days، 3Days، 4Days، 5Days وعند درجة حرارة 20°C .



شكل 13: العلاقة بين التيار والفولتية المسطرة على المطاط NBR المطعم بالرصاص $Pb=40$ عند درجة الحرارة $t=20^{\circ}C$ مشععة بالنيوترونات وبازمنة تشعيع مختلفة



شكل 12: العلاقة بين التيار والفولتية المسطرة على المطاط NBR المطعم بالرصاص $Pb=10\%$ عند درجة الحرارة $t=20^{\circ}C$ مشععة بالنيوترونات وبازمنة تشعيع مختلفة



شكل 14: العلاقة بين التيار والفولتية المسطرة على المطاط NBR المطعم الرصاص $Pb=50\%$ عند درجة الحرارة $t=20^{\circ}C$ مشععة بالنيوترونات وبازمنة تشعيع مختلفة

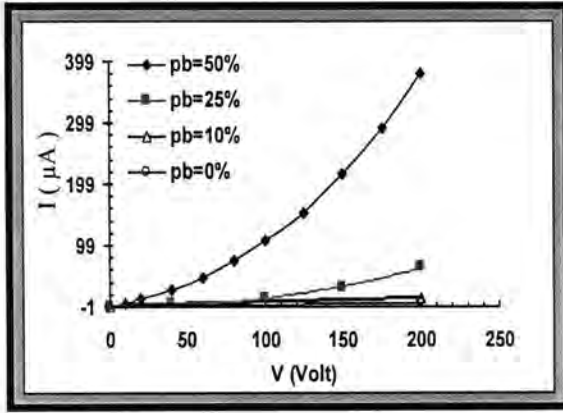
ومن الأشكال السابقة نلاحظ انه كلما ازدادت الفولتية المسطرة كلما ازداد التيار المتسرب وكذلك كلما ازدادت نسبة التطعيم بالرصاص ازداد التيار المتسرب مع البقاء على آلية التوصيل التيار المحدد بالشحنة الفراغية (SCLC) وهو يشبه التصرف الذي يسلكه مطاط NBR عند التسخين الاعتيادي. ويمكن تفسير ذلك أنه عندما تسقط أشعة على البوليمرات المطاطية فأنها تؤدي إلى حدوث تكسر في السلاسل البوليمرية، كما يؤدي ذلك إلى ترابط الجذور الحرة المتكونة نتيجة

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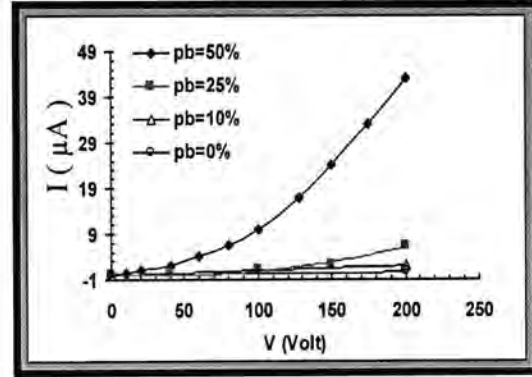
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التشعيع مع بعضها البعض مكونة روابط (أواصر) ، فضلا عن أن عملية التشعيع تهيئ الأيونات وتنقلها إلى نطاق حزمة التوصيل ومن ثم تزداد التوصيلية [18].

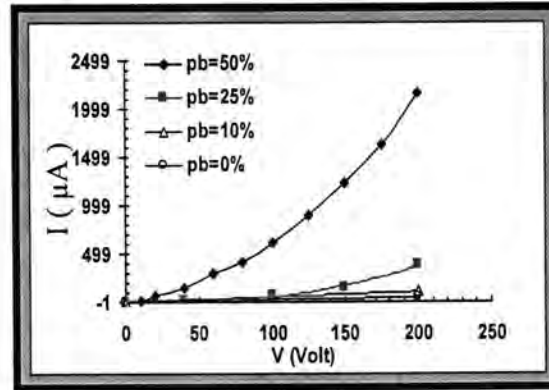
وتبين الأشكال (15) و(16) و(17) العلاقة بين التيار والفولتية المسطرة على المطاط NBR النقي والمطعم بتركيز مختلفة من الرصاص للسلك 1.4mm ولأزمنة تشعيع مختلفة 5Days، 3Days، 1Day) على التعاقب.



شكل 16: العلاقة بين التيار والفولتية المسطرة على المطاط NBR النقي والمطعم بتركيز مختلفة من الرصاص وزمن التشعيع ثلاثة ايام



شكل 15: العلاقة بين التيار والفولتية المسطرة على المطاط NBR النقي والمطعم بتركيز مختلفة من الرصاص وزمن التشعيع يوم واحد



شكل 17: العلاقة بين التيار والفولتية المسطرة على المطاط NBR النقي والمطعم بتركيز مختلفة من الرصاص وزمن التشعيع خمسة ايام

من الاشكال (15) و(16) و(17) نلاحظ ان قيمة التيار المتسرب للعينات المشعة تزداد مع زيادة التطعيم بالرصاص وهذا يعزى الى التأين غير المباشر لذرات الرصاص عند تعرضها

للنيوترونات ومن ثم زيادة ناقلات التيار في المطاط NBR المطعم بالرصااص اكثر مما هي عليه في المطاط NBR النقي.

تمت دراسة تأثير كل من درجة الحرارة والتشعيع النيوتروني على الخواص الكهربائية للمطاط NBR النقي والمطعم بالرصااص في المجالات الكهربائية المستمرة . ومن النتائج العملية التي تم التوصل إليها نستنتج الاتي:

- 1- عند دراسة خواص (I-V) للمطاط NBR النقي عند درجة حرارة معينة لوحظ زيادة في التيار المتسرب كلما ازدادت الفولتية المسلطة.
- 2- يزداد التيار المتسرب في المطاط NBR النقي كلما ازدادت درجة الحرارة. ويعزى السبب إلى زيادة الحركة الاهتزازية للجزيئات المطاطية حول مواقع اهتزازها مما يسبب زيادة في تحركية انتقال الشحنات.
- 3- أما بالنسبة للمطاط NBR المطعم فلقد وجد أن التيار المتسرب أكثر مما ورد في الفقرتين الأولى والثانية، وتعزى هذه الزيادة الإضافية في التيار المتسرب إلى دور الرصااص كمادة ذات توصيلية اكبر من توصيلية مطاط الـ NBR.
- 4- وعند دراسة تأثير الأشعة النيوترونية على الخواص (I-V) للمطاط NBR النقي والمطعم، أظهرت النتائج أن التيار المتسرب يزداد بزيادة زمن التشعيع في حالة المطاط النقي. أما في حالة المطاط NBR المطعم فيلاحظ أن التيار المتسرب أكبر مما هو عليه في المطاط النقي المشع. ولقد تم تفسير الزيادة الإضافية في التيار المتسرب إلى التهيج أو التأين غير المباشر للرصااص.
- 5- عند دراسة خواص (I - V) للمطاط النقي والمطعم وجدنا أنها تتكون من منطقتين: المنطقة الأولى تكون منطقة اومية إذ إن $(I \propto V)$. أما المنطقة الثانية فهي منطقة التيار المحدد بالشحنة الفراغية (SCLC) حيث $(I \propto V^2)$.
- 6- كما بينت النتائج أن قيمة طاقة التنشيط في المطاط NBR تقل بزيادة نسبة التطعيم.

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دراسة وقياس المعلمات الفيزيائية لاستخدام الليزر في تفتيت الحصى

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ABSTRACT

In order to applied laser technology in lithotripsy, and to study the effected parameters on it. In this work different samples of stones from different patients in age , sex and health conditions, were studied after making all laboratory processing for samples properties , also spectroscopic (FTIR) structural (X-Ray) Flouresance and Biological measurements are taken for samples before shotting by laser beam. Samples shotted by train of (Nd:YAG) laser at (1.06 μ m) wavelength, and energy ranges (100-1600)mj with repitation (10-100) pulses with (1pps) frequency. Effecting of laser beam interaction with stones are absorbed and through spectroscopic measurements and results obtained are very acceptable and compatible with other researchs in field, we can improve the ability of using such lasers (Nd:YAG) as one effective tools for lithotripsy. Threshold energy were determined about (150mj) with 25 pulses repitition which increased in effect by increasing the energy and repitition rate which depend upon different stone structure.

الخلاصة

لغرض توظيف تقنية استخدام الليزر في تفتيت الحصى للجهاز البولي ودراسة العوامل المؤثرة عليها، تم في هذا البحث أخذ عدة عينات من الحصى لمختلف المرضى من حيث الاعمار والاجناس والحالة الصحية. واجراء المعالجات المختبرية لهذه النتائج وتهيئتها واجراء الفحوصات الطيفية (FTIR) والتركيبية (X-Ray Flouresence) والبايولوجية قبل معالجتها بالليزر. تم تعريضها لنبضات ليزرية من ليزر Nd:YAG العامل بالطول الموجي (1.06) مايكرومتر وبمديات طاقة (100-1600) ملي جول وبمعدل تكرار (10-100) نبضة وبتردد نبضة في الثانية. تم تحديد وملاحظة تأثير الاشعة المسلطة في عملية تفتيت الحصى ومن خلال اجراء الفحوصات الطيفية للنماذج والحصول على نتائج مشجعة لاثبات امكانية توظيف الليزر اعلاه في تفتيت الحصى وتحديد عتبة التفتيت وكانت بمديات (150) ملي جول وبمعدل (25) نبضة وتزداد تاثير عملية التفتيت بزيادة مديات الطاقة ومعدل التكرار وتعتمد على تركيبة الحصى المختلفة ومقارنة النتائج مع النشريات العلمية في هذا المجال وتبين ملائمة الليزر المستخدم كاحدى الخيارات المتاحة.

المقدمة

ان ميكانيكية تكون حصى الكلية كانت موضع اهتمام العديد من البحوث والتجارب العلمية والتي تطورت بالتزامن مع التطور العلمي في مجال المعدات المستخدمة للتشخيص والمعالجة. حصاة الكلية (kidney stone) هي عبارة عن جسم صلب يتشكل في الكليتين ويتفاوت حجم هذه الحصى من صغير كحبيبات الرمل وصولاً الى حجم كبير يمكن ان يشغل تجويف الكلية وهي تتكون بشكل رئيسي وشائع عند الرجال وقد تسبب ألماً شديداً اذا انحشرت في مجرى ومخرج البول. وفي العديد من الحالات لا يستطيع الاطباء تحديد سبب تكون الحصى حيث ان بعض المرضى تكون لديهم القابلية على تكوين الحصى القلوية لحصولهم على كمية من الكالسيوم عن طريق غذائهم والذي يطرح الزائد منه في البول ولكن قد يتبلور البعض منه قبل ان يغادر الجسم مشكلاً حصاة [1].

تمر معظم حصى الكلى مع البول الى خارج الجسم وعندما تتحشر في طريق خروجها تسبب معاناة مؤلمة للمريض الامر الذي يتطلب معونة الطبيب لاستخراجها باحدى الطرق المتبعة وقد يتطلب الامر تدخلاً جراحياً.

تكمّن فوائد استخدام تقنية الليزر في تفتيت الحصى مقارنة مع التقنيات الاولى بما يلي:

1. بالنظر لمرونة الليف البصري وصغر قطره يعطي قابلية كبيرة لاستخدامه وبفاعلية اكبر

لكل انواع الحصى.

2. حركة الحصى تكون أقل خلال المعالجة.

3. ذو كفاءة عالية في ازالة ومعالجة الحصى المغروسة داخل جدار الكلية.

4. احتمالية حصول نزيف خلال المعالجة تكون قليلة جداً مقارنة مع الطرق التقليدية.

المفاهيم النظرية لاستخدامات الليزر في تفتيت الحصى:

تتم عملية التفتيت للحصى باستخدام الليزر بواسطة التأثير المباشر لشعاع الليزر المستخدم وتفاعله مع مادة الحصى ومكوناتها او عن طريق الموجة الصدمية (Shock wave) الناتجة من امتصاص شعاع الليزر من قبل طبقة رقيقة من السائل المحيط بالحصى بالقرب من نهاية الليف البصري حيث يحصل ارتفاع متزايد لدرجة حرارة السائل خلال زمن قصير مما يؤدي الى حدوث اجهادات ميكانيكية على شكل موجات صدمية (فوق صوتية Super sonic).

وفي كلا الحالتين تعتمد كفاءة عملية التفتيت على عاملين اساسيين هما:

1- الليزر المستخدم مثل الطول الموجي (λ) وأمد النبضة وشدها.

2- الخصائص الطيفية والحرارية لمكونات حصى الجهاز البولي.

ان أمد النبضة وزمن تعرض الحصى للشعاع الليزري له الدور الحيوي في تحديد ديناميكية توازن الطاقة لتفاعل الشعاع مع مادة الحصى وعليه فان هنالك ثلاث انواع من عمليات تفتيت الحصى بالليزر وهي:

1. التفتيت بالموجات المستمرة contentious waves lithotripsy
2. التفتيت بالنبضة الطويلة (ويكون أمد النبضة من مايكروسملي ثانية) long pulse lithotripsy
3. التفتيت بالنبضة القصيرة (أمد النبضة بمديات النانوثانية) short pulse lithotripsy

ان استخدام موجة الليزر المستمرة تؤدي الى رفع درجة حرارة الحصى وتعمل على صهر وتبخير المادة وتعتمد على مقدار امتصاصية مكونات الحصى للطول الموجي وبالتالي فانها تتحدد بمعرفة المركبات الداخلة في تكوين الحصى وان زمن التأثير يكون بطيء نسبيا وبالتالي فان الحرارة المتولدة يمكن ان تؤثر على الاجزاء المحيطة بالحصى ويؤدي الى حصول اضرار غير مرغوب فيها.

أما طاقة الليزر النبضي فيؤدي الى انتقال معظم الطاقة المستخدمة الى مادة الحصى والتي تنتقل اليها عن طريق البلازما المتولدة والتي ينتج عنها توليد موجات صدمية (Shock Waves) وبالتالي فانها لا تعتمد مباشرة على المركبات الداخلة في تركيب الحصى، وبوقت قصير يؤدي الى تفتيتها ويعتمد تأثيرها الجانبي على الاجزاء المحيطة على زمن النبضة. ويوضح الجدول [1] أدناه انواع الليزرات وخصائصها المستخدمة في تفتيت الحصى.

جدول 1: انواع الليزرات وخصائصها المستخدمة في تفتيت الحصى

1-Alexandrite	5-Nd:YAG	10-Multi Nd:YAG
1- wavelength =(380-830)nm	1- wavelength =(532)nm	1- wavelength =(1440)nm
2- pulse duration =(100-1000)ns	2- pulse duration =(100)micro s	2- pulse duration =(650)micro s
3- Q-switch =(30-1000)ns	3- Q-switched =(8-20)ns	11-KTP
4- energy =(80-110)mj	3- energy =(30)mj	1- wavelength =(532)nm
2-Er:Cr:YSGG	6-Ruby	2- pulse duration =(6)ns
1- wavelength =(2.79)micro m	1- wavelength =(694)nm	3- energy =(15)mj
2- pulse duration =(250-500)micro s	2- pulse duration =(170)ns	12-Co ²⁺
3- energy =<1j per pulse	3- Q-switched =(20)ns	1- wavelength =(10.6)micro m
3-Excimer	4- energy =(2)j	2- high eff. =up to 30%
1- wavelength =(120-500)nm	7-FREDDY	3- cw - pulse
2- pulse duration =(160)ns	(frequency-doubled double pulse ND:YAG	4- power =(50)W
3- energy =(80-110)mj	1- wavelength =(532)nm	13-Dye
4- Pav =up to 1j	2- energy =(120)mj	1- wavelength
4-Ho:YAG	8-Ti:Sappher	coumarin =(504)nm
1- wavelength =(2.12)micro m	1- wavelength =(792)nm	Rhodamin 6G =(540)nm
2- pulse duration =(6)micro s	2- pulse duration =(2)micro s	Rhodamin 700 =(720)nm
3- energy =(0.2-2.8)j	3- energy =up to (160)mj	2- pulse duration =(1-300)micro s
4- optical penteration =(400)micro m	9-Nd:Glass	3- energy =(3)mj at (437)nm
5- energy density =(160) j/cm2	1- wavelength =(1055)nm	14-Dual Wave length Ruby laser

دراسة وقياس المعلمات الفيزيائية لاستخدام الليزر في تفتيت الحصى

شروق وشهاب وروى وزينب ومعاذ

2- pulse duration =(30)ns

3- energy =(10)j

1- wavelength =(694-347)nm

2- pulse duration =(170)ns

3- energy =(3)mj at(437)nm

4- energy =(16)mj at(694)nm

أما فيما يتعلق بالخصائص الطيفية للمكونات الداخلة في تركيب الحصى فان العامل الاساسي المؤثر في آلية تفاعل الليزر مع الحصى هو مقدار الامتصاصية لمادة الحصى للطول الموجي لشعاع الليزر المستخدم وهي التي تحدد مقدار الحرارة المتولدة والاجهاد الميكانيكي الحاصل، وان الذي يحدد طاقة الامتصاص يتمثل في الفيض الليزري الساقط وخصائص التوهين البصري (الحصى والماء) وبالاكتفاء على قانون (بير-لامبرت) فان مقدار الامتصاصية (A) تتحدد بالعلاقة التالية [2]:

$$A = \epsilon bc$$

----- (1)

حيث ϵ تمثل الامتصاصية المولارية ووحدتها (لتر / مول سم)

b تمثل طول المسار ويقاس (سم)

c تمثل التركيز المولاري ويقاس (مول / لتر)

اما الامتصاصية الطيفية $\mu_a(\lambda)$ فهي معامل الامتصاص المعتمد على الطول الموجي ويساوي

$$\mu_a(\lambda) cm^{-1} = c * \epsilon$$

----- (2)

ان توزيع شعاع الليزر داخل المادة الماصة يعتمد على الفيض الساقط ومعامل الامتصاص وكمية الشعاع المنعكس عند السطح.

وطبقا لقانون بير فان الفيض الممتص يتناقص اسيا مع العمق Z فان :-

$$F(z) = H_0 (1 - R) e^{(-\mu_a z)}$$

----- (3)

حيث F(z) : الفيض الممتص ووحدته (جول / سم²)

H₀ : الفيض الساقط ووحدته (جول / سم²)

$\mu_a(\lambda)$: معامل الامتصاص ووحدته (سم⁻¹)

R : كمية الشعاع المنعكس عند السطح

اما بالنسبة الى عمق الاختراق البصري فهو العمق الذي يتناقص عنده فيض الليزر الساقط الى 37% من قيمته الأصلية ويرمز له δ_λ وهو مقلوب معامل الامتصاص الذي يقيس معدل المسار الحر للتوهين

$$\delta_\lambda = \frac{1}{\mu_a(\lambda)}$$

----- (4)

حيث δ_λ : عمق الاختراق البصري ووحدته (سم)

بالنسبة للماء فان عمق الأختراق البصري والامتصاصية باستخدام ليزر النيديميوم - ياك هي 8 مايكرومتر لذا فهي تسمح بارتفاع الديناميكيات اللاخطية (non-linear dynamics) مما تزيد من معامل الامتصاص :

$$\delta_\lambda = 8\mu m, \quad \mu_{a(\lambda)} = 0.0125 \text{ cm}^{-1}$$

ان الذي يحدد حجم التشعيع هو عمق الأختراق البصري و المقطع العرضي لحزمة الليزر المستخدم.

العمليات الحرارية - البصرية:

عند امتصاص مادة الحصى لفوتونات اشعة الليزر الساقطة يحدث تهيجا في النظام الذي والجزئي لها ويحدث انتقالات الى مستويات طاقية عليا تؤدي الى زيادة في الطاقة الحركية مع وجود حالة من التوازن الحراري وعليه فان بزيادة الطاقة الحركية ترتفع درجة الحرارة داخل المادة . يحصل التفتيت بالليزر للحصى المغمورة داخل سائل حيث تحدث عملية التبادل الحراري بين بخار السائل ومادة الحصى حيث طبقا لصغر حجم بقعة الليزر وقصر عمق الأختراق البصري تبدأ الحرارة بالارتفاع موضعيا لكنها تنبدد الى المناطق المجاورة بواسطة عملية الانتشار الحراري , حيث ان الزمن اللازم لانتشار الحرارة داخل العينة (الحصى + الماء) بواسطة عملية التوصيل الحراري الى المناطق المجاورة تعتمد على الانحدار الحراري الذي يعرف بـ زمن الانتشار الحراري τ_{th} [3]، ويعرف بأنه دالة على نصف قطر بقعة الليزر وعمق الأختراق البصري .

$$\tau_{th} = \frac{s^2}{4\alpha} \quad \text{where } r_0 \geq S \quad \text{----- (5)}$$

$$\tau_{th} = \frac{r_0^2}{4\alpha} \quad \text{where } r_0 < S \quad \text{----- (6)}$$

حيث α : الانتشارية الحرارية وتقاس (ملم²/ثانية)

r_0 : نصف قطر بقعة الليزر (ملم)

δ_λ : عمق الاختراق (سم)

لذا فان الزمن اللازم لمرور الشعاع داخل السائل واحداث طاقة الحفر والاستئصال هو اطول من زمن المرور داخل مادة الحصى حيث يصل زمن الانتشار الحراري للماء عند استخدام ليزر النيديميوم-ياك لحجم بقعة 0.15 ملم (اقل من عمق الأختراق) الى 38ms.

ان الارتفاع الحاصل بدرجة الحرارة لمادة الحصى تكون دالة لمعامل الامتصاص والعمق وتعطى بالعلاقة التالية [4] :

$$\Delta T(x) = \frac{\mu_a(\lambda) H_0}{\rho C_p} \exp(-\mu_a(\lambda) Z) \quad \text{----- (7)}$$

حيث ΔT : التزايد الحراري ويقاس (درجة مئوية)

ρ : كثافة المادة (كغم / م³)

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C_p : السعة الحرارية النوعية بثبوت الضغط وتقاس (جول درجة مئوية / كغم)

حيث بزيادة درجة الحرارة الى اكثر من 100 درجة مئوية يحصل تبخر للماء والذي يؤدي بدوره الى حصول انحلالات كيميائية في تركيبة مادة الحصى للمنطقة المعرضة للاشعاع الليزري.

العمليات الميكانيكية - البصرية

تحصل التفاعلات الميكانيكية-البصرية نتيجة الارتفاع السريع في درجة حرارة حجم معين متعرض لنبضات ليزرية قصيرة جدا تتسبب في احداث تمدد حراري مرن يعمل على خلق موجات اجهادية على شكل موجات صوتية او فوق صوتية (صدمية) "تنتشر الموجة الصوتية في الماء بسرعة 1.5 $\text{mm } \mu\text{s}^{-1}$ عند 37 °م بينما الموجات الصدمية تكون فائقة السرعة " اما الماء فيعاني من تبخير يؤدي الى احداث ضغط بخاري نتيجة لأمتصاصه الطول الموجي.

للحصول على التأثير الميكانيكي يجب ان تكون امد النبضة لليزر اقصر من الزمن الازم لأحداث موجة اجهاد تنتشر خارج منطقة الأمتصاص الفوتوني وهو ما يعرف بزمن الانتشار الصوتي τ_a وطبقا لمقياس التولد الحراري فان الطاقة الميكانيكية تبقى داخل المنطقة المعرضة للاشعاع خلال فترة بقاء نبضة الليزر فيتولد ما يعرف بشرط " ولادة الاجهاد " وهذا المقياس يعبر عنه [5]:

$$\tau_p < \tau_a = \frac{s}{\sigma} \quad \text{----- (8)}$$

حيث: σ : the speed of sound in material ($\text{mm } \mu\text{s}^{-1}$)

ففي حالة ليزر Nd:YAG ذات التشغيل المفتاحي في الماء (الذي له عمق اختراق بصري 8 ملم وسرعة صوت 1.5 ملم لكل مايكروثانية) يمتلك زمن تولد الاجهاد يصل الى 5 مايكروثانية حيث يكون اطول من نبضة الليزر البالغة 6 نانوثانية. لذا فانه مع طاقة نبضة ليزر Nd:YAG ذات التشغيل المفتاحي يتوقع توليد موجات صدمية قوية في الماء مع كفاءة تحويل هذه الطاقة الضوئية الى طاقة ميكانيكية .

ان التولد الاجهادي يحتاج الى تولد حراري ولذا فان التغير في الضغط يحسب من خلال التغير الحراري وحسب المعادلة

$$\Delta P = \sigma^2 \rho \beta \Delta T \quad \text{----- (9)}$$

حيث:


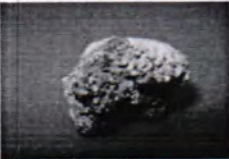

β : the volumetric thermal expansion coefficient (K^{-1})

اذن يعتمد الضغط المتولد على الحرارة المتولدة ولذا فان معامل الأمتصاص والفيض الليزري هما من سيحددان قيمة موجه الضغط المتولدة داخل الحجم الساخن . مع ذلك هذه العلاقة تطبق فقط للاجهاد المتولد من التغير الجزئي في الحجم والنواتج من التمدد الحراري وهي غير مهمة بالمقارنة مع الضغط المرتفع من عمليات التبخير.

النتائج والمناقشة

لغرض دراسة المعلمات الفيزيائية لاستخدام الليزر في تفتيت الحصى للجهاز البولي تم اجراء القياسات الطيفية والتحليلية لمكونات نماذج (عدد / 3) من الحصى التي تم الحصول عليها من المرضى بعد اجرائهم عملية جراحية لاستخراجها. كخطوة اولى تم اجراء القياسات لتحديد الابعاد الهندسية لنماذج الحصى المستخدمة وقياس اوزانها و اجراء التحاليل البايولوجية والطيفية لمعرفة مكوناتها وكما مدرجة في الجدول [2] في ادناه:

الجدول 2: يمثل القياسات الفيزيائية والتحليل البايولوجية لنماذج الحصى المستخدمة في البحث

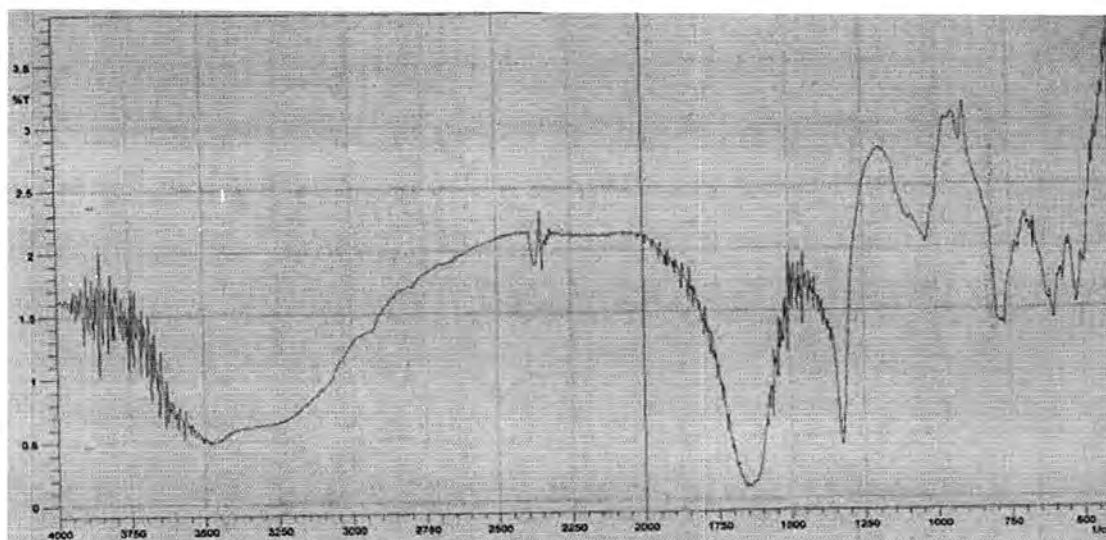
Sample no.	Dimensions in(mm)	Figures	Samles biological analysis
1	Length=5.25mm Width=5mm Hight=4.4mm		1. Amorphas urate 70% 2. Uric acid 30%
2	Length=17.1mm Width=12.45mm Hight=11.4mm		1. uric Acid 60% 2. Amorphas urate 30% 3. Calcium Oxalat 10%
3	Length=12.6mm Width=9.7mm Hight=5.4mm		1. Amorphas urat 60% 2. Uric acid 40%

القياسات الطيفية :

لغرض معرفة ديناميكية تفاعل اشعة الليزر مع الحصى، كان لابد من معرفة الخصائص الطيفية لها وبالتحديد طيف الامتصاص لمديات الاطوال الموجية ومن ضمنها الطول الموجي لليزر النيدميوم - ياك المستخدم وبالتالي سيتم تحديد خصائص الامتصاص الطيفي لكل نوع من انواع الحصى المستخدمة.ولهذا الغرض تم اجراء فحوصات طيفية باستخدام منظومة التحليل الطيفي (FTIR) المصنع من قبل شركة شيمادزو وحسب المخططات الطيفية الموضحة بالاشكال (1) و(2) و(3) للنماذج الثلاثة المستخدمة في البحث.

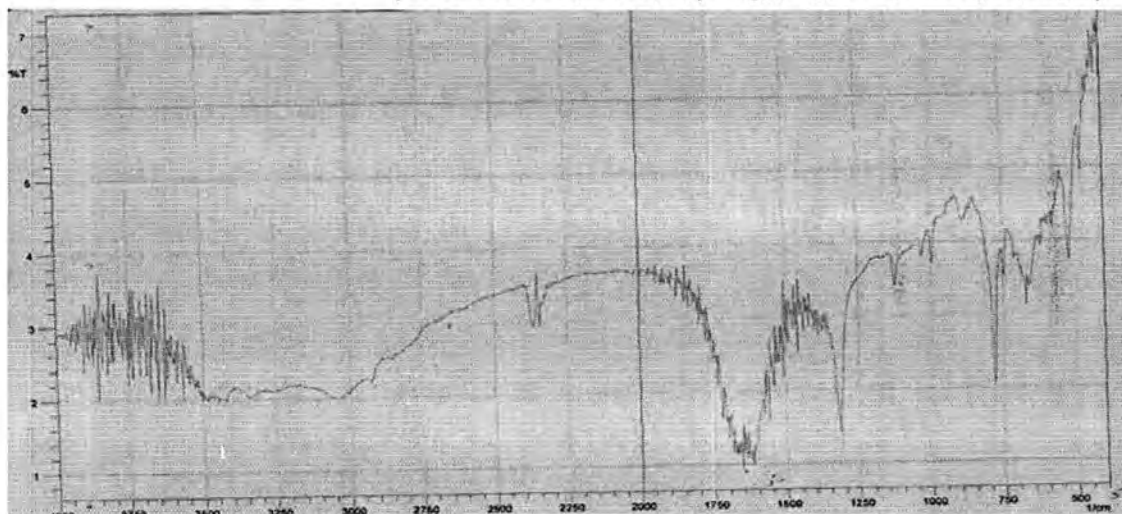
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شكل 1: قمم الامتصاص الطيفية في النقاط عند مديات الاعداد الموجية [521, 600, 760, 800, 1050, 1325, 1620, 4350] cm^{-1}

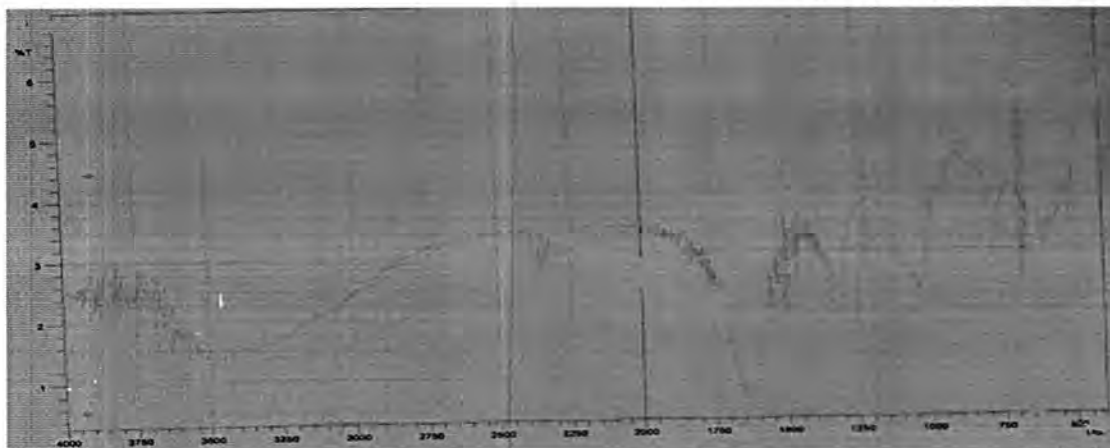
يوضح الشكل (1) قمم الامتصاص الطيفية في النقاط عند مديات الاعداد الموجية [521, 600, 760, 800, 1050, 1325, 1620, 4350] cm^{-1} بالنسبة لنموذج الحصى رقم (1) ويستدل من هذه القيم على وجود احماض الكالسيوم احادية الهيدروجين (Caliciumoxalatemonohydrate) وحمض اليوريك ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$) وحمض اليوريك ($\text{Uric Acid } \text{C}_5\text{H}_4\text{N}_4\text{O}_3$)



شكل 2: قمم الامتصاص الطيفية في النقاط عند مديات الاعداد الموجية [600, 775, 1050, 1325, 1650, 2360, 3460] cm^{-1}

يوضح الشكل (2) قمم الامتصاص الطيفية في النقاط عند مديات الاعداد الموجية [600, 775, 1050, 1325, 1650, 2360, 3460] cm^{-1} بالنسبة لنموذج الحصى رقم (2) ويستدل من هذه

القيم على وجود احماض الكالسيوم ثنائية الهيدروجين (Caliciuinoxalatedehydrate) وحمض اليوريك ($\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) واورسالات الكالسيوم الفوسفاتية ثنائية الهيدروجين ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$).



شكل 3: قمم الامتصاص الطيفية في النقاط [480, 520, 670, 750, 800, 1000, 1050, 1150, 1310, 1650, 2360, 3050, 3450]

يوضح الشكل (3) قمم الامتصاص الطيفية في النقاط [480, 520, 670, 750, 800, 1000, 1050, 1150, 1310, 1650, 2360, 3050, 3450] بالنسبة لنموذج الحصى رقم (3) ويستدل من هذه القمم على وجود اورسالات الكالسيوم الفوسفاتية ثنائية الهيدروجين ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) وحمض اليوريك ($\text{Uric Acid C}_5\text{H}_4\text{N}_4\text{O}_3$).

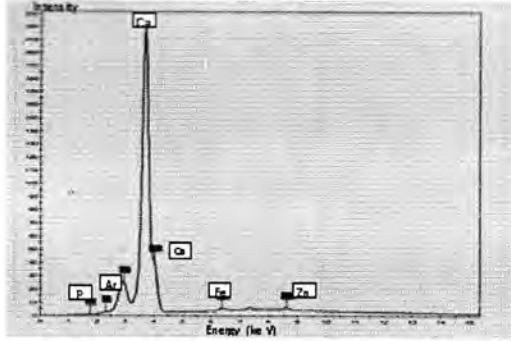
ويأتي هذا الاستنتاج من مقارنة النتائج المستحصلة من القياسات الطيفية باستخدام منظومة ال FTIR للنماذج المستخدمة في البحث مع النتائج المنشورة للقياسات المماثلة في النشريات العلمية [6] حيث هنالك تطابق ملحوظ في تحديد المكونات الداخلة في تركيب الحصى من مقارنة قمم الامتصاص لكل منها.

فحوصات الاشعة السينية

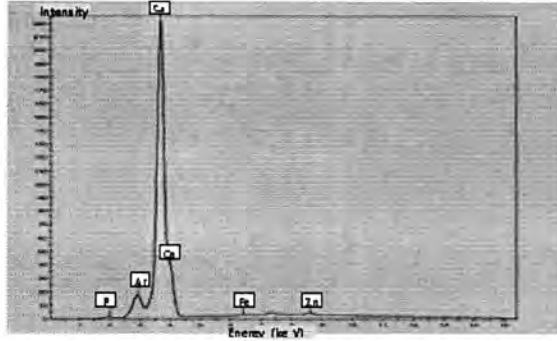
تم اجراء فحص تحليلي للعينات المستخدمة في البحث وباستخدام منظومة [Ray Flouresance X-] لتحديد المكونات الاساسية الداخلة في تركيب الحصى وتحديد نسب تراكيزها وكما موضحة بالاشكال أدناه:

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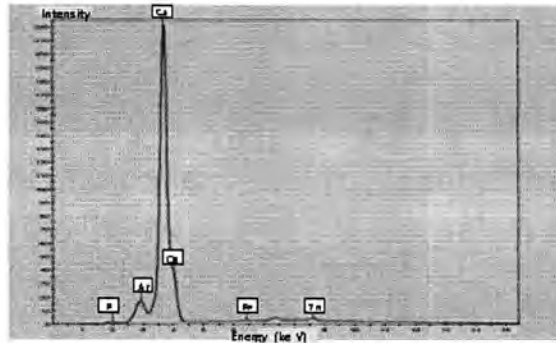
شروق وشهاب وروى وزينب ومعاذ



شكل 5: نسب عناصر الكالسيوم والركون والزنك والحديد والكبريت والسليكون



شكل 4: نسب عناصر الكالسيوم والركون والزنك والحديد والكبريت والسليكون



شكل 6: نسب عناصر الكالسيوم والركون والزنك والحديد والكبريت والسليكون

نلاحظ من الشكل 4 وجود عنصر الكالسيوم بأعلى نسبة عند 3.7Kev اما الأركون بنسبة أقل عند 3Kev وكذلك نسب قليلة من عناصر (Zn, Fe, S, Si). ومن الشكل 5 نلاحظ وجود عنصر الكالسيوم بأعلى نسبة عند 3.5Kev اما الأركون بنسبة أقل عند 2.9Kev وكذلك نسب قليلة من عناصر (Zn, Fe, P). ومن الشكل 6 نلاحظ وجود عنصر الكالسيوم بأعلى نسبة عند 3.75Kev اما الأركون بنسبة أقل عند 3Kev وكذلك نسب قليلة من عناصر (Zn, Fe, P)

وتعد هذه الخطوة ضرورية لتحديد مدى ملائمة الطول الموجي لليزر المستخدم وعلى مبدأ ان تفاعل الليزر مع المادة يتحدد بمديات الامتصاص الطيفي للمكونات الداخلة في تركيب الحصى. وهذا يتحدد من مطابقة النتائج أعلاه مع ماتم الحصول عليه من القياسات الطيفية باستخدام منظومة FTIR.

عملية تفتيت الحصى بالليزر

بعد اجراء الفحوصات الطيفية والتركيبية للعينات المستخدمة في البحث تم تهيئة المنظومة الليزرية مع مكوناتها البصرية الملحقة لغرض اجراء عملية التفتيت لكل عينة ولتحديد عتبة التفتيت لكل نوع تم استخدام مصدر ليزر النيديميوم - ياك موديل ADSS المصنع من شركة Globel والعامل

بالطول الموجي $\mu m (1.06)$ وبمدى طاقات خارجة $mj (100-1600)$ والمصدر الليزري يعمل بمعدل تكرار $Hz (1-6)$ وركزت حزمة الليزر المنبعثة على نماذج الحصى بمقطع عرضي يبلغ $mm^2 (1)$ باستخدام منظومة بصرية لتركيز الحزمة لضمان الحصول على كثافة طاقة ليزرية مؤثرة على الحصى. تتلخص عملية التفتيت لكل نموذج في الحصى المستخدمة بأن تم تعريض النموذج الى نبضات ليزرية وبمعدل تكرار ثابت مع تغيير في طاقة الليزر وملاحظة مدى تأثيرها على الحصى لكل حالة وكانت بالمديات التالية:

1. (10 نبضة بمعدل نبضة لكل ثانية) بطاقات $(100-1600)$ ملي جول
2. (20 نبضة بمعدل نبضة لكل ثانية) بطاقات $(100-1600)$ ملي جول
3. (30 نبضة بمعدل نبضة لكل ثانية) بطاقات $(100-1600)$ ملي جول
4. (50 نبضة بمعدل نبضة لكل ثانية) بطاقات $(100-1600)$ ملي جول
5. (100 نبضة بمعدل نبضة لكل ثانية) بطاقات $(100-1600)$ ملي جول

ومن الملاحظة البصرية على مكان تسليط الليزر على الحصى المستخدمة في البحث تم ملاحظة انه بزيادة الطاقة المسلطة على جسم الحصى بنفس معدل التكرار يزداد مساحة وعمق الحفر مع زيادة الطاقة الى الحد الذي ينجم عنه تذرية الحصى عند المديات الطاقية 1600 ملي جول ويزداد بشكل خطي مع زيادة مديات الطاقة ولكل انواع الحصى مع وجود تباين ملحوظ باختلاف انواع الحصى ويعزى ذلك الى طبيعة مكونات الحصى المختلفة حيث كانت أقل قيمة للطاقة المؤثرة على جسم الحصى لا تقل عن (150) ملي جول ويتكرر (15) نبضة على الاقل. كما ان زيادة معدل التكرار للنبضات الليزرية المسلطة على العينات لنفس مديات الطاقة اوضحت زيادة تأثير معدل التكرار على مساحة وعمق الحفر للمنطقة التي تم معالجتها بالليزر وكانت بداية التأثير لشعاع الليزر على الحصى والذي نجم عنه بداية عملية التفتيت كانت بالمعدلات التالية:

بداية ظهور تأثير هيكل الحصى والشروع بالتذرية (التفتيت) كان بطاقة (150) ملي جول وبمعدل تكرار لا يقل عن (15-20) نبضة وتزداد التذرية وعملية التفتيت بشكل خطي وملحوظ بزيادة الطاقة لنفس معدل التكرار. تم جمع فئات الحصى الناجم عن التفتيت والتذرية وكانت باحجام يمكن الاستنتاج من فعالية عملية المعالجة بالليزر حيث كان واضحاً حصول تفاعل بين الليزر ومادة الحصى وفق المراحل المشار اليها بالجزء النظري، حيث تم تعليق الحصى بخيط وكانت حرة بالحركة وتم ملاحظة اهتزاز الحصى من جراء تسليط نبضات الليزر المتلاحقة والناجمة عن موجة الصدمة اضافة الى وضوح البلازما المتكونة عند منطقة التعرض وشدة اضاعتها.

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من خلال النتائج العملية والفحوصات المشار إليها في الجزء العملي يمكن الاستنتاج بأنه من الممكن اعتماد ليزر النيديميوم -ياك ذو الطول الموجي $1.06\mu\text{m}$ وبمعدل تكرار من (15) نبضة لكل ثانية وصعودا الى قيم أعلى وبمديات طاقة (150) ملي جول وصعودا في تفتيت حصى الجهاز البولي وان لم يكن هو الخيار الافضل مقارنة مع الدراسة النظرية التي تم اجراء ذكرها بالجزء النظري للبدائل الاخرى ولكن لعدم توفرها تم الاكتفاء عمليا بهذا النوع من الليزر. كما ويمكن الاشارة الى ان شدة تأثير الحصى بالاشعة المسلطة يعتمد على نوع مكونات الحصى وتحديد عتبة التفتيت بطاقة (150) ملي جول وبمعدل تكرار (25) نبضة للشروع بعملية التفتيت وبالمقارنة مع النشريات المستحصلة [6] .

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دراسة الخصائص الكهربائية لأغشية البزموت الرقيقة المحضرة بطريقة التبخير الحراري الفراغي مع دراسة تأثير عملية التلدين الحراري عليها

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ABSTRACT

In the research a study of I-V characteristics of (Bi) thin films evaporated on glass substrat at room tamperture at dark conditions for forwards and reversal sides ,they have an ohmic contact behavior but this differ by applying heat treatment for the range of $(50-250)^{\circ}\text{C}$ the resistivity decreases when the degree of heat treatment increases, the films shown a constant resistance when temperature increasing but the resistance slowly increasing for the rang $(170-200)^{\circ}\text{C}$. The (Bi)films have a conductors and semiconductor behavior at $(40-170)^{\circ}\text{C}$ range, the seebeck coefficient is positive and itsvalue between $(17-49.2\mu\text{V/K})$, The electric activation energy is (0.0433eV) and the thermoelectric activation energy is (0.0357eV)

الخلاصة

في هذا البحث تم دراسة علاقة تيار-جهد في حالة الظلام بالاتجاهين الأمامي والعكسي لأغشية البزموت المرسبة على قواعد زجاجية في درجة حرارة الغرفة وظهر انها ذات سلوك مشابه لسلوك الأتصال الخارجي. وعند اجراء عملية التلدين الحراري للمدى $(50-250)^{\circ}\text{C}$ اختلف سلوك الأغشية عن الحالة التي كان عليها. وقد نقصت المقاومة الكهربائية مع ازدياد درجة حرارة التلدين. ان علاقة المقاومة بدرجة الحرارة فانها تميل الى الثبات عند زيادة درجة حرارة الغشاء مع زيادة طفيفة جداً فيها عند درجات الحرارة $(170-200)^{\circ}\text{C}$ فأغشية البزموت تسلك سلوكاً وسطاً بين المعادن وأشباه الموصلات ضمن المدى الحراري $(140-170)^{\circ}\text{C}$ تبين لدينا ان معامل سيبك (موجب) وتراوح قيمته المقاسة بين $17-49.2\mu\text{V/K}$. وفي ظروف البحث كانت قيمة طاقة التنشيط الكهربائية 0.0433eV وان طاقة التنشيط الكهروحرارية تساوي 0.0357eV .

المقدمة

البزموت من عناصر المجموعة الخامسة من اشباه المعادن $(E_g \approx 24.9-28.7)\text{m eV}$ تظهر خصائصه شبه المعدنية في الحالة الحجمية بسبب تطابق حزم التكافؤ مع حزم التوصيل (1). وقد لاحظ (2) تغير مقاومة أغشية البزموت مع درجة الحرارة و تناقص المقاومة مع زيادة سمك الأغشية.

دراسة الخصائص الكهربائية لأغشية البزموت الرقيقة المحضرة بطريقة التبخير الحراري الفراغي مع دراسة تأثير عملية التلدين الحراري عليها

هنا

وقد درس (1) تغير المقاومة مع درجة الحرارة لأغشية البزموت الرقيقة ذات سمك ($\approx 70\text{nm}$) ووجدوا ان مقاومة الغشاء تقل ثم تزداد بشكل طفيف في نهاية المدى الحراري لبحثهم وكان سمك الأغشية يتراوح بين 23nm (225-23) كالملاحظ (1) عند ترسيبهما للبزموت على قواعد زجاجية بالتبخير الحراري الفراغي ان مقاومة الأغشية الملدنة تقل مع ازدياد درجة الحرارة مظهرة خصائص شبه موصلة. عند التلدين يحصل نمو حبيبي وأختفاء بعض العيوب ومساحات من الحدود الحبيبية وربما يكون هذا سبباً للنقص في المقاومة الكهربائية (3-4) ووجدوا أيضاً ان علاقة ($\log p$) ومقلوب درجة الحرارة ($1/T$) تكون خطية. ان علاقة التوصيلية الكهربائية مع تغير درجة الحرارة لأغشية البزموت الرقيقة تعطى بالعلاقة الآتية (5)

$$\sigma = \sigma_{01} \exp[-\Delta E / K_B T] \dots\dots\dots (1)$$

$E_a = \Delta E = E_C - E_f$ وتمثل طاقة التنشيط

E_f, E_C حزمة التوصيل ومستوى طاقة فيرمي

σ_{01} التوصيلية الصغرى للمعدن وهي كمية ثابتة

K_B ثابت بولتزمان T درجة الحرارة المطلقة

لدراسة عمليات التوصيل الكهربائية الرئيسية المختلفة يمكن رسم علاقة تغير ($\ln \sigma$) مع مقلوب درجة الحرارة $1000/T$ K⁻¹ (6) وفيه تظهر مناطق التوصيل المختلفة بشكل واضح اعتماداً على نوع مادة الغشاء ونوع التوصيلية ومن ميل الخط المستقيم يمكن حساب طاقة التنشيط الكهربائية (7).

لاحظ بعض العلماء (8) ان خصائص تيار-جهد من السمات الخاصة بآلية التوصيل الكهربائي فعلاقة تيار-جهد في حالة الظلام تكون مؤشراً للمقاومة او المقاومة والتوصيلية الكهربائية للغشاء الرقيق . عند مقارنة خصائص تيار-جهد للأغشية الرقيقة المختلفة لنفس المادة يمكن الدلالة على وجود العيوب والتشوهات في الأغشية وملاحظة تأثير ظروف الترسيب المختلفة على هذه الخصائص وتحديد الظروف الملائمة لإنتاج أغشية ذات مواصفات مرغوبة (9).

القدرة الكهروحرارية هي القوة الدافعة الكهربائية لوحدة الفرق في درجة الحرارة بين طرفي غشاء رقيق او مادة معينة (10). وقد وجد بعض الباحثين ان اعظم قوة دافعة كهربائية حرارية يستحصل عليها عندما يكون سمك الغشاء اكبر من 250nm (11-12) ويعرف معامل سيبيك بأنه النسبة بين فرق الجهد (ΔV) والفرق في درجات الحرارة (ΔT) بين الطرف البارد والساخن بين طرفي الغشاء كما في المعادلة الآتية (13).

$$\alpha = \Delta V_{12} / \Delta T \dots\dots\dots (2)$$

ماتعطى (α) بوحدات $\mu V/K$

ان اشارة معامل سيبك تعطي اشارة حاملات الشحنة الرئيسة في اشباه الموصلات غير النقية (14). ففي حالة اشباه الموصلات غير النقية تكون اشارة معامل سيبك نفس اشارة ناقلات الشحنة الرئيسة ولأشباه الموصلات النقية تكون الأشارة نفس اشارة ناقلات الشحنة ذات التحريكية العالية (15). بالنسبة للمواد ذات التوصيلية القليلة يكون معامل سيبك عادةً أكبر منه للمواد ذات التوصيلية الكهربائية العالية (16).

وقد درس (17) علاقة فرق الجهد الخارج بتغير سمك أغشية البزموت ولاحظوا ان فرق الجهد الخارج يزداد خطياً مع السمك كونه يتناسب مع الانحدار الحراري عبر سطح الغشاء الرقيق فعندما يزداد السمك فأن الفرق في درجات حرارة الغشاء يزداد وبالتالي يزداد فرق الجهد. وقد بحث (18) تأثير تغير سمك اغشية البزموت على القدرة الكهروحرارية عند درجات حرارية مختلفة ولاحظا زيادة القدرة الكهروحرارية عند زيادة درجة الحرارة وقد درس (17) العلاقة بين تغير فرق الجهد الخارج كدالة لعرض اغشية البزموت مختلفة السمك ووجدوا ان فرق الجهد يتغير عكسياً مع عرض غشاء البزموت .

لحساب طاقة التنشيط الكهروحرارية E_s (التي يجب ان تكون مساوية لطاقة التنشيط التوصيلية الكهربائية) يمكن رسم العلاقة بين معامل القدرة الكهروحرارية (S) مع مقلوب درجة الحرارة اعتماداً على المعادلة الآتية (19)

$$S = -K_B/e [(E_C - E_F) / K_B T + A] \dots\dots\dots (3)$$

حيث A مقدار ثابت ($A \approx 1$)

المواد وطرائق العمل

تم استخدام شرائح المجهر البصري الزجاجية كقواعد وتم تقطيعها بأبعاد حسب نوع الفحص المطلوب وبعد تنظيفها يتم ترسيب أغشية البزموت بأستخدام منظومة التبخير الحراري الفراغي نوع (Balzers Bae 370) بفراغ يصل الى (10^{-6} Torr) وبأستخدام حويض تبخير من المولبدنيوم (Mo). تجري نفس العملية لترسيب اقطاب الألمنيوم بسمك حوالي 200nm. تم اعتماد الطريقة الوزنية لقياس سمك الأغشية. تجري عملية التلدين الحراري بدرجات حرارية $250^\circ C$, 200, 150, 100, 50) لزمن 15min في فرن انبوبي كهربائي يرتبط بمفرغة دوارة لخفض الضغط لحدود (10^{-3} Torr) قبل وحتى بعد انتهاء عملية التلدين الحراري لغرض تحديد علاقة التيار بالجهد المسلط على طرفي الغشاء بالاتجاهين الأمامي والعكسي لأغشية البزموت في درجة حرارة الغرفة وللأغشية المملنة نستخدم مقياس التيار نوع Keithely 616 Digital Electrometer ومجهز قدرة متغيرة نوع Griffin اجريت عملية قياس مقاومة الأغشية عند التسخين بفرن كهربائي

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هنا

بوجود مزدوج حراري يرتبط بمقياس رقمي نوع (Comark 2502) لقراءة درجة الحرارة وتم التسخين لدرجات حرارة بين $^{\circ}\text{C}$ (200-30) وحددت مقاومة الغشاء بمقياس رقمي متعدد الأغراض نوع (Keithley, 179 TRMS Digital multimeter).

اجريت قياسات القدرة الكهروحرارية لأغشية البزموت المرسبة على قواعد زجاجية بأبعاد $(45 \times 4 \text{ mm})$ المثبت على طرفيها اتصالات أومية من الألمنيوم بسمك (200 nm) . يكون احد طرفي الغشاء بارداً عند درجة حرارة T_1 بينما يسخن الطرف الثاني الى درجة حرارة T_2 ومثبت عليه مزدوج حراري لقياس درجة الحرارة مع تسجيل الجهد الناشئ نتيجة الانحدار الحراري بين طرفي الغشاء.

النتائج والمناقشة

تظهر طبيعة مادة غشاء البزموت عند ملاحظة التوصيل الأومي من خلال العلاقة الخطية للتيار مع الجهد في حالة الظلام في الشكل (1) وهذا متوقع لكون البزموت من اشباه المعادن (1) حيث يتصرف تصرف المعادن علاوة على سلوكه كشبه موصل ذو فجوة طاقة صغيرة جداً . يلاحظ (20) تأثير عملية التلدين على خصائص تيار - جهد في حالة الظلام من الشكل (2). نلاحظ التذبذب في قيمة التيار مقابل الجهد وهذا يعزى الى حدوث اكسدة للأغشية سمكها (200 nm) حيث تم ملاحظة ارتفاع درجة حرارة بعض الأغشية مع زيادة فرق الجهد البسيط المسلط عليها . وهذا موافق لما أكدته بعض الباحثين (2)(21) وقد وجدوا ايضاً ان المقاومة تتناقص (يزداد التيار) مع زيادة سمك أغشية البزموت .

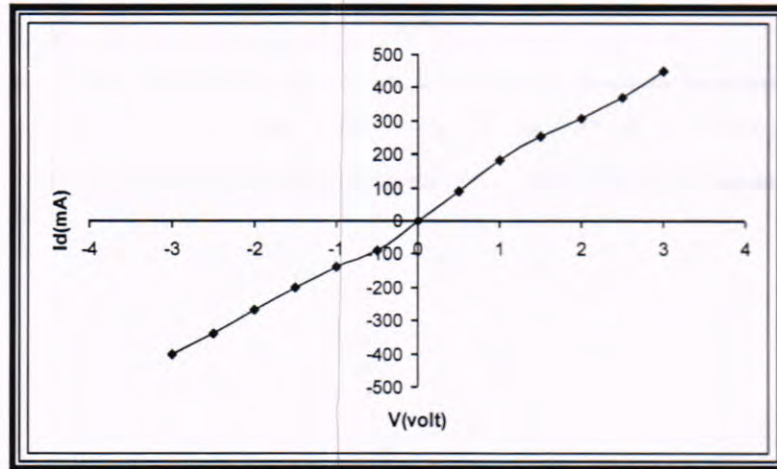
يرجع التوصيل الكهربائي في المعادن الى الألكترونات وتتولد المقاومة الكهربائية في استطارة هذه الألكترونات بالشبيكة فعندما ترتفع درجة الحرارة يزداد اهتزاز الذرات حول مواقعها الرئيسية مما يزيد من استطارة الألكترونات وهذا يعني زيادة المقاومة عند ارتفاع درجة الحرارة وان الجزء الأعظم من قيمة المقاومة الكلية في الأغشية العشوائية التركيب تأتي من الاستطارة عند الحدود الحبيبية (22-23) الشكل (3) يبين اعتماد المقاومة الكهربائية على درجة الحرارة لأغشية البزموت حيث نلاحظ حصول تقعر بسيط في منحنى المقاومة عند تغير درجة الحرارة وتكون قيمة المقاومة في نهاية المدى اكبر بشكل بسيط من بدايته وبذلك يكون سلوكها اقرب الى سلوك المعادن بينما في وسط المدى الحراري تكون اقرب الى سلوك اشباه الموصلات . وهذا موافق لما ذكره بعض الباحثين (24) اذ وجدوا ان مقاومة أغشية البزموت تقل أولاً ثم تزداد مع درجة الحرارة فهي تظهر قيمة دنيا (تقعر). الشكل (4) يبين علاقة $(\ln \sigma)$ و $(1000/T)$ التي تفسرها المعادلة (1) بعد اخذ

اللوغارتم الطبيعي ($\ln \sigma$) لطرفيها ومن ميل الخط المستقيم يمكن حساب طاقة التنشيط الكهربائية (E_a) (25) وظهر لنا انها تساوي (0.0433eV).

يمكن ملاحظة زيادة قيمة معامل سيببك مع زيادة الفرق في درجات الحرارة للمدى الحراري المستخدم كما في الشكل (5) الذي يبين علاقة معامل سيببك بتغير درجة حرارة أغشية البزموت ذات سمك (200nm) وابعاد (45×5) mm وتبين ان قيمة معامل سيببك موجبة وهذا يتفق مع ما وجدته بعض الباحثين (18). وكانت قيمة معامل سيببك المقاسة تتراوح بين (20-46.2 $\mu V/K$) اعتماداً على درجة الحرارة. ان القيمة العظمى لمعامل سيببك مقارنة للقيمة المستنتجة في البحث (17) حيث وجدوا ان قيمة معامل سيببك للبزموت تساوي (50 $\mu V/K$) لغشاء عرضه (5mm).

الشكل (6) يبين علاقة معامل سيببك (S) مع (1000/T) والتي تمثلها المعادلة (3) ومن ميل الخط المستقيم يمكن حساب طاقة التنشيط الكهروحرارية (E_s) وكانت تساوي (0.0357eV). وهذا يتفق مع ما وجدته بعض الباحثين (26-27).

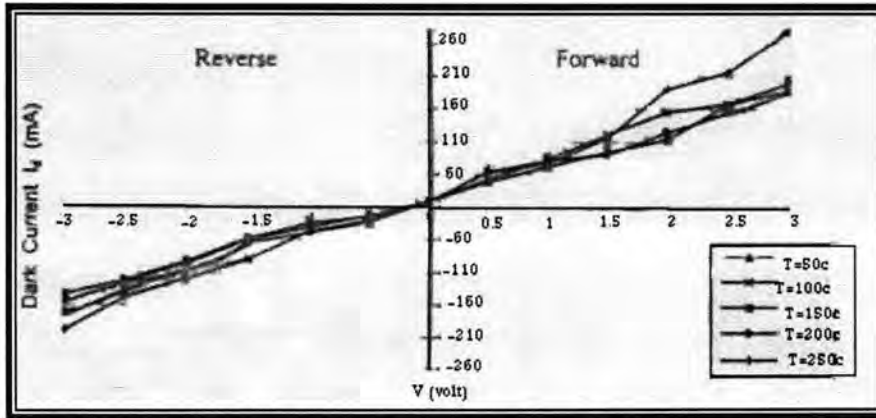
تبين عند دراسة خصائص تيار-جهد في حالة الظلام ودراسة تأثير الحرارة على المقاومة الكهربائية لأغشية البزموت انها تظهر سلوكاً اقرب الى سلوك المعادن مع انها تبدي خصائص شبه موصلة في بعض الأحيان فهي تسلك سلوكاً وسطاً بين المعادن وأشباه الموصلات كونها من أشباه المعادن. ظهر لدينا ان عملية التلدين الحراري بالظروف المستخدمة في بحثنا لها نتائج ايجابية في نقص المقاومة الكهربائية. من نتائج القدرة الكهروحرارية تبين ان معامل سيببك موجب وذو قيمة عالية تعتمد على درجة الحرارة



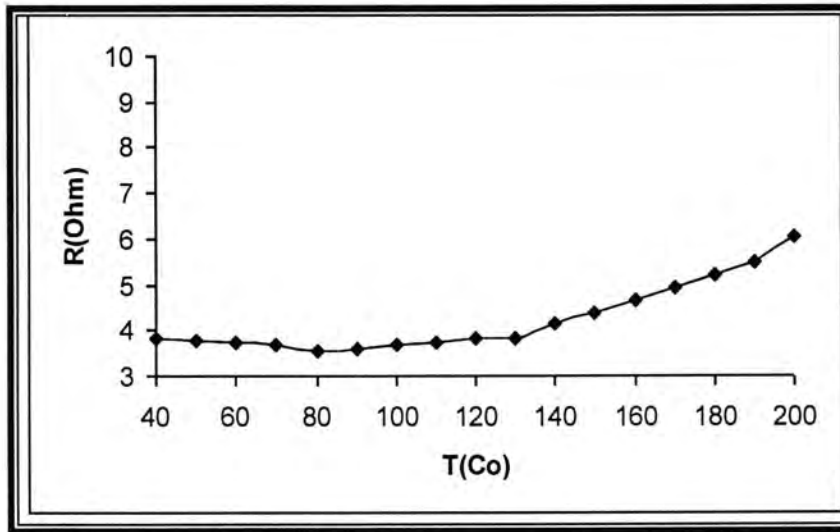
شكل 1: يبين خصائص تيار -جهد في حالة الظلام لأغشية البزموت المرسبة بدرجة حرارة الغرفة وبالاتجاهين الامامي والعكسي

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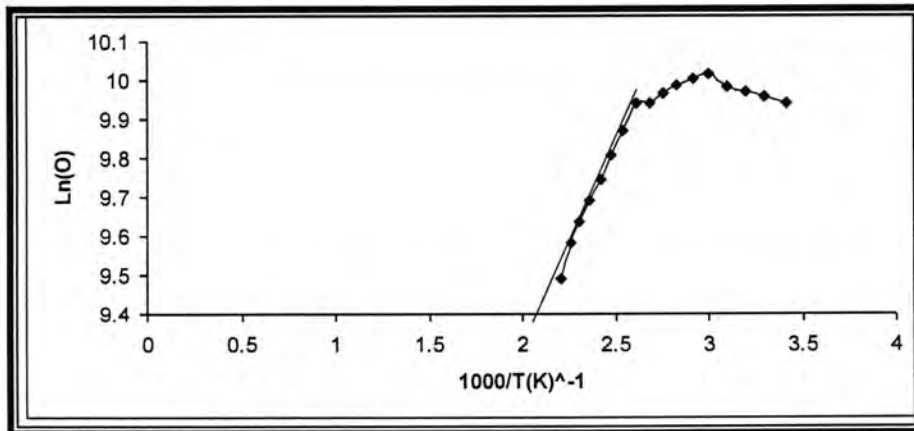
هنا



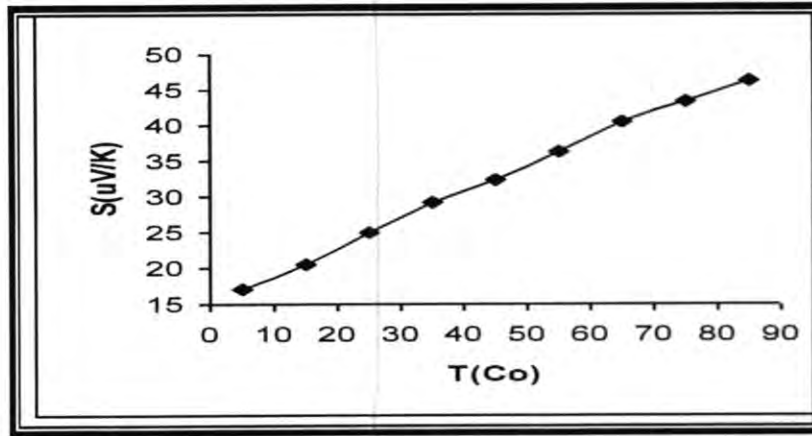
شكل 2: خصائص تيار-جهد في حالة الظلام لأغشية البزموت المبلدة حرارياً بالاتجاهين الامامي والعكسي



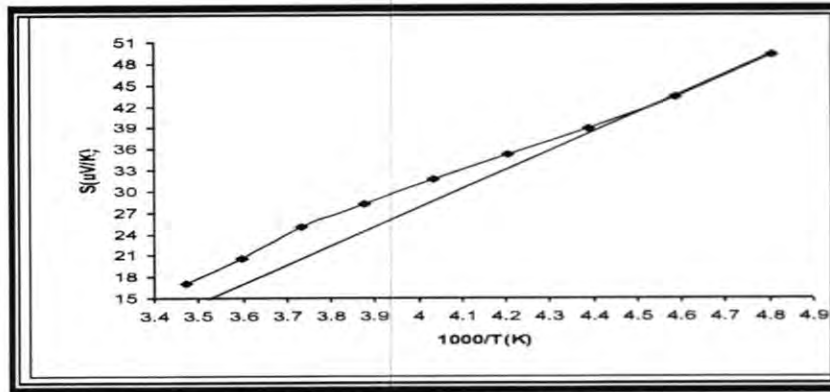
شكل 3: يبين علاقة المقاومة الكهربائية مع درجة الحرارة



شكل 4: يبين علاقة $\ln(\sigma)$ مع $1000/T$



شكل 5: يبين علاقة معامل سيبك مع تغير درجة الحرارة



شكل 6: يبين علاقة معامل سيبك مع 1000/T

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دراسة تحليلية للمطبات الهوائية الحرارية فوق مدينة بغداد

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ABSTRACT

By using the upper observing for two times 00 and 12 UTC for two months, March and April, for three years recorded at meteorological International Baghdad airport. The location and intensity have determined the thermal air turbulence for two layers such that 0-3 km and 3-6 km. The results show that the number of frequencies of severe and moderate turbulences at the months in the first layer is more than those at 00 UTC. In the second layer frequency of severe turbulence at 12 UTC and 00 UTC are equal. In addition, empirical expressions between thermal turbulences and some thermodynamic parameters such as the difference between air temperature and dew point temperature and the height of convective condensation level have been concluded.

الخلاصة

باستخدام بيانات الرصد العلوي للرصدتين 00 و 12 لشهري آذار ونيسان ولمدة ثلاث سنوات المسجلة عند محطة مطار بغداد الدولي الانوائية. تم تعيين موقع وشدة المطبات الهوائية الحرارية لطبقتين جويتين هما 0-3 km و 3-6 km. وقد بينت النتائج إن عدد تكرارات المطبات الشديدة والمتوسطة في 12 UTC للشهرين في الطبقة الأولى أكثر تكراراً من 00 UTC. وفي الطبقة الثانية فإن تكرار المطبات الشديدة في الرصدتين 00 و 12 متساوية. بالإضافة إلى ذلك تم استنتاج علاقات تجريبية بين المطبات وبعض المتغيرات الترموديناميكية مثل الفرق بين درجة حرارة الهواء ودرجة حرارة نقطة الندى عند سطح المحطة وارتفاع مستوى التكاثف الحملي.

المقدمة

منذُ بزوغ فجر الطيران كانت رداءة الطقس السبب الرئيس في تحطم العديد من الطائرات بأنواعها المختلفة ووقوع حوادث كثيرة نجم عنها إعطاب العديد منها ووقوع إصابات متفرقة بركابها، إذ يزداد تأثيرها عند وجود العواصف الرعدية. تعتبر التطورات الحولية المصدر الرئيسي لنشوء المطبات الهوائية الحرارية حيث أنها تنشأ من تطور عملية الحمل الحراري في الغلاف الجوي ومن التيارات الرأسية ضمن وحول الغيوم الحولية [1].

منعم وأركان

تحديد مواقع المطبات الهوائية وشدتها لها أهمية كبرى في الطيران، إذ تعمل على عرقلة واهتزاز الطائرات أثناء إقلاعها وهبوطها مما قد تسبب حدوث بعض المشاكل على المسافرين ونقل البضائع. إن تحديد مواقعها له أهمية للطيارين في اتخاذ المسار الصحيح والأمن أثناء حركة الطائرات لاجتناب المطبات خصوصاً الشديدة. وأخيراً توفر هذه الدراسة سلوكاً مناخياً عن طبيعة المطبات خلال المنطقة. أما شدة المطبات فأنها تختلف خلال اليوم الواحد فأقصى شدة لها تحدث عند العصر وأقلها عند الليل، بينما في العواصف الرعدية تدوم خلال وقت الليل مع الانتشار لمسافات كبيرة تبلغ عدة آلاف الكيلومترات.

ارتبط فهم ميكانيكية نشوء المطبات الهوائية عند تطور وسائل نقل الخطوط الجوية في العالم خصوصاً عند اخذ التقارير الخاصة بالمطبات (مثل رياح القصى العمودية والاستقرارية الجوية ومواقع التيار النفاث وسرعة الرياح القصوى والأخاديد التي تصاحب المنظومات الضغطية) من قبل الطيارين وقد حلت هذه التقارير عند المستويات القياسية 300-500 hPa لأشهر نيسان مثل باحثين Smigiecki [2] و Kronebach [3] ويعدها قام الباحثان Endlich and Mancuso [4] بمقارنة نتائج تقارير الطيارين مع رياح القصى الأفقية والعمودية المحسوبة من رصدات الرياح المقاسة بواسطة الراديو سوند للطبقة الممتدة بين 200-400 hPa ووجدوا أن القصى العمودي أفضل مؤشر للدلالة عن وجود المطبات الهوائية. وقدم الباحثان Belson و Knox طرق جديدة للكشف عن المطبات بتحديد الموجات المتكسرة الناتجة عن الجبال [5] ونظرية عدم التوازن التلقائي المتواجدة مع موجات الجاذبية [6] على الترتيب.

من خلال الاعتماد على الأساليب القياسية المعتمدة في تشخيص مواقع المطبات في طبقات الجو العليا وتحليل بيانات الراديو سوند لعدة سنين ركز البحث على تعيين المطبات وشدتها في جو مدينة بغداد بطريقة بيانية ومن ثم حساب النسب المئوية لتكراراتها. وأخيراً دراسة العلاقات البيانية بين المطبات ومتغيراتها وبعض المتغيرات الترموديناميكية.

الطريقة والبيانات المستخدمة

تعيين شدة المطبات الهوائية الحرارية باستخدام مخطط Emagram من خلال تعيين درجة الحرارة الحملية ومستوى التكثيف الحملية (T_c و Z_{cc})، إذ تحدث المطبات في النصف السفلي من طبقة التروبوسفير نتيجة تيارات الحمل الحراري الناتجة بفعل تسخين الهواء قرب سطح الأرض، وعدم ثبوت الانحدار الحراري. وتحدث المطبات الحرارية في الليل والنهار وفي جميع فصول السنة خصوصاً عند وجود الغيوم الركامية والركامية المزنية والعواصف الرعدية. إن الأسلوب المتبع للتنبؤ عن هذا النوع من المطبات هو غير مناسب للتنبؤ عن مطبات الهواء الصافي. كما انه يمكن تحديد شدة المطبات الحرارية خلال طبقتين جويتين [7]:

1. الطبقة الممتدة من سطح الأرض إلى ارتفاع 3km: تتم بتحديد مستوى التكثيف الحملّي Convection Condensation Level CCL وإيجاد درجة الحرارة الحملية (T_c) Convective Temperature بالنزول من نقطة (CCL) مع خطوط التغير الاديباتيكي الجاف D.A.L.R إلى السطح. وي طرح (11°C) من (T_c) نحصل على فرق درجة الحرارة التي تثبت على مخطط الذاتيات عند تقاطع خط الذاتيات المار عند (T_c) وصعوداً من نقطة التقاطع هذه مع خطوط التغير الاديباتيكي المشبع S.A.L.R. إلى ارتفاع (3 km) نعين درجة حرارة هذه النقطة ولتكن (T_3)، ثم نطرحها من درجة الحرارة الحقيقية ولتكن (T_A) عند المستوى نفسه، ومن قيمة الفرق (ΔT_3) وباستخدام جدول 1 نحصل على شدة المطبات. لأجل دراسة الخصائص الفيزيائية لهذه الطبقة وللسهولة تم الرمز لها بالرمز (A).

جدول 1: شدة المطبات الهوائية الحرارية حسب فروقات درجات الحرارة وسمك الطبقة الجوية.

الشدة	فرق درجة الحرارة (ΔT ($^\circ\text{C}$))	
	3 - 6 (km)	0 - 3 (km)
خفيفة	0 - 2.5	0 - 6
متوسطة	2.5 - 7	6 - 11
شديدة	>7	>11

2. الطبقة الممتدة من (3 - 6) km يتم الحصول على شدة المطبات بالصعود مع خط التغير الاديباتيكي المشبع من نقطة (CCL) إلى إن يقاطع مستوى 6 km وتعيين درجة حرارة هذه النقطة لتكن (T_6) التي تطرح من درجة الحرارة الحقيقية لتكن (T_B) عند المستوى نفسه، ومن قيمة الفرق الأخيرة (ΔT_6) وباستخدام جدول 1 نحصل على شدة المطبات. وبالأسلوب نفسه للطبقة السابقة تم الرمز لهذه الطبقة بـ (B).

في هذا البحث تم اعتماد بيانات رصد طبقات الجو العليا المقاسة بواسطة الراديو سوند المسجلة عند محطة مطار بغداد الدولي التابعة الى الهيئة العامة للأنواء الجوية العراقية. تم تحليل البيانات فقط لشهري هما آذار ونيسان ولثلاث سنين هما: 1988 و 1989 و 1999 وللرصدتين 00 UTC و 12. تم اختيار هذين الشهرين كونهما يتميزان بنشاط للعواصف الرعدية في العراق. تشمل البيانات المستخدمة درجات الحرارة والارتفاعات المقاسة بالأمطار الجهدية وكذلك استخدمت البيانات السطحية للمحطة نفسها لكل من درجة الحرارة ودرجة حرارة نقطة الندى ولنفس الفترة الزمنية أعلاه.

النتائج والمناقشة

باستخدام البيانات أعلاه تم رسم أولاً درجات الحرارة على مخطط Emagram حسب الارتفاعات الجهدية وكذلك درجة حرارة نقطة الندى عند السطح ومن ثم تطبيق الطريقة أعلاه تم تحديد المطبات لمدة شهري آذار ونيسان وللوقتتين وبهذا يصبح العدد الإجمالي 360 حالة حساب للثلاث سنوات.

تكرارات المطبات الهوائية الحرارية

تم تصنيف شدة المطبات الهوائية الحرارية للنتائج اعتماداً على جدول 1 المستخدم في طريقة إيجاد المطبات، فقد وضعت النتائج في جدول 2. من ملاحظة الجدول وجد أن عدد التكرارات لمجموع سنوات الدراسة ولعدد حالات (364) حالة من ضمنها الأيام التي لا يوجد بها مطبات حرارية. بالتركيز على المطبات الهوائية الحرارية الشديدة والمتوسطة في الوقت 00 UTC للطبقة الأولى (A)، وجد أن عدد تكرارات المطبات يكون (18) حالة وبنسبة (19%) من أصل (92) حالة لشهر آذار، أما بالنسبة للمطبات الحرارية المتوسطة فعدد تكراراتها تكون (30) وبنسبة (33%) من عدد الحالات الكلية نفسها، أما في الوقت 12 UTC فنجد أن عدد تكرارات المطبات الشديدة تكون (29) حالة وبنسبة (32%) من مجموع حالات للشهر آذار (90) حالة، وبنسبة للمطبات المتوسطة هناك (32) حالة وبنسبة (36%) من مجموع عدد الحالات الكلية.

يتبين لنا مما تقدم أن في طبقة (A) المطبات الهوائية الحرارية الشديدة والمتوسطة يكونان في الوقت 00 UTC أكثر تكراراً من الوقت 12 UTC. هذا بسبب عملية الحمل، وأن عملية الحمل تتم بصعود الهواء أدبياتيكياً من الأرض يصاحبه انخفاض في درجة حرارته بسبب تمدده نظراً لانخفاض الضغط مع الارتفاع، غالباً ما نحتاج إلى خاصية ثابتة للهواء الجاف المتمد أدبياتيكياً هذه الخاصية تسمى درجة الحرارة الجهدية، وبالرغم من أن العمليات الحرارية في الجو لا تكون أدبياتيكية بسبب عمليات المزج والإشعاع مع ذلك فإن استخدام درجة الحرارة الجهدية مهمة لدراسة حياه كتلة هوائية جاف من مكان إلى آخر فوق سطح الأرض في فترة زمنية قصيرة (12 ساعة) لذلك فإنها تعد كمية محافظة ولذلك استخدمت في إيجاد المطبات الهوائية، إن هذه النسب التي حصلنا عليها من أسبابها التسخين الشديد في النهار مما يؤدي إلى حدوث عمليات الحمل للهواء التي تساهم بدورها في تكوين المطبات الحرارية.

إن من الأسباب الأخرى لحدوث المطبات الهوائية في النهار هو أنه بعد الظهر يتطير الغبار والبخار والدخان إلى الأعلى ثم ينتشر أفقياً فيصل إلى نقطة معينة وتسمى هذه النقطة الطبقة المستقرة التي يكون فيها انقلاب حراري، وتكون هذه النقطة واطئة عادة 300-500 m في العراق. ففي الليل يبرد الهواء المجاور للأرض بالإشعاع ويبقى الهواء العلوي دافئاً نسبياً فيكون انقلاب

ضحل لا يلبث أن يتبدد عند طلوع الشمس واستئناف تيارات الحمل الحرة نشاطها عند تسخين الأرض، وهذا هو السبب الرئيس الذي يجعل المطبات الهوائية في UTC 12 هي أكثر حدوثاً من UTC 00. كما هو معروف أن المطبات تحدث مرافقة للعواصف الرعدية، وأن أغلب العواصف الرعدية التي تحدث في العراق تكون بفعل الجبهات أو المنخفضات غير الجبهوية التي تتحرك من منخفض السودان وشمال شرق البحر الأحمر وبعض المنخفضات الحرارية التي تتكون فوق أواسط الجزيرة العربية والمتحركة باتجاه العراق، إن أكثر فترة مناسبة لتكرار حدوث العواصف الرعدية هي الفترة الواقعة ما بين آذار ونيسان.

بالنسبة للطبقة الثانية (B) نجد أن من أصل (92) حالة أن المطبات الهوائية الحرارية الشديدة هي أقلها حدوثاً إذ تكون عدد تكرارات المطبات الهوائية الشديدة (2) حالة بنسبة (2%) ويليه المطبات الهوائية المتوسطة بعدد حالات (25) حالة وبنسبة (27%) هذا في الوقت 00 UTC، أما بالنسبة للمطبات في الوقت 12 UTC أيضاً نجد أنه من أصل (90) حالة المطبات الشديدة هي الأقل تكراراً بعدد تكرارات (2) وبنسبة (3%)، ويليه المطبات المتوسطة بعدد تكرارات (21) وبنسبة (23%). في هذه الطبقة ولاسيما فوق طبقة الاحتكاك يكون الهواء أقل اضطراباً، ولذلك تكون سرعة الرياح عالية ولذا عندما تحدث المطبات الهوائية الحرارية فإن المطبات الشديدة تكون ذا تأثير قوي على الملاحية.

من الجدول 1 وعند اخذ نظرة على المطبات الهوائية الحرارية الشديدة والمتوسطة نجد أن عدد تكرارات المطبات الشديدة في UTC 00 للطبقة (A) هي أكثر تكراراً بعدد حالات (41) وبنسبة (46%) من أصل (89) حالة بعد استبعاد الأيام التي لا تحدث فيها مطبات هوائية حرارية، ويأتي في المرتبة الثانية المطبات المتوسطة بعدد حالات (33) حالة وبنسبة (37%). أما بالنسبة للمطبات الحرارية التي تحدث في UTC 12 للطبقة نفسها وكذلك المطبات الشديدة نجدها أكثر عدد تكرارات (55) حالة وبنسبة (63%) من أصل (87) حالة، وفي حين أن المطبات المتوسطة تكون بالمرتبة الثانية بعدد تكرارات (21) حالة وبنسبة (24%). أما بالنسبة للطبقة الثانية (B) فنجد أن في الليل المطبات الهوائية الشديدة تحدث بنسبة أقل من أصل (89) حالة وتكون المطبات الحرارية الشديدة (7) حالات وبنسبة (8%)، لكن المطبات الحرارية المتوسطة تكون بأكثر عدد حالات فقد كانت (42) حالة وبنسبة (47%). أما في UTC 12 ومن أصل (87) حالة نجد أيضاً أن المطبات الشديدة قد حصلت بأقل عدد تكرارات (5) وبنسبة (5%) والمطبات المتوسطة هي أيضاً حدثت بأكثر عدد حالات (35) حالة وبنسبة (40%).

عند إجراء مقارنة للمطبات الهوائية الحرارية الشديدة والمتوسطة بين أشهر الدراسة ورصدتي UTC 00، 12، يتبين إن للطبقة (A) المطبات الشديدة في UTC 00 و 12 تحدث بنسبة أكبر في شهر نيسان أكثر من شهر آذار. بينما المطبات المتوسطة تكون في وقتي شهر آذار أكثر

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حدوثا من شهر نيسان. أما بالنسبة للطبقة (B) المطبات الشديدة والمتوسطة في UTC 00 و 12 لشهر نيسان أكثر من شهر آذار.

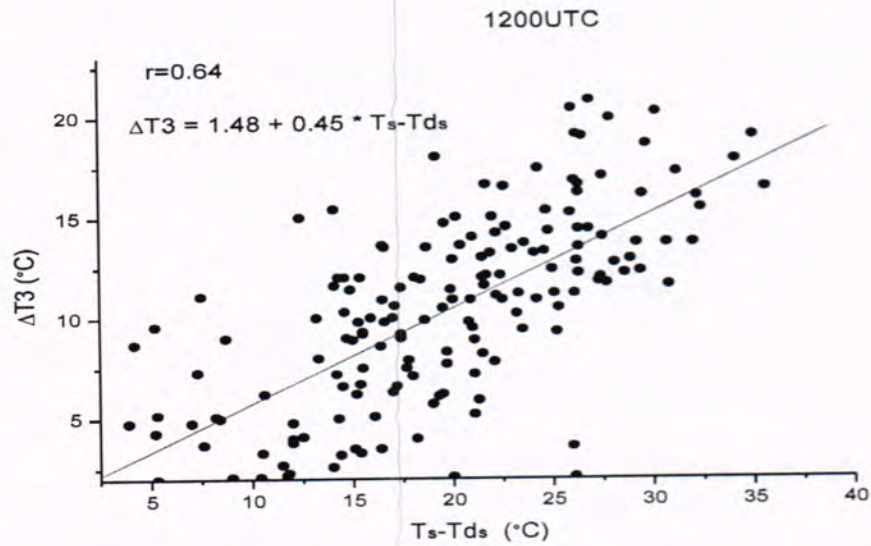
العلاقة بين المطبات الهوائية الحرارية وبعض المتغيرات الترموديناميكية

بعد الحصول على النتائج من المخطط البياني Emagram وجد أن هناك بعض المتغيرات الترموديناميكية التي تعتمد عليها شدة المطبات الهوائية في أثناء الرسم، من هذه المتغيرات هي الفرق بين درجة الحرارة ودرجة حرارة الندى على السطح بملاحظة أنه عندما توجد هناك مطبات هوائية حرارية، يكون الفرق بين درجة الحرارة ودرجة حرارة الندى على السطح كبيراً، إذ تزداد شدة المطبات الهوائية. أما بالنسبة للمتغير الآخر وهو ارتفاع مستوى التكثيف الحملّي فيلاحظ أنه عندما توجد هناك مطبات هوائية حرارية فكلما أزداد ارتفاع هذا المستوى كلما ازدادت شدة المطبات الهوائية. لذلك وضعت هذه المتغيرات في برنامج من أجل إيجاد العلاقة التي تربط بين المطبات الهوائية الحرارية وهذه المتغيرات الترموديناميكية المذكورة، من خلال الأشكال 1 و 2 و 3 و 4 باستخدام برنامج (Origin) وجدت العلاقات الرياضية بأنها من الدرجة الأولى الموجودة في شكل 1 و 2 و 3 و 4، هذه العلاقات أعطت أفضل خطوط تمر بين نتائج المطبات الحرارية والمتغيرات الترموديناميكية المأخوذة من الرسم. وقد وجدت العلاقات للطبقة (A) فقط أما الطبقة (B) فلا توجد فيها علاقات تربط المطبات الحرارية وهذه المتغيرات.

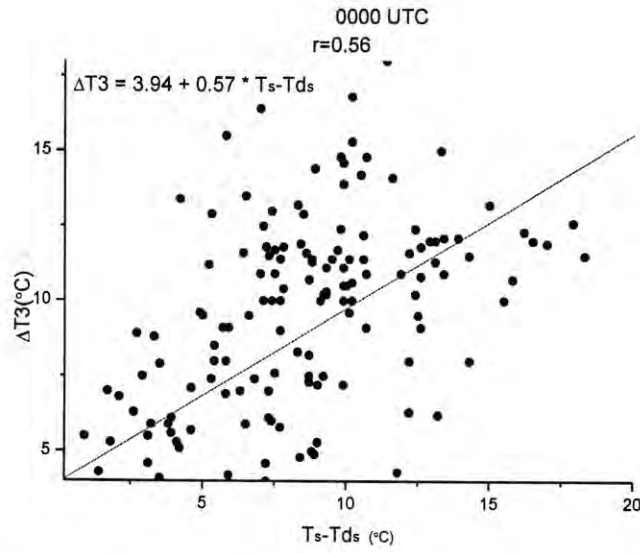
عند إجراء مقارنة للعلاقات التي تربط بين المطبات الهوائية الحرارية وبعض المتغيرات الترموديناميكية التي هي (الفرق بين درجة الحرارة ودرجة حرارة الندى على السطح والمتغير الآخر وهو ارتفاع مستوى التكثيف الحملّي) في UTC 00 و 12. بالنسبة للمتغير الأول نجد أن في 12 UTC تكون العلاقة أقوى من UTC 00 وذلك من خلال معامل الارتباط في 12 UTC الذي يكون أكبر من UTC 00، ومعامل الارتباط في UTC 00 (0.56) وفي 12 UTC يكون معامل الارتباط (0.64). وبالنسبة للمتغير الآخر وهو ارتفاع مستوى التكثيف الحملّي فإنه يعطي النتيجة نفسها في 12 UTC وتكون العلاقة أقوى في 12 UTC حيث معامل الارتباط في 12 UTC يكون (0.84) ومعامل الارتباط في UTC 00 يكون (0.80).

جدول 2: النسبة المئوية لتكرارات المطبات الهوائية الحرارية لأوقات 00 و 12 UTC ونشهر آذار ونيسان

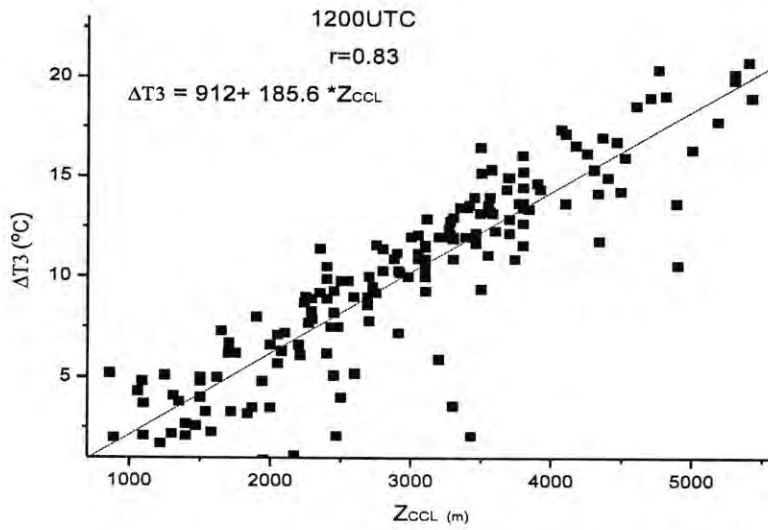
12 UTC				00 UTC				الشدة	رمز الطبقة
شهر نيسان		شهر آذار		شهر نيسان		شهر آذار			
نسبة (%)	عدد الحالات	نسبة (%)	عدد الحالات	نسبة (%)	عدد الحالات	نسبة (%)	عدد الحالات		
12	10	23	21	16	14	37	34	خفيفة	A
24	21	36	32	37	33	33	30	متوسطة	
63	55	32	29	46	41	19	18	شديدة	
01	01	09	08	01	01	11	10	لا توجد	
100	87	100	90	100	89	100	92	المجموع	
33	29	24	22	30	27	27	25	خفيفة	B
40	35	23	21	47	42	27	25	متوسطة	
06	05	03	02	08	07	02	02	شديدة	
21	18	50	45	15	13	44	40	لا توجد	
100	87	100	90	100	89	100	92	المجموع	



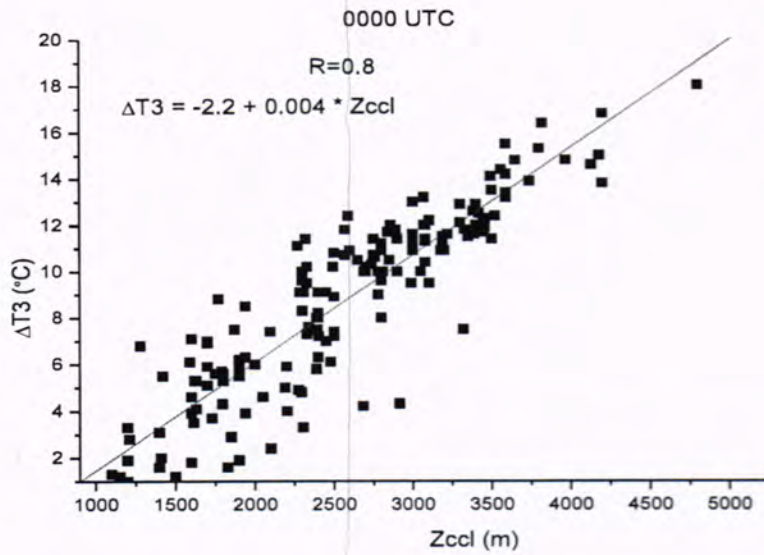
شكل 1 : العلاقة بين المطبات الحرارية والفرق بين (Ts-Tds) في وقت 12 UTC



شكل 2: العلاقة بين المطبات الهوائية الحرارية والفرق بين (TS-Tds) في 00 UTC



شكل 3: العلاقة بين المطبات الهوائية الحرارية وارتفاع (Zccl) في وقت 12 UTC



شكل 4: العلاقة بين المطبات الهوائية الحرارية وارتفاع (Zccl) في وقت 00 UT
الاستنتاجات

من خلال رسم بيانات درجات الحرارة ودرجات حرارة نقطة الندى على المخطط Emagram وإيجاد المطبات الهوائية الحرارية من بيانات الراديو سوند لوقتتين (00 UTC و 12) تم التوصل إلى النتائج الآتية:

1. عند جمع تكرارات المطبات لشهري آذار ونيسان للطبقة الأولى وهي طبقة (A)، يكون عدد تكرارات المطبات الشديدة في 12 UTC أكثر من 00 UTC والمطبات المتوسطة بالعكس، من ذلك نستنتج أن المطبات المتوسطة أكثر تكراراً في 00 UTC من 12 UTC وبذلك فإن نسبة حدوث المطبات الشديدة في 12 UTC أكثر من 00 UTC، ونسبة حدوث احتمالية المطبات المتوسطة في 00 UTC أكثر من 12 UTC.
2. للطبقة الثانية وهي الطبقة (B) وعند جمع تكرارات المطبات لشهري آذار ونيسان نجد أن عدد تكرارات المطبات الشديدة والمتوسطة تحدث في 00 UTC بنسبة أكثر من 12 UTC وبذلك نستنتج أن نسبة حدوث المطبات في 00 UTC أكثر من 12 UTC.
3. توجد هناك علاقات تربط بين المطبات الهوائية الحرارية وبعض المتغيرات الترموديناميكية كالفرق بين درجة الحرارة ودرجة حرارة نقطة الندى على السطح، فكلما ازداد هذا الفرق ازدادت شدة المطبات الهوائية بحيث معامل الارتباط $r=0.56$ في الوقت 00 UTC و $r=0.64$ في وقت 12 UTC. بالنسبة للمتغير الآخر هو ارتفاع مستوى التكثيف الحلمي فوجدت علاقة طردية من الدرجة الأولى حيث وجد أنه ازدياد ارتفاع هذا المستوى ازدادت

منعم وأركان

شدة المطبات الهوائية بمعامل ارتباط قوي $r=0.8$ و $r=0.83$ في الوقتين UTC 00 و 12 على الترتيب.

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استخدام بولي ميثا اكريلات المطعم بمعقدات الداينين كمفتاح عامل نوعية السليبي لليزرات Nd^{2+} :YAG, Nd^{2+} :Glass

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وزارة العلوم والتكنولوجيا

تاريخ التقديم: 2011/ 3/31

تاريخ القبول: 2011/ 5/29

ABSTRACT

In this research prepared Dithine complexes have been prepared from dithiol benzyl ligand and central ion to the Ni,Pd,Pt ,element the ligand and complexes have been investigated using FTIR spectrophotometer and UV-VIS-NIR spectral reigns show higher intensity represents the $\pi-\pi^*$ transition in the chromophore cycle .These absorption which appear in visible and near IR spectral regions , PMMA doping by these complexes to prepared foils, these foils have been implemented in Nd^{2+} :YAG laser cavity because each posses resonant absorption band near Nd^{2+} :YAG, Nd^{2+} :Glass emitting at (1060nm .(pulse duration measured to complexes dissolved in chloroform³⁻¹⁰ M) is very short compared with free running Pulse duration ,therefore the complexes work as Q-switch to the NIR lasers.

الخلاصة

يتناول هذا البحث تحضير معقدات الداينين لليكاند الداينول بنزيل وايون مركزي لعناصر Ni,Pd,Pt ثم شخّصت المعقدات المحضرة بمطياف FTIR ومطياف NIR-VIS-UV حيث أظهرت حزمة امتصاص بشدة عالية والتي تعود إلى الانتقال الإلكتروني (*) للمجموعة الكروموفورية والتي تمثل حزمة امتصاص تشبع حيث ظهرت عند المنطقة الطيفية المرئية والقريبة من الحمراء. نظرا لأمتلاك الصبغات المحضرة حزم امتصاص تشبع عند المنطقة القريبة من (1060nm) والتي تمثل حزمة انبعاث لليزر Nd^{2+} :YAG و Nd^{2+} :Glass تم تشويب بولي ميثا أكريلات بصبغة الداينين وضمنت داخل تجويف منظومة ليزر Nd^{2+} :YAG وأجريت قياسات لحساب أمد النبضة للصبغات مذابة بكلوروفورم وبتركيز (10⁻³ M) وتم الحصول على نبضة ليزرية بأمد قصير مقارنة بالتشغيل الحر وبذلك عملت هذه الصبغات كمفتاح عامل نوعية لليزرات القريبة من الحمراء.

استخدام بولي ميثا اكريلات المطعم بمعقدات الداينين كمفتاح عامل نوعية السليبي لليزرات $YAG:2+$.
Nd .Glass: $2+$ Nd

أشواق وشذى ومروج وأشواق

المقدمة

نظراً للخصائص الطيفية لمعقدات الداينين التي تتميز بها عن بقية المعقدات حيث تمتلك حزم امتصاص في المنطقة القريبة من تحت الحمراء والتي تعود الى الانتقالات الالكترونية للاواصر $C=C$ و $C=S$ للمجموعة الكروموفورية لمعقدات الداينين مثل معقدات ثنائي ثايول بنزيل المعوضة وثلاثي ثايوبنزيل المعوضة وغيرها من معقدات الداينين [1] . فالخواص الطيفية لبعض معقدات الداينين ملائمة جداً لاستخدامها لمجموعة اصباغ ماصة مشبعة تعمل كمفتاح عامل نوعية لاطوال موجية مختلفة تخدم انواع متعددة لليزرات القريبة من الحمراء . ولأهمية النبضة الليزرية العملاقة ذات القدرة العالية والتي تم الحصول عليها من خلال تقنية تحويل مفتاح عامل النوعية سلبياً حيث تدخل المواد الماصة المشبعة في تحضيرها، لذا أنصب جهود الباحثين في تحضير صبغات الداينين ذات صفة الامتصاص حد التشبع [2] .

تتميز الماصة المشبعة بخاصية امتصاص غير خطي يتناقض مع زيادة شدة الضوء الساقط عليها والذي يؤدي إلى إشباع المستوي المتهيج العلوي لها والوصول إلى حالة القصر (Bleaching) حيث اعتمدت عملية التشغيل المفتاحي على صفة القصر (bleaching) للاصباغ الماصة المشبعة، تعمل الصبغات الماصة المشبعة على امتصاص الاشعة الساقطة عليها وخصوصاً عند المستويات الطاقة الرنينية الى حد اشباع هذه المستويات وعند الوصول الى حد الاشباع فانها تعمل على امرار اشعة الليزر تحدث حالة القصر ولهذا الانخفاض المفاجئ للامتصاص له تأثير في توليد نبضة عملاقة او سلسلة من النبضات العملاقة. طبقت هذه العملية لرفع المستوى الاقصى للقدرة البصرية من منطقة الكيلو واط الى منطقة الميكرواواط [3].

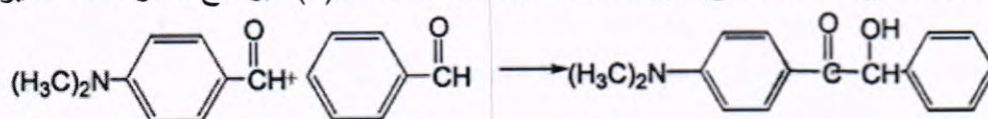
المواد وطرائق العمل

طريقة تحضير المعقدات

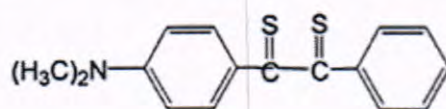
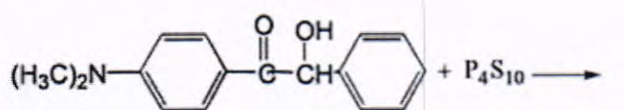
مزج (0.1) مول من البنزالدهايد الاروماتي و (0.1) مول من 4-ثنائي ميثل أمينو الدهايد الاروماتي الثاني مذاب في (35) مل من الكحول الايثيلي اضيف الى هذا المزيج (0.037) مول من سيانيد البوتاسيوم مذاب في (18) مل من الماء المقطر في دورق (250) مل ذو فوهة واحدة ووضع المكثف التصعيدي وسخن المزيج تصعيداً ولمدة تتراوح بين (1-4) ساعة اعتماداً على نوع البنزوين المحضر. وبعدها يبرد المزيج في حمام ثلجي ولمدة نصف ساعة فتظهر بلورات يمرر بخار الماء خلال المحلول للتخلص من الالدهايد الغير متفاعل. بعدها تغسل البلورات بالكحول الايثيلي ثم تعاد البلورة بالايثانول فنحصل على بلورات صفراء اللون او بيضاء اللون مائلة الى اللون

الاصفر تمثل المادة 4-داي ميثل أمينو بنزوين تم تحضير معقدات I-BDM يخطوات كما مبينة في المخطط (1) اعتماداً على طريقة التحضير الآتية [4]:-

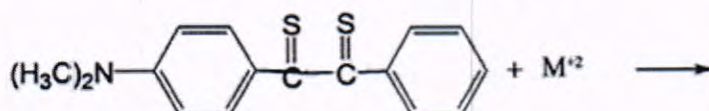
يضاف (mol0.003) من خماسي كبريتيد الفسفور الى محلول مكون من (mol0.1) بنزوين مذاب في (ml10) دايوكسان في دورق دائري سعة (250) مل. ركب مكثف تصعيد ملائم على الدورق وسخن المزيج بخلاط مغناطيسي مجهز بمسخن كهربائي واستمر التسخين لحين تحول لون المزيج الى اللون الاحمر اوقف التفاعل ثم برد المزيج في حمام ثلجي لمدة (min15) انفصلت مادة لزجة ذات لون احمر وفصل المحلول عن المادة اللزجة ثم غسلت المادة اللزجة بالماء المقطر عدة مرات. اضيف الى المادة اللزجة ملح الايون المركزي للمعقد وبكمية (gm3) مذاب في (ml5) من الماء المقطر ثم اضيف (ml4) حامض الهيدروكلوريك المركز وسخن المزيج على حمام مائي مع التحريك لمدة تتراوح بين (30-40) دقيقة. وبتصاعد غاز كبريتيد الهيدروجين بشكل رغوة فوق محلول بني اللون. بعد تبريد المزيج انفصلت مادة لزجة بنية اللون، فصلت المادة اللزجة عن المزيج وغسلت بالماء المقطر عدة مرات. بعد اعادة البلورة نحصل على بلورات خضراء اللون مائلة الى اللون البني. رشحت وجففت في فرن التجفيف عند درجة حرارة (C60) ولمدة (min45)، اضيف (ml10) محلول قاعدي لهيدروكسيد الصوديوم وبعيارية (N6) مع مذيب عضوي الى البلورات السابقة ويتسخن المزيج لمدة (min20) وعند درجة حرارة (C 70) انفصلت طبقتين احدهما عضوية تحتوي على المعقد واخرى مائية فصلت الطبقة العضوية عن المائية وجففت في فرن تجفيف ولمدة زمنية تتراوح (1-1.5) ساعة وكان الناتج عبارة عن بلورات (BDM-I) خضراء اللون، تعاد البلورة لنحصل على بلورات ذات نقاوة عالية المخطط (1) يوضح خطوات التحضير.



4-dimethyl Amino Bnzoin

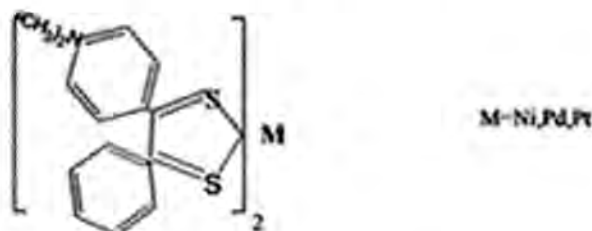


Dimethylamino ditho benzoin



أستخدام بولي ميثل ميثا اكريلات المطعم بمعقدات الدايتين كمفتاح عامل نوعية السليبي لليزرات $YAG:2+$,
Nd ,Glass: $2+$ Nd

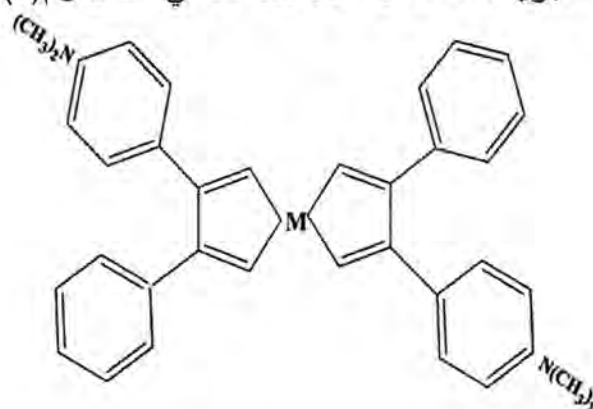
أشواق وشذى ومروج وأشواق



Bis(dimethyl amino dithio benzol) M

مخطط 1: خطوات تحضير المعقدات

ويمكن ملاحظة الصيغة الجزيئية لمعقدات I BDM- كما في الشكل رقم (1)



BDM-I

$C_{32}H_{30}S_4M$

Pd,Pt,Ni=M

الشكل 1 : الصيغة الجزيئية لمعقد BDM-I

تشخيص الليكنادات المحضرة والمعقدات بطيف الأشعة تحت الحمراء

شخصت المواد المحضرة باستخدام جهاز Perkin Elmer FT-IR Spectrophotometer model – 1720X

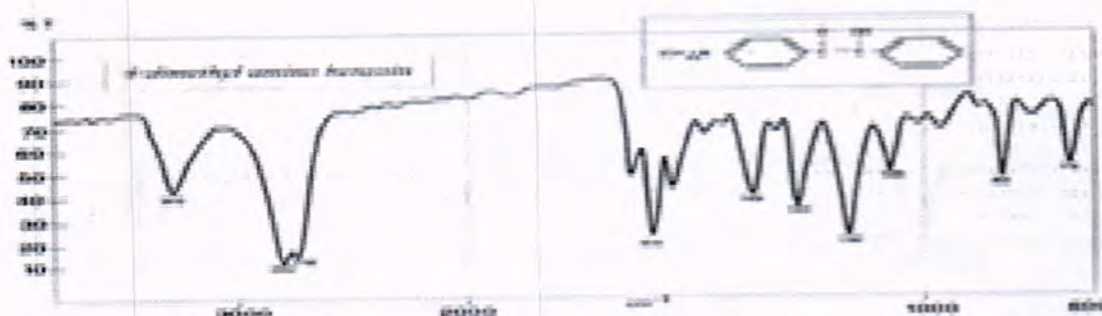
طيف الاشعة تحت الحمراء للمركب 4 - ثنائي ميثل أمينو بنزوين

اظهرت القياسات الطيفية للأشعة تحت الحمراء للمركب 4-ثنائي ميثل أمينو بنزوين حزم الامتصاص الموضحة في الجدول (1). الشكل (2) يوضح طيف الامتصاص للأشعة تحت الحمراء.

جدول 1: اهم حزم الامتصاص للمركب 4-ثنائي ميثل أمينو بنزوين

حزمة الامتصاص (سم ⁻¹)	المجموعة المهتزة
3410	حزمة الاهتزاز المطي (O-H)

3030	حزمة اهتزاز مط (C-H) الاروماتية
2850 , 2790	حزمة اهتزاز مط (C - H) الاليفاتية
1680	حزمة اهتزاز مط (C=O) لمجموعة الكينون
1610 , 1585	حزمة اهتزاز مط (C=C) لحلقة البنزين
1405	حزمة اهتزاز مط (C - C) الاليفاتية
1303	حزمة انحناء (C-H) لحلقة البنزين
1050	انحناء مطي N-ph
802	حزمة انحناء C-H لحلقة بنزين ثنائية التعويض
715	حزمة انحناء C-H لحلقة بنزين احادية التعويض



الشكل 2: يوضح طيف الامتصاص للأشعة تحت الحمراء لمركب 4 - ثنائي ميثل أمينو بنزوين

تشخيص المعقد Bis (4-benzil dithio dimethyl amino-4) (I-BDM)

شخصت معقد BDM-I بدراسة اطياف الأشعة تحت الحمراء (FT-IR) واطياف الأشعة فوق البنفسجية والمرئية والقريبة من تحت الحمراء Spectro Shimadzu UV-Visible Recording Photometer UV 160 .

نتائج التحليل الطيفي للأشعة تحت الحمراء لهذه المعقدات وكما مبين في الجدول (2).

والأشكال (5)، (4)، (3) تمثل طيف الأمصاص للمعقدات عند المنطقة FTIR

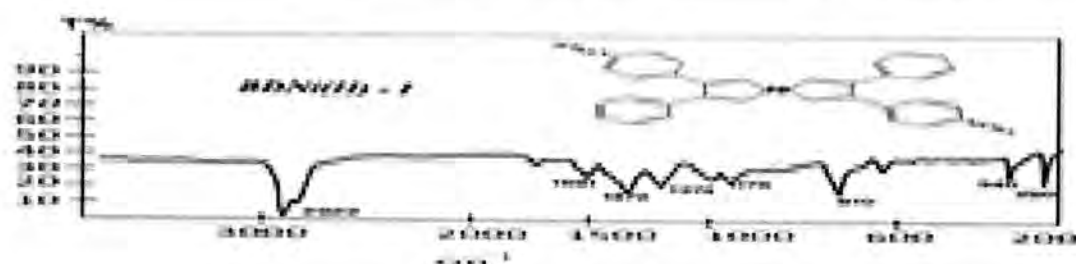
الجدول 2: حزم الامتصاص لمعقد I-BDM

حزمة الامتصاص (سم ⁻¹)	المجموعة المهتزة
3000	حزمة الاهتزاز المطي (C-H) الأروماتية
2900	حزمة الاهتزاز المطي (C-H) الاليفاتية
1600-1592	حزمة الاهتزاز المطي (C=C) الأروماتية
1472	حزمة الاهتزاز المطي (C=C) الكيليتية
1210, 1175	حزمة الانحناء (C-H) الأروماتية
810	حزمة الاهتزاز المطي للأصرة (C-S)

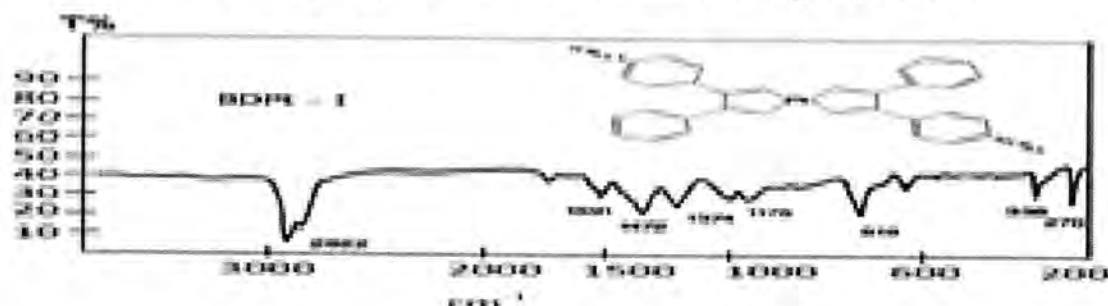
أستخدام بولي ميثا اكريلات المطعم بمعقدات الداينين كمفتاح عامل نوعية السليبي لليزرات $YAG: Nd^{2+}$, Glass: Nd^{2+}

أشواق وشذى ومروج وأشواق

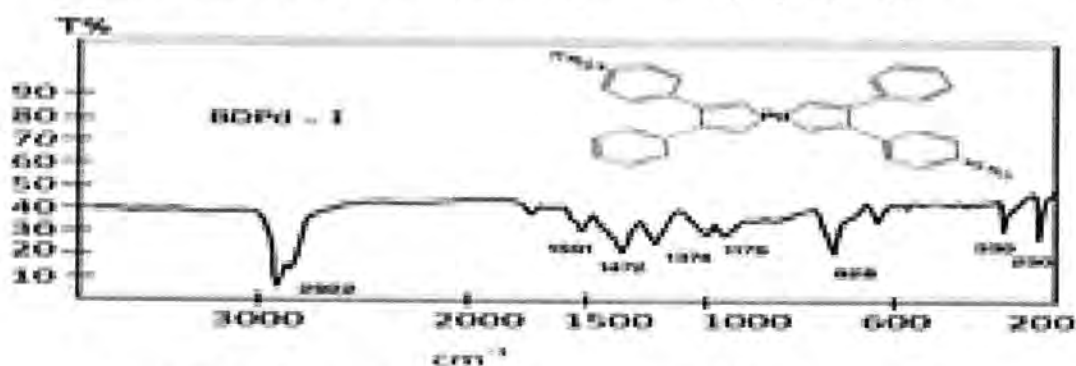
حزمة الاهتزاز ألمطي للأصرة (S - M)	360-320
حزم انحناء (S - Pd)	220 - 250



الشكل 3 : يوضح طيف الامتصاص للأشعة تحت الحمراء لمركب I-BDNi

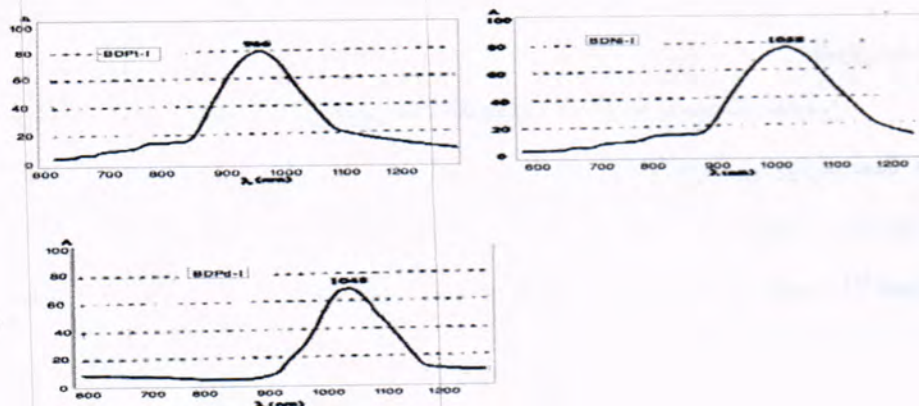


الشكل 4 : يوضح طيف الامتصاص للأشعة تحت الحمراء لمركب I-BDPt

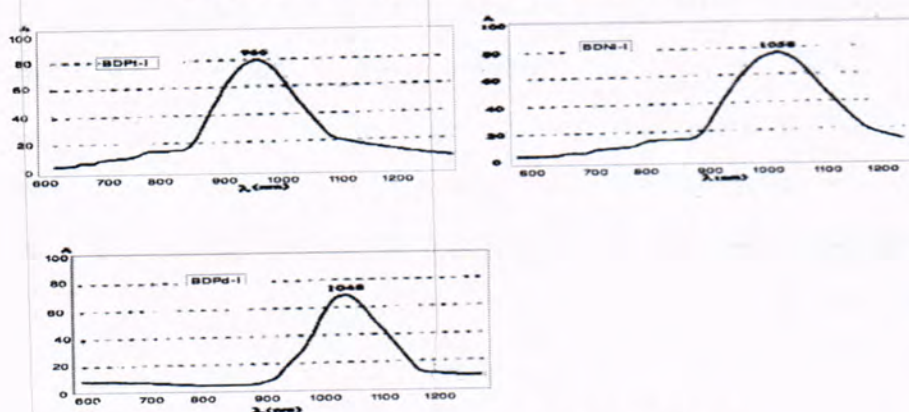


الشكل 5 : يوضح طيف الامتصاص للأشعة تحت الحمراء لمركب I-BDPd

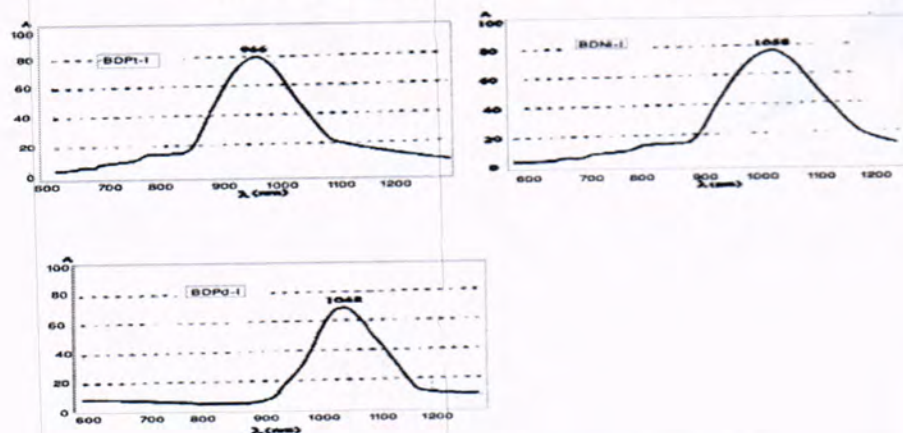
الفحوصات الطيفية لمعقدات الداينين في المنطقة المرئية والقريبة من الحمراء
جريت الفحوصات الطيفية في المنطقة المرئية والقريبة من تحت الحمراء وقد اظهرت عدد من
المعقدات حزمة امتصاص التشعب في المنطقة في المنطقة القريبة من تحت الحمراء وتمثل الانتقال
الالكتروني (*) للمجموعة الكروموفورية الخاصة بالمعقدات المحضرة [5,6] وكما موضحة في
الأشكال (6)، (7)، (8) التالية :



الشكل 6: يمثل قمة الامتصاص للمعقد I-BDNi



الشكل 7: يمثل قمة الامتصاص للمعقد I-BDPd



الشكل 8: يمثل قمة الامتصاص للمعقد I-BDPt

جدول 3: أعلى قيم الامتصاص للمعقدات عند المنطقة القريبة من الحمراء.

	R, R	$\max \text{Ni}^{+2}(\text{nm})$	$\max \text{Pd}^{+2}(\text{nm})$	$\text{Pt}^{+2}(\text{nm})^{\max}$
	$\text{N}(\text{CH}_3)_2 = \text{R} = \text{H}, \text{R}$	1056	1048	966

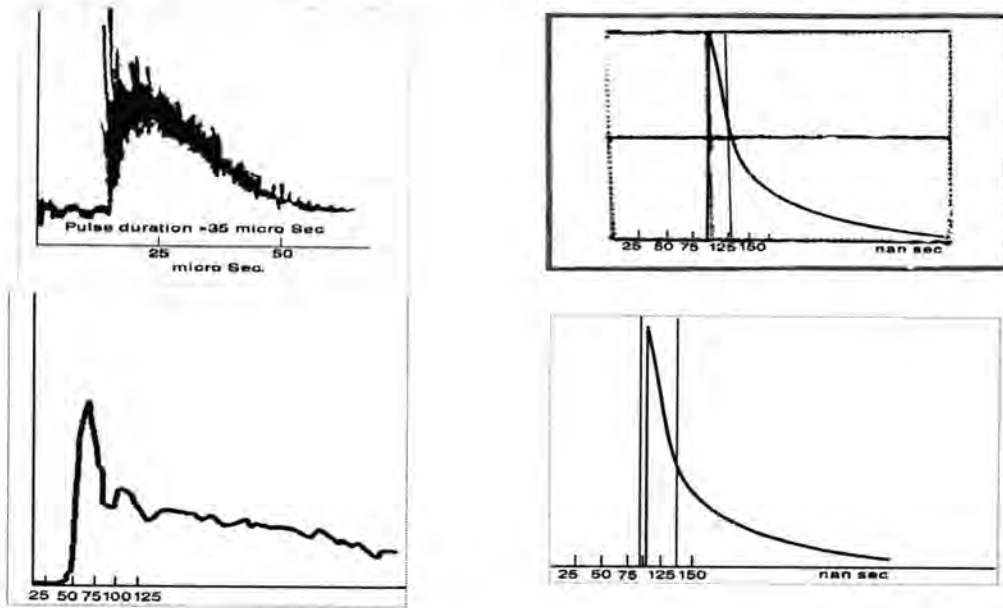
أستخدام بولي ميثل ميثا اكريلات المطعم بمعدات الدايئين كمفتاح عامل نوعية السليبي لليزرات $YAG:2^{+}$,
Nd ,Glass: 2^{+} Nd

أشواق وشذى ومروج وأشواق

طريقة تحضير أغشية البولي ميثل ميثا أكريلات المشوبة بصبغات الدايئين
يذاب 3 غم من البولي ميثل ميثا أكريلات في 5 مل من الكلوروفورم ويترك لمدة 24 ساعة يضاف
 M^{3-10} من الصبغة مذابة بالكلوروفورم الى البوليمر وتصب بصحون زجاجية ثم تجفف بفرن
تجفيف عند درجة (C40) ولدة ثلاث ساعات بعدها تترك 12 ساعة وتفصل الأغشية عن القواعد ثم
تضمن داخل التجويف الليزري

تضمن الصبغات داخل التجويف الليزري

نظراً لامتلاك الصبغات (I-BDPt , I-BDPd , I-BDNi) حزم امتصاص تشبع عند
المناطق الطيفية التالية (1056، 1048، 966 nm) [9,8,7]. على التوالي القريبة من الطول
الموجي لليزر Nd:YAG و Nd:Glass الباعث للطول الموجي (1060 nm) ضمننت هذه
الصبغات الثلاثة بشكل رقائق بوليمرية مطعمة بالصبغة التجويف الليزري حيث تزداد عملية الضخ
العكسي للوسط الليزري مما يؤدي إلى توليد نبضات ليزرية بأمد نبضة ليزرية ذات امد قصير جداً
بوحدة (38,44,50 nanosec)) نسبة إلى امد النبضة الليزرية بالتشغيل الحر free running
بوحدة 35sec. الشكل (9) التالي يوضح منظومة ليزر النيوديميوم - ياك



شكل 9 : منظومة ليزر النيوديميوم - ياك

وقد سجلت النبضة الليزرية بأستخدام الصبغات (I-BDPt , I-BDPd , I-BDNi) المذابة
في الكلوروفورم نبضات ذات امد قصير جداً بوحدة nanosec كما بالأشكال (11,12,13) مقارنة

بالتشغيل الحر ذات امد النبضة 35 sec كما بالشكل (10) وبذلك يكون المبدأ قد تحقق مفتاح عامل النوعية [9].

النتائج والمناقشة

نظراً لامتلاك الصبغات (I-BDPt , I-BDPd , I-BDNi) حزم امتصاص تشبع قريبة من (nm 1060) عند الاطوال الموجية (1056 , 1048 , nm966) على التوالي ضمنت داخل التجويف الليزري لليزر YAG:²⁺Nd الباعث للطول الموجي (nm 1060). ومقارنة قدرة وأمد النبضة عند التشغيل الحر مع قدرة وأمد النبضات عند تضمين الصبغات كما موضح في الجدول (4) لوحظ ان قدرة النبضة في التشغيل الحر اقل بكثير من قدرة النبضات الناتجة عن تضمين الصبغات وبذلك تحقق مبدأ مفتاح عامل النوعية لهذه الصبغات، ويلاحظ أيضاً أن أمد النبضة باستخدام الصبغتان I-BDPt , I-BDPd هو أكثر منها باستخدام الصبغة I-BDNi مذابة في نفس المذيب وفي نفس التراكيز [9].

درس أهم العوامل المؤثرة على الزحزحة الطيفية ومنها:

الأيون العدد الذري المركزي من حيث قوة منح الكثافة الالكترونية حيث لوحظ تأثير الأيون المركزي لمعقدات ذات ليكندرات ذات قوة منح كثافة الكترونية ثابتة، حضرت معقدات باستخدام ايونات لنفس المجموعة هي ²⁺Pt , ²⁺Pd , ²⁺Ni لنفس الليكندرات، حدثت زحزحة طيفية نحو الأطوال الموجية الأقصر عند الانتقال عمودياً ضمن الزمرة ويمكن تفسير ذلك باعتبار أيون ²⁺Pt أثقل من ²⁺Pd وهذا أثقل من ²⁺Ni وبذلك تكون الطاقة اللازمة لرفع معقد I-BDPt الى المستويات المثيجة أكبر فتظهر حزمة الامتصاص عند الطول الموجي الأقصر أما معقد I-BDNi فيظهر عند الطول الموجي الأطول.

نظراً لأهمية النبضات الليزرية ذات القدرة العالية في المجالات العلمية لازالت هذه العملية في طريقها الى التطور ونخص هنا طريقة مفتاح عامل النوعية السلبي ذو عملية تشغيل غير معقدة تتضمن استخدام مواد ماصة مشبعة. تم تطوير العمل في هذا المجال والاعتماد على طريقة تحضير سلسلة من معقدات الدايتين تعمل كمفتاح عامل نوعية لليزرات الحالة الصلبة في متن هذا البحث لكونها معقدات ذات حزم امتصاص رنينية قريبة من الاطوال الموجية المنبعثة من هذه الليزرات. كذلك يمكن اعتماد هذه الطريقة لتحضير صبغات ماصة مشبعة عند اطوال موجية محددة اعتماداً على نوع الايون المركزي والمجاميع المعوضة على حلقة البنزين لليكاند. ولموائمة مواقع حزم الامتصاص الرنينية مع الاطوال الموجية لليزرات اعتماداً على اختيار المذيب المناسب وبتراكيز محددة.

استخدام بولي ميثا اكريلات المطعم بمعدّات الدايثين كمفتاح عامل نوعية السليبي لليزرات YAG:^{2+} ,
 $\text{Nd ,Glass:}^{2+}\text{Nd}$

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حول بعض مفاهيم مصفوفتي الحذف والنسخ مع التطبيقات

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ABSTRACT

In this work, we have studied the elimination and duplication matrices, using a proposed approach depends on some principle bases for n -Euclidean space. And, a connection has been made between these two matrices with each of the vec and v operators and kronecker product for matrices and commutation of these two matrices. We have adopted definition and specialties of these two matrices in some applications. The usefulness of the two matrices is demonstrated is mathematical statistics and matrix algebra fields which are the Maximum likelihood estimation of the multivariate normal distribution for each the symmetric matrices and lower triangular matrices.

الخلاصة

تم في هذا العمل، دراسة مصفوفتي الحذف والنسخ بأسلوب مقترح يعتمد بعض المفاهيم الجبرية، وقد تم الربط بينهما وبين كل من عمليتي vec و v وعملية ضرب كرونكر للمصفوفات وكما تم تعريف مصفوفة التبديل بنفس الأسلوب المقترح ومن ثم تطرقنا إلى خصائص مصفوفة التبديل. وقد اعتمدنا تعريف وخصائص هاتين المصفوفتين مع مصفوفة التبديل في بعض التطبيقات حيث تم تبين فائدتهما في مجال الإحصاء الرياضي وجبر المصفوفات والتي هي تقدير الإمكان الأعظم للتوزيع الطبيعي متعدد المتغيرات المصفوفات المتناظرة والمصفوفات المتثلثة السفلى.

المقدمة

تتخذ دراسة المصفوفات مكانة مهمة من حيث توظيفها في مجالات المعرفة بصورة عامة فهي أداة مهمة في تنظيم العلاقات بين مجموعتين (Relation between two sets) من الأشياء فهي تستخدم في حل أنظمة المعادلات (systems of equations) والتعبير عن العمليات في تحليل المتجهات (Vector analysis) كما تستعمل في دراسة تنظيم الدوائر الكهربائية (Electrical circuits) وشبكات البث (Networks) والاتصال communication ولها استعمالات في الكيمياء الكمية chemical quantitative [1].

سامي ونوال

استخدام الباحثون مصفوفتي الحذف والنسخ في بحوثهم منهم [2] vetter 1975، [3] Magnus and Neudecker 1979، [4].

استخدم الباحث (1981) Graham، [5] مصفوفتي الحذف والنسخ الى جانب عمليتي vec و U وضرب كرونكر للمصفوفات $kronecker$ product for matrices في كتابه الذي يتطرق فيه الى حسابان المصفوفة (Matrix calculus) مع التطبيقات.

استخدم الباحثان (1983) Neudecker and Wansbeek، [6] مصفوفتي الحذف والنسخ مع عملية vec والمصفوفات التبديلية (commutation matrices) في برهنة بعض خواص هذه المصفوفات ومن ثم عملا تطبيقات في احصاء متعدد المتغيرات Multivariate statistics.

استخدم الباحث Magnus عام (1988)، [7] مصفوفتي الحذف والنسخ والمصفوفات المثلثية السفلى (Lower triangularity matrices) وربطها مع المصفوفات التبديلية وعملية ضرب كرونكر وعملية vec في مناقشة العديد من المفاهيم.

استخدم الباحثان (1993) Tracy and Sultan، [8] مصفوفتي الحذف والنسخ كما استخدموا عملية vec في حساب وإيجاد الصيغة العامة للعزوم المركزية ذات الرتب العالية (Higher orders central moments) للتوزيع الطبيعي متعدد المتغيرات وذلك بأشتقاق دالته المميزة (Characteristic function) باستخدام تفاضل المصفوفات.

بين الباحثون (1999) Sydsaeter, Stron and Berik، [9] في كتابهم أن دراسة عملية ضرب كرونكر للمصفوفات وعمليتي متجه المصفوفة ونص متجه المصفوفة ومصفوفتي الحذف والنسخ تتطلب معرفة واسعة المدى للصيغ الرياضية والاحصائية.

تطرق الباحثان (2002) Abader and Magnus، [10] في بحثهما الى مصفوفتي الحذف والنسخ في بيان اختلاف الرموز الرياضية التي استخدمت في المصطلحات مثل عملية vec وضرب الكرونكر للمصفوفات .

ان الهدف الاساسي من هذا البحث هو تعريف مصفوفتي الحذف والنسخ وبرهنة خواص مصفوفتي الحذف L والنسخ D باستخدام اسلوب يوظف بعض المفاهيم الجبرية مع بيان علاقتهما بعملية ضرب كرونكر وعمليتي vec و v . حيث تم استخدام هاتين المصفوفتين في بعض التطبيقات و هي تقدير الامكان الاعظم للتوزيع الطبيعي لمتعدد المتغيرات المصفوفات المتناظرة والمصفوفات المثلثية السفلى .

المصفوفات 0-1 Matrices [11]

يوجد العديد من المصفوفات (المربعة وغير المربعة) التي عناصرها فقط الصفر والواحد والتي تستخدم في مجالات عديدة في العلوم ، و لبيان مصفوفتي الدراسة التي تشترك مع بقية المصفوفات

بنفس الصفة وهي احتواءها على عنصر الصفر والواحد ويطلق عليهما تسمية مصفوفة الحذف Elimination Matrix ومصفوفة النسخ Duplication Matrix وسنرمز لهما بالرمز L و D على التوالي، وقبل اعطاء تعريف لكل L و D نحتاج ان نعرف عمليتي $vec(.)$ و $v(.)$ للمصفوفات أولاً، حيث ان vec هو مختصر (Matrix vector) وبالعربي تعني متجه المصفوفة و v وهو مختصر vector half of a matrix وبالعربي تعني نصف متجه المصفوفة، وفيما يأتي تعريف هاتين العمليتين

عملية متجه المصفوفة *Matrix Vector Operation*، [12]

المتجهات تكون أدوات ضرورية حيث إنها على سبيل المثال تصف كميات فيزيائية التي تحتوي على الاتجاه مع كمية المقدار، المتجهات يمكن أن تعد حالة خاصة من المصفوفة وقد تكون متجهات صفية أو متجهات عمودية. إن تحويل المصفوفة إلى متجه ما هي إلا عملية وضع الأعمدة للمصفوفة الواحد تحت الآخر بدا من أول عمود من اليسار وهكذا، يمكن استخدام المتجهات لمعالجة كميات كبيرة من البيانات ويتضح ذلك في عدد من لغات برامج الحاسبة.

عملية نصف متجه المصفوفة *Matrix half vector operation*، [12]

تعريف عملية نصف متجه المصفوفة يكون مشابهاً لتعريف عملية متجه المصفوفة، لكن هذه العملية مختصة بالمصفوفات المربعة فقط، والاختلاف الآخر هو إن لكل عمود للمصفوفة x يتم حذف العناصر التي تقع تحت القطر أو فوقه عند تشكيل المتجه لأنه المصفوفة X تكون متناظرة، symmetric أي انه $v(X)$ يحتوي فقط العناصر المختلفة.

$$v(A) = \begin{pmatrix} a_{11} \\ a_{21} \\ \vdots \\ a_{n1} \\ \dots \\ a_{22} \\ \vdots \\ a_{n2} \\ \dots \\ \vdots \\ \dots \\ a_{nn} \end{pmatrix} \dots\dots\dots(1)$$

اثر المصفوفة *Trace of a Matrix*، [9]

لنكن A مصفوفة مربعة فان مجموع العناصر القطرية للمصفوفة A يسمى بأثر المصفوفة A ويرمز له بالرمز $tr(A)$ ويكتب .

$$tr(A) = \sum_{i=1}^n a_{ii} \quad \dots\dots\dots (2)$$

الخصائص الآتية حول اثر المصفوفة لها أهمية حيث يتم الاعتماد عليها في بعض براهين
خاصية (1)

$$tr(A) = tr(A') \quad \dots\dots\dots (3)$$

حيث ان $(\cdot)'$ تعني مدور المصفوفة .

خاصية (2): لتكن B, A مصفوفتين من نفس الدرجة $(n \times n)$ فان

$$trAB' = \sum_i \sum_j a_{ij} b_{ij} = trB'A = trA'B = trBA' \quad \dots\dots\dots (4)$$

خاصية (3): لتكن A مصفوفة من الدرجة $(n \times n)$ فان

$$trAA' = \sum_i \sum_j a_{ij}^2 = trA'A \quad \dots\dots\dots (5)$$

خاصية (4): لتكن A, B, C ثلاث مصفوفات من الدرجة $m \times n, n \times p, p \times m$ على التوالي فان

$$trABC = trCAB = trBCA \quad \dots\dots\dots (6)$$

حيث ان الضرب معرف تماما (well-defined) .

خاصية (5):

$$tr(I_c) = c \quad \dots\dots\dots (7)$$

حيث ان I_c تمثل مصفوفة واحدة (Identity Matrix) .

خاصية (6): لتكن A مصفوفة مربعة فان

$$tr(\Gamma A \Gamma') = tr(A) \quad \dots\dots\dots (8)$$

حيث ان Γ مصفوفة عمودية Orthogonal matrix .

خاصية (7): لتكن A مصفوفة من الدرجة $n \times n$ و x متجه من الدرجة $n \times 1$ فان

$$X'AX = tr(xx'A) \quad \dots\dots\dots (9)$$

ضرب كرونكر للمصفوفات [10] Kroncker product of Matrix

ضرب كرونكر للمصفوفات

لتكن $A = (a_{ij})$ مصفوفة من الدرجة $m \times n$ ، ولتكن $B = (b_{ij})$ مصفوفة من الدرجة $r \times s$ ،
يعرف ضرب كرونكر للمصفوفتين A و B بأنه مصفوفة من الدرجة $(mr \times ns)$ ويكتب
 $A \otimes B$ كما يأتي

$$A \otimes B = (a_{ij}B) = \begin{pmatrix} a_{11}B & a_{12}B & \dots & a_{1n}B \\ a_{21}B & a_{22}B & \dots & a_{2n}B \\ \vdots & \vdots & \ddots & \vdots \\ a_{m1}B & a_{m2}B & \dots & a_{mn}B \end{pmatrix} \dots\dots\dots (10)$$

بعض القواعد الأساسية لفضاء n الاقليدي، [11]

Some principle Basis of n Euclidean Space

بالإمكان استخدام بعض القواعد الأساسية لفضاء n الاقليدي في التعبير عن المصفوفات وكذلك في التعبير عن العمليات التي مر ذكرها في البندين السابقين وسوف نرسم لهذه القواعد بالرمز e وكما يأتي.

$$e_i^n = (0, \dots, 0, 1, 0, \dots, 0)' \dots\dots\dots (11)$$

حيث ان e_i^n متجه من الدرجة $n \times 1$ وان جميع عناصره اصفارا عدا العنصر في الموقع i فانه واحد. كما يمكن ان ينظر الى e_i^n على انه العمود ذو الرتبة i للمصفوفة الاحادية I_n .
تعريف المصفوفة E_{ij}^n , [12]

E_{ij}^n مصفوفة من الدرجة $n \times n$ جميع عناصرها اصفارا ما عدا العنصر في الموقع (ij) فانه واحد، وبالرموز فان

$$E_{ij}^n = e_i^n \cdot e_j^{n'} = e_i^n \otimes e_j^{n'} \dots\dots\dots (12)$$

إذا كانت A مصفوفة مربعة من الدرجة $n \times n$ فانه يمكن التعبير عن A و \bar{A} (المصفوفة المثلثية السفلى) و $dg(A)$ (المصفوفة القطرية) A عندما تكون جميع عناصرها غير القطرية اصفارا) باستخدام مصفوفة E_{ij}^n وكما يأتي

$$A = \sum_{i=1}^n \sum_{j=1}^n a_{ij} E_{ij}^n \dots\dots\dots (13)$$

$$\bar{A} = \sum_{i=1}^n \sum_{j=1}^n a_{ij} E_{ij}^n \dots\dots\dots (14)$$

$i \leq j$

$$dg(A) = \sum_{i=1}^n a_{ii} E_{ii}^n \dots\dots\dots (15)$$

سامي ونوال

سنجزأ المصفوفة الواحدة من الدرجة $\frac{1}{2}n(n+1) \times \frac{1}{2}n(n+1)$ على شكل متجهات كقواعد لفضاء $\frac{1}{2}n(n+1)$ الاقليدي ولكن بترميز مختلف وكما يأتي

$$I_{\frac{1}{2}n(n+1)} = (u_{11}u_{21}\dots u_{n1}u_{22}u_{23}\dots u_{2n}u_{33}\dots u_{nn}) \dots\dots\dots (16)$$

حيث ان u_{ij} متجه وحدة من الدرجة $\frac{1}{2}n(n+1) \times 1$ جميع عناصره اصفار ما عدا العنصر في الموقع $((j-1)n+i-\frac{1}{2}j(j-1))$ فانه واحد، مع $1 \leq j \leq i \leq n$.
الآن باستخدام (13) فان (1) يمكن إعادة كتابتها كما يأتي

$$v(A) = \sum_{j=1}^n \sum_{i=1}^n a_{ij} u_{ij} \dots\dots\dots (17)$$

$j \leq i$

تعريف مصفوفة التبديل K Definition of Commutation Matrix K

(1) **التعريف الضمني [12] The Implicit Definition**

K مصفوفة من الدرجة $mn \times mn$ ، وتكتب $K(m, n)$ ويمكن الحصول عليها من التحويل

$$K(m, n) vecA = vecA' \dots\dots\dots (18)$$

حيث ان A مصفوفة من الدرجة $(m \times n)$ أي ان $K(m, n)$ تنقل المتجه $vecA$ الى $vecA'$

(2) **التعريف الظاهري [12] The Explicit Definition**

يمكن التعبير عن مصفوفة التبديل $K(m, n)$ باستخدام المصفوفة E_{ij}^n وكما يأتي

$$K(m, n) = \sum_{i=1}^m \sum_{j=1}^n (E_{ij}^m \otimes E_{ij}^{n'}) \dots\dots\dots (19)$$

ويمكن تعريف $k(m, n)$ على شكل أعمدة باستخدام القواعد الأساسية لفضاء n الاقليدي بالشكل الآتي

$$k(m, n) = (e_{1+0n} e_{1+n} \dots e_{1+(m-1)n} : e_{2+0n} e_{2+n} \dots e_{2+(m-1)n} : \dots : e_{n+0n} e_{n+n} \dots e_{n+(m-1)n}) \dots\dots\dots (20)$$

أو على شكل صفوف وكما يأتي

$$k'(m, n) = \begin{bmatrix} e'_{1+0n} \\ e'_{1+n} \\ \vdots \\ e'_{1+(m-1)n} \\ \dots \\ e'_{2+0n} \\ e'_{2+n} \\ \vdots \\ e'_{2+(m-1)n} \\ \dots \\ \vdots \\ \dots \\ e'_{n+0n} \\ e'_{n+n} \\ \vdots \\ e'_{n+(m-1)n} \end{bmatrix} \quad (21)$$

معكوس مور- بنروز Moor-Penrose Generalized Inverse [14]

لنكن U مصفوفة من الدرجة $n \times r$. معكوس مور- بنروز العام للمصفوفة U هو مصفوفة U^+ من الدرجة $r \times n$ تحقق الشروط الأربعة الآتية

$$UU^+U = U \quad -1$$

$$U^+UU^+ = U^+ \quad -2$$

$$UU^+ \text{ مصفوفة متناظرة} \quad -3$$

$$U^+U \text{ مصفوفة متناظرة} \quad -4$$

المصفوفة N ، [12]

التعريف الضمني للمصفوفة N The Implicit Definition of N

المصفوفة N هي مصفوفة من الدرجة $n^2 \times n^2$ والتي تعمل لكل مصفوفة A من الدرجة $n \times n$ التحويل الآتي:

$$N \text{ vec } A = \text{vec} \frac{1}{2}(A + A') \quad \dots\dots\dots(22)$$

التعريف الظاهري للمصفوفة N The Explicit Definition of N

يعتمد هذا التعريف على مصفوفة التبديل $K_{(n,n)}$ والمصفوفة الواحدية I_{n^2} حيث ان المصفوفة N تعرف من خلال هاتين المصفوفتين وكما يأتي.

$$N = \frac{1}{2}(I_{n^2} + K_{(n,n)}) \dots\dots\dots(23)$$

مصفوفة الحذف L ، The Elimination matrix L [13]

التعريف الضمني للمصفوفة L The Implicit Definition of L

مصفوفة الحذف L مصفوفة من الدرجة $\frac{1}{2}n(n+1) \times n^2$ والتي تعمل لكل مصفوفة A من الدرجة $n \times n$ التحويل الآتي

$$LvecA = v(A) \dots\dots\dots(24)$$

ان تسمية الحذف للمصفوفة L نتجت بسبب حذف للعناصر التي تقع فوق أو تحت القطر للمصفوفة A من $vecA$ لينتج $v(A)$. سنبين فيما يأتي بان المصفوفة L وحيدة (unique) ويمكن تحديد وحدانيتها باستخدام (24) وكما يأتي

لتكن A مصفوفة اعتباطية (Arbitrary Matrix) من الدرجة $n \times n$ ولنفرض ان L و L_1 كلاهما يعمل على تحويل $vecA$ الى $v(A)$. أي ان

$$Lvec(A) = v(A)$$

$$L_1vec(A) = v(A)$$

ويطرح الصيغة الثانية من الاولى ينتج

$$(L - L_1)vec(A) = 0 \quad \forall A$$

ونستنتج من ذلك ان $(L - L_1) = 0$ وبالتالي فان $L = L_1$. بالامكان اشتقاق التعبير الظاهري للمصفوفة L وكما يأتي: لتكن A مصفوفة من الدرجة $n \times n$ فان

$$v(A) = \sum_{i \geq j} \sum_{i \geq j} a_{ij} u_{ij} \dots\dots\dots(25)$$

$$= \sum_{i \geq j} \sum_{i \geq j} u_{ij} (e'_i A e_j)$$

$$\begin{aligned}
&= \sum_{i \geq j} \sum_{i \geq j} u_{ij} \text{tr}(e_j e_i' A) \\
&= \sum_{i \geq j} \sum_{i \geq j} u_{ij} \text{tr}(E_{ij} A) \\
&= \sum_{i \geq j} \sum_{i \geq j} u_{ij} (\text{vec} E_{ij})' \text{vec} A \\
&= \sum_{i \geq j} \sum_{i \geq j} (u_{ij} \otimes e_j' \otimes e_i') \text{vec} A \quad \dots\dots\dots (26)
\end{aligned}$$

وهذا يقودنا الى التعريف الظاهري لمصفوفة الحذف L

التعريف الظاهري لمصفوفة الحذف L
من (26) نستنتج

$$L = \sum_{i \geq j} \sum_{i \geq j} (u_{ij} \otimes e_j' \otimes e_i') \quad \dots\dots\dots (27)$$

يمكن التعبير عن المصفوفة L على شكل مصفوفات جزئية وبالشكل التالي

$$L = (L_{ij}) \quad i, j = 1, 2, \dots, n \quad \dots\dots\dots (28)$$

حيث ان

$$L_{ij} = \begin{cases} L_{ii} = (0_{(n-i+1) \times (i-1)} \dots I_{(n-i+1)}), i = j, i = 1, 2, \dots, n \\ L_{ij} = (0_{(n-i+1) \times n}), i \neq j, i, j = 1, 2, \dots, n \end{cases} \quad (29)$$

بتعويض (29) في (28) نحصل على

$$L = dg(L_{ii}) \quad i = 1, 2, \dots, n \quad (30)$$

مقدمة (1), [13]

لتكن A مصفوفة اعتباطية من الدرجة $n \times n$ فإن

$$(1) \quad LN \, vec A = \frac{1}{2} \nu(A + A') \quad (31)$$

ويشكل خاص اذا كانت A متناظرة فإن

$$(2) \quad LN \, vec A = \nu(A) \quad (32)$$

مقدمة (2), [13]

$$(1) \quad L \text{ تمتلك رتبة صفية كاملة تساوي } \frac{1}{2}n(n+1) \quad (33)$$

$$(2) \quad LL' = I_{\frac{1}{2}n(n+1)} \quad (33)$$

$$(3) \quad L^+ = L' \quad (34)$$

حيث ان L^+ تدعى بمعكوس مور - بنروز (Moore-Penrose) للمصفوفة L

مقدمة (3), [13]

المصفوفات $L'L$ ، LKL' ، $L'LKL'L$ تكون مصفوفات قطرية ومتساوية القوى (idempotent) من الدرجة $\frac{1}{2}n(n+1)$ ، n ، n على الترتيب

مقدمة (4), [13]

لتكن A مصفوفة اعتباطية من الدرجة $n \times n$ فإن

$$(1) \quad L'L \, vec A = vec(\bar{A}) \quad (35)$$

$$(2) \quad L'L = \sum_{i \geq j} (E_{ij}'' \otimes E_{ji}'') \quad (36)$$

$$(3) \quad LKL' \, \nu(A) = \nu(dg(A)) \quad (37)$$

$$(4) \quad LKL' = \sum_{i=1}^n u_{ii} u_{ii}' \quad (38)$$

$$(5) \quad L'LKL'L \, vec(A) = vec(dg(A)) \quad (39)$$

$$(6) \quad L' L K L' L = \sum_{i \geq j} (E_{ii}'' \otimes E_{jj}'') \quad (40)$$

ممهدة (5)، [13]

المصفوفة LNL' تكون قطرية ويكون محددها ومعكوسها معطى كما يأتي

$$1- \quad |LNL'| = 2^{-\frac{1}{2}n(n-1)} \quad (41)$$

$$2- \quad (LNL')^{-1} = 2I - LKL' \quad (42)$$

مصفوفة النسخ D [13] The Duplication Matrix D

من الجدير بالذكر ان المصفوفة L هي التحويل الوحيد الذي يقوم بنقل $vecA$ الى $v(A)$ حيث ان

$$LvecA = v(A)$$

لكن معكوس التحويل عموماً غير موجود، إذ بإمكاننا وبسهولة تحويل $v(A)$ الى $vecA$ للمصفوفة المثلثية السفلى او المصفوفة القطرية

حسب التعريف الضمني للمصفوفة L والممهدة (4) فرع (1) نحصل

$$L'v(A) = vec(\bar{A})$$

ويضرب المعادلة من اليسار بالمصفوفة K نحصل

$$KL'v(A) = vec(\bar{A}')$$

حسب التعريف الضمني للمصفوفة L والممهدة (4) فرع (5) نحصل

$$L' L K L' L vec(A) = vec(dg(A))$$

ويدمج هذه التحويلات نحصل على ما يأتي:

$$(L' + KL' - L' L K L') v(A) = vec(\bar{A} + \bar{A}' - dg(A)) \quad (43)$$

وبذلك قد نكون وجدنا مصفوفة تقوم بتحويل $v(A)$ الى $vecA$ مصفوفة متناظرة. ولنعرف هذه المصفوفة بشكل ضمني وكما يأتي

التعريف الضمني للمصفوفة D

مصفوفة النسخ D من الدرجة $n^2 \times \frac{1}{2}n(n+1)$ والتي تعمل لكل مصفوفة A من الدرجة $n \times n$ التحويل الآتي

$$(44) Dv(A) = \text{vec}(\bar{A} + \bar{A} - dg(A))$$

من السهولة أن نلاحظ إن المصفوفة D وحيدة، ومن العلاقتين (43) و(44) ينتج

$$D = L' + KL' - L'LKL' \quad (45)$$

$$= (I + K)L' - L'LKL'$$

$$(46) = 2NL' - L'LKL'$$

نلاحظ انه وبشكل خاص، إذا كانت المصفوفة A متناظرة فإن

$$DL\text{vec}(A) = Dv(A) = \text{vec}(A) \quad (47)$$

تكون هذه خاصية مهمة وسنستخدمها غالباً، والعكس يكون صحيحاً أيضاً، أي إن أي مصفوفة A تحقق العلاقة (47) تكون مصفوفة متناظرة.

الممهدات الآتية توضح خصائص المصفوفة D

ممهدة (6), [13]

$$(1) LD = I_{\frac{1}{2}n(n+1)} \quad (48)$$

$$(2) DLN = N \quad (49)$$

$$(3) D = 2NL' - L'LKL' = NL'(LNL')^{-1} \quad (50)$$

التعريف الظاهري للمصفوفة D The Explicit Definition of Matrix D

لتكن T_{ij} مصفوفة من الدرجة $(n \times n)$ مع العنصر 1 في الموقعين $(ij), (ji)$ وبقيّة العناصر اصفار. عند ذلك

$$D' = \sum_{i \geq j} \sum_j u_{ij} (\text{vec} T_{ij})' \quad (51)$$

نلاحظ أن

$$\begin{aligned} T_{ij} &= E_{ij}^n + E_{ji}^n & i \neq j \\ T_{ii} &= E_{ii}^n & i = j \end{aligned}$$

كما يمكن تعريف المصفوفة D بالشكل الآتي

$$D = (D_{ij}) \quad i, j = 1, 2, \dots, n \quad (52)$$

حيث أن

$$D_{ij} = \begin{cases} 0_{n \times (n-j+1)} & \text{if } i < j \\ \begin{pmatrix} 0_{(i-1) \times (n-i+1)} \\ I_{n-i+1} \end{pmatrix} & \text{if } i = j \\ \begin{pmatrix} 0_{(j-1) \times (n-j+1)} \\ E_{i-j+1}^{n-j+1} \end{pmatrix} & \text{if } i > j \end{cases} \quad (53)$$

حيث أن E_{ij}^n معرفة في (12)تتضمن الممهدتان الاتيتان خواص أخرى حول المصفوفة D

ممهدة (7), [13]

$$\frac{1}{2}n(n+1)(1) \text{ تمتلك رتبة عمودية كاملة تساوي } D \text{ المصفوفة}$$

$$(2) KD = D = ND \quad (54)$$

$$(3) D'D = (LNL')^{-1} \quad (55)$$

$$(4) D^+ = LN \quad (56)$$

ممهدة (8), [13]

لتكن A مصفوفة اعتباطية من الدرجة $(n \times n)$ فإن

$$(1) D' \text{vec} A = v(A + A' - dg(A)) \quad (57)$$

$$(2) DD' \text{vec} A = \text{vec}(A + A' - dg(A)) \quad (58)$$

$$(3) DD' = 2N - L' L K L' L \quad (59)$$

ممهدة (9), [13]

لتكن X مصفوفة من الدرجة $(n \times n)$ فان

$$(1) \frac{\partial \text{vec} X}{\partial v(X)} = \begin{cases} L' & X \text{ Lower Triangular Matrix} \\ D' & X \text{ symmetrix} \end{cases} \quad (60)$$

$$(2) \frac{\partial v(X)}{\partial \text{vec} X} = L' \quad (61)$$

الجانب التطبيقي

سنبين فائدة مصفوفتي الحذف L والنسخ D في عدد من التطبيقات. ونظرا لاستخدامنا بعض خصائص مشتقة المصفوفة أثرنا ذكرها، علما ان X و Y مصفوفتين من الدرجة $(n \times n)$

$$d(XY) = (dX)Y + XdY \quad (62)$$

$$d \log |X| = \text{tr} X^{-1} dX \quad (63)$$

حيث ان X مصفوفة غير معتلة

$$dX^{-1} = -X^{-1}(dX)X^{-1} \quad (64)$$

تطبيقات احصائية Statistical Applications [13]

مقدر الامكان الاعظم للتوزيع الطبيعي متعدد المتغيرات.

Maximum Likelihood estimation of the multivariate normal distribution. لنعتمد عينة ذات حجم m بالمتغيرات y من التوزيع الطبيعي ذو البعد n مع معدل μ ومصفوفة تباين مشترك موجبة تماما Φ . مقدرات الامكان الاعظم Maximum Likelihood estimators الى μ و Φ معروفة، لكن اشتقاق هذه المقدرات غالبا ما يكون غير صحيح حيث ان المشكلة ان يتم الاخذ بشروط التناظر على Φ وقد بين ذلك من قبل كل من

Balstera و Richard عام (1957)، [15] وبشكل أكثر دقة يجب ان لا نشق دالة الامكان بالنسبة الى $vec(\Phi)$ لكن يجب ان نشق بالنسبة الى $v(\Phi)$ اولا نشق مقدرات الامكان الاعظم الى μ و Φ وهذاما سنثبتته في تطبيق التطبيق: اذا كانت لدينا عينة عشوائية ذات حجم m من التوزيع الطبيعي ذو البعد n للمتغير y مع معدل μ ومصفوفة تباين مشترك موجبة تماما Φ فان مقدرات الامكان الاعظم الى μ و Φ تكون

$$(65) \hat{\mu} = \left(\frac{1}{m} \right) \sum_{i=1}^m y_i = \bar{y}$$

$$(66) \hat{\Phi} = \left(\frac{1}{m} \right) \sum_{i=1}^m (y_i - \bar{y})(y_i - \bar{y})'$$

البرهان: دالة الامكان لعينة هذا التوزيع تكون

$$L(y, \mu, v(\Phi)) = \left(\frac{1}{(\sqrt{2\pi})^m |\Phi|^{m/2}} \right)^n e^{(-\frac{1}{2} \text{tr} \Phi^{-1} Z)} \dots\dots\dots(67)$$

$$\log L(Y, \mu, v(\Phi)) = -\frac{1}{2} nm \log 2\pi - \frac{1}{2} nm \log |\Phi| - \frac{1}{2} \text{tr} \Phi^{-1} Z$$

$$Z = \sum_{i=1}^m (y_i - \mu)(y_i - \mu)' \quad (68)$$

باستخدام الخواص المعروفة لمشتقات المصفوفة والاثار المعطاة في (63) و (64) على التوالي فان المشتقة الاولى الى L يمكن كتابتها بالشكل

$$\partial \log = 0 - \frac{1}{2} \partial \log |\Phi| - \frac{1}{2} \text{tr} (\partial \Phi^{-1}) z - \frac{1}{2} \text{tr} \Phi^{-1} \partial z$$

$$\begin{aligned}
 &= -\frac{1}{2} m(tr\Phi^{-1}\partial\Phi) + \frac{1}{2} tr\Phi^{-1}(\partial\Phi)\Phi^{-1}z \\
 &\quad + \frac{1}{2} tr\Phi^{-1} \left[\sum_i (y_i - \mu)(\partial\mu)' + (\partial\mu) \sum_i (y_i - \mu)' \right] \\
 &= \frac{1}{2} tr(\partial\Phi)\Phi^{-1}(z - m\Phi)\Phi^{-1} + (\partial\mu)' \Phi^{-1} \sum_{i=1}^m (y_i - \mu) \\
 &= \frac{1}{2} (vec\partial\Phi)'(\Phi^{-1} \otimes m\Phi^{-1})vec(z - \Phi) + (\partial\mu)' \Phi^{-1} \sum_{i=1}^m (y_i - \mu) \\
 &= \frac{1}{2} [\partial v(\Phi)]' D'(\Phi^{-1} \otimes \Phi^{-1})vec(z - m\Phi) + (\partial\mu)' \Phi^{-1} \sum_{i=1}^m (y_i - \mu)
 \end{aligned}$$

الشرط الضروري لإيجاد أكبر قيمة بأن يكون $\partial L = 0$ لكل $\partial\mu \neq 0$ و $\partial v(\Phi) \neq 0$ وهذا يعطي

$$\Phi^{-1} \sum_{i=1}^m (y_i - \mu) = 0 \quad (69)$$

$$D^1(\Phi^{-1} \otimes \Phi^{-1})vec(z - m\Phi) = 0 \quad (70)$$

$$\hat{\mu} = \frac{1}{m} \sum_{i=1}^m y_i \equiv \bar{y}$$

$$D^1(\Phi^{-1} \otimes \Phi^{-1})vec(z - m\Phi) = 0$$

$$D^1(\Phi^{-1} \otimes \Phi^{-1})Dv(z - m\Phi) = 0 \quad (71)$$

بضرب طرفي المعادلة (4.10) من اليسار بالمصفوفة $(D'(\Phi^{-1} \otimes \Phi^{-1})D)^{-1}$ لأن $(D'(\Phi^{-1} \otimes \Phi^{-1})D)^{-1}$ مصفوفة غير معتلة (نحصل على

$$\hat{\Phi} = \frac{1}{m} \hat{z} = \frac{1}{m} \sum_{i=1}^m (y_i - \hat{\mu})(y_i - \hat{\mu})'$$

$$= \frac{1}{m} \sum_{i=1}^m (y_i - \bar{y})(y_i - \bar{y})'$$

$$\Psi_m \equiv -E \frac{\partial^2 L}{\partial \theta \partial \theta'} \quad (72)$$

$$\theta' = (\mu', (v(\Phi))') \quad (73)$$

مقلوب العلاقة (72) يكون القيد الأدنى (Lower bound) لمصفوفة التباين المشترك لأي مقدر غير متحيز (unbiased estimator) μ و $\nu(\Phi)$ وهذه في الحقيقة ماهي الا متراجحة كريمر (The Gremer - Rao inequality) مصفوفة المعلومات المحاذية تكون معرفة بالصيغة

$$\Psi = \lim_{m \rightarrow \infty} \frac{1}{m} \Psi_m \quad (74)$$

الاستنتاجات التي توصلنا اليها من خلال هذه الدراسة هي

1. ان تعريف مصفوفتي الحذف L والنسخ D باستخدام القواعد الاساسية لفضاء n الاقليدي كان المفتاح لبرهنة خصائص هذه المصفوفات بشكل سلس وسهل واكثر وضوحا.
2. ان دراسة مصفوفتي الحذف L والنسخ D كانت ذات فائدة كبيره من حيث توظيفها في إيجاد مقدر الامكان الاعظم للتوزيع الطبيعي المتعدد المتغيرات.

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التلوث البكتيري للافرازات المهبلية عند المرأة الحامل اثناء الولادة وعلاقتها مع مكونات صالات الولادة

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ABSTRACT

This study had been conducted to assess the extent of bacterial contamination of Labor rooms revealed in the number and types of bacteria existent there, as well as those identified among pregnant and non-pregnant women utilizing these wards of some hospitals in Baghdad for the period from October 2008 till March 2009. The total number of the collected isolates were 294 from different swabs, 112 from disinfected Labor rooms before it will be use for normal vaginal delivery and 112 swabs from the same rooms after being utilized for such deliveries. 50 swabs were taken from pregnant women delivered at the same rooms, and another 20 swabs from non-pregnant women of escorts of these patients as control group. The results showed that bacterial growth was found in 12 swabs from a sterile Labor room (10.7%) and in 40 swabs (35.7%) from it after is used. At the same time the vaginal swabs from pregnant and non-pregnant women, bacterial growth were different qualitative and quantitative values, pregnant women found to be the main source of bacterial contamination of Labor rooms. Various types of bacteria had been identified, most frequently Staphylococci and Gram negative bacilli.

الخلاصة

شملت هذه الدراسة اجراء مسح لمستويات التلوث البكتيري من حيث انواع واعداد البكتريا الملوثة لصالات الولادة وكذلك للنساء الحوامل وغير الحوامل المستخدمين لصالات الولادة في بعض مستشفيات مدينة بغداد خلال الفترة من شهر تشرين الأول 2008 ولغاية شهر آذار 2009، حيث تم جمع 294 عينة من مسحات مختلفة توزعت بواقع 112 عينة من صالات الولادة المعقمة قبل استخدامها لعمليات ولادة طبيعية، و 112 عينة اخرى لنفس المواقع بعد اجراء عمليات الولادة الطبيعية فيها، و 50 عينة من نساء حوامل استخدموا صالات الولادة المشمولة بالدراسة مع 20 عينة من نساء غير حوامل متواجدين مع المرضى استخدمت كعينات سيطرة. في 12 مسحة مأخوذة من صالة الولادة المعقمة قبل استخدامها، وجد فيها نمو بكتيري (10.7%) وفي

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40 مسحة مأخوذة من الصالة بعد استخدامها اصبحت النسبة (35.7%) من العدد الكلي للمسحات ، مما يدل على حصول تلوث بكتيري اثناء استخدام صالة الولادة. ايضا أظهرت المسحات المهبلية للنساء الحوامل وغير الحوامل تباين في محتواها البكتيري كما ونوعا، وبالمقارنة مع عينات السيطرة تبين وجود مصدر رئيسي للتلوث البكتيري في الصالة مصدره المرأة الحامل، بكتريا المكورات العنقودية كانت في مقدمة الانواع الملوثة للمسحات تليها عصيات السالبة لصبغة كرام.

المقدمة

يشكل التلوث الجرثومي احدى أكبر المشاكل الصحية للمرضى الراقدين في المستشفيات Nosocomial infections (1)، اذ يتسبب عنها اخماج مختلفة قد تجبر المريض على قضاء وقت أطول للعلاج (4-5) ايام أو أكثر (2). مصادر هذا النوع من التلوث البكتيري للمرضى ، قد يكون خارجيا بالاحتكاك مع المكونات المحيطة بالمريض بشكل مباشر أو غير مباشر بالاثاث والادوات الطبية والاشخاص المتواجدين مع المريض عند عدم توفر شروط النظافة أو التعقيم بالشكل المطلوب مما يحتم على الجميع الالتزام بكافة الوسائل المطلوبة للمحافظة على النظافة والتعقيم في مقدمتها غسل الايدي واستعمال الكفوف المطاطية المعقمة وفق الضوابط العالمية في المجال الطبي والرعاية الصحية (3)، أو داخليا من النبيت المجهري في جسم الانسان، او كائنات مجهرية انتهازية تنمو في او على جسم الانسان مستفيدة من فترة ضعف دفاعات الجسم الطبيعية (4).

أن تعرض المرأة الحامل خلال فترة حملها الى متغيرات فسلجية عديدة (5) نتيجة الافرازات الهرمونية ابتداء من الاسبوع الثاني للحمل ولغاية ساعة الولادة (6) ، تتغير خواص البيئة المهبلية من حيث الكائنات المجهرية الملوثة لها (7) ، بعضها تعتبر من النبيت المجهري الطبيعي في بيئة المهبل مثل بكتريا الموجبة لصبغة كرام *Lactobacillus sp.* (8) وأخرى من الانواع الانتهازية والتي تحتاج الى المعالجة الطبية مثل بكتريا *Neisseria gonorrhoeae* و *Chlamydia sp.* (9) والتي قد ينتج عنها اصابة الوليد اثناء الولادة عند ملامسته للاغشية المخاطية والافرازات المصاحبة لعملية الولادة (10). وقد تضمنت هذه الدراسة عزل وتشخيص لانواع البكتريا في البيئة المهبلية لدى نساء غير حوامل كعينات سيطرة ونساء حوامل عند دخولهم الى صالة الولادة وذلك لغرض تحديد مصادر التلوث البكتيري و انواعه اثناء الولادة وعلاقة ذلك بالمرأة الحامل وبمكونات صالة الولادة .

المواد وطرائق العمل

تم جمع العينات بأخذ مسحات مهبلية Vaginal swabs (بإشراف طبية اختصاص) من نساء حوامل، وكذلك من نساء غير حوامل كعينات سيطرة في صالة الولادة، و أخذت مسحات لملابس الكادر الطبي المشرف على الولادة ومن معظم محتويات الصالة من أثاث وأدوات طبية، وذلك خلال الفترة من تشرين أول 2008 ولغاية آذار 2009 من مستشفيات الهلال الأحمر للولادة والكاظمية التعليمية والكرامة التعليمي والكرخ العام في مدينة بغداد.

نقلت المسحات المذكورة الى المختبر باستخدام مرق نقيع الدماغ كوسط ناقل (11) وزرعت على اوساط اكار الدم و اكار ماكونكي (هوائية) و اكار الجوكليت (لاهوائية)، ثم وضعت في الحاضنة في 37°م ولمدة (24-48) ساعة، للمستعمرات البكتيرية النامية تم اجراء عزلها وتنقيتها في مزارع نقية ثم تشخيصها من دراسة خواصها المظهرية والمزرعية والمجهريه وصفاتها البايوكيميائية (12)، وقد حفظت في الثلجة (4°م) أثناء خطوات دراسة خواصها.

النتائج والمناقشة

العدد الكلي للمسحات بلغ 294 مسحة، توزعت الى 112 مسحة من محتويات صالة الولادة بعد اجراءات تعقيمها قبل الاستخدام، و 112 مسحة أخرى من نفس محتويات صالة الولادة بعد استخدامها في حالات الولادة الطبيعية، كما تضمنت 50 مسحة مهبلية من نساء حوامل في حالة الولادة الطبيعية و 20 مسحة مهبلية من نساء غير حوامل مرافقات المريضات في المستشفى، استخدمت كعينات سيطرة.

نتائج عزل البكتريا النامية من المسحات المذكورة تضمنت 12 مسحة فقط احتوت على نمو بكتيري مأخوذة من صالة الولادة المعقمة قبل استخدامها بنسبة (7,10%) من العدد الكلي لمسحات الصالة يوضح الجدول (1) يوضح انواع مصادر العينات قيد الدراسة، مع اعداد وانواع العزلات البكتيرية الملوثة لها . في حين تضمنت (40) مسحة حاوية على نمو بكتيري من محتويات صالة الولادة بعد استخدامها وكانت نسبتها (7,35%) من العدد الكلي للمسحات، ويوضح الجدول (2) نسبة التلوث الحاصل فيها مع اعداد وانواع البكتريا الملوثة لها لمسحات صالة الولادة المعقمة بعد استخدامها . البكتريا النامية، الملوثة لمسحات عينات الصالة بعد استخدامها للولادة، تظهر حصول تلوث خارجي بدلالة زيادة في اعداد العزلات البكتيرية المعزولة والمشفحة.

المسحات المهبلية للنساء الحوامل وغير الحوامل أظهرت تباينا واضحا في محتواها البكتيري من حيث الاعداد و الانواع للعزلات النامية فيها، والجدول (3) يوضح هذه النتائج من حيث عدد ونسبة تواجد كل نوع من العزلات البكتيرية وبالمقارنة مع مسحات السيطرة . وعند

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دراسة لمعطيات هذه النتائج ، ظهر لنا اعداد العزلات البكتيرية النامية عند النساء قبل وبعد الولادة ، و بمقارنتها مع العزلات النامية لمكونات الصالة قبل وبعد استخدامها ، وجد مصدر رئيسي للتلوث البكتيري في جميع العينات المدروسة تقريبا وهو المرأة الحامل عند دخولها الى صالة الولادة . ويوضح جدول(4) أعداد العزلات المدروسة لكل تلك العينات .

أن دورة حصول عدوى المستشفيات في بيئة الرعاية الصحية تبدأ عادة في اصابات الجهاز البولي ثم الجهاز الهضمي ثم الجهاز الرئوي لذلك يتطلب احيانا استخدام طريقة تبخير بيروكسيد الهيدروجين (H_2O_2) لتمييز تأثيره الفعال ضد العوامل المرضية المكونة للسيوربات الداخلية مثل بكتريا *Clostridium* sp. والتي تعتبر مقاومة لتأثير الكحول عليها (13) .

أن شروط النظافة والتعقيم في صالات الولادة تعتبر شرط اساسي لتوفير ظروف آمنة لسلامة الأم وابنها الوليد لما يتعرضان له من حالات جروح أو حالات نزيف قد يرافقها احتمالات التلوث بما يتواجد من كائنات مجهرية مرضية أو غير مرضية أثناء عملية الولادة (3). لذلك فإن نسبة تلوث الصالة بعد تعقيمها وقبل استخدامها (10,7%) يشير الى وجود خلل أو قلة كفاءة في اجراءات تعقيمها . أما ارتفاع تلك النسبة الى (35,7%) اثناء اجراء عملية الولادة ومايتبعها من اجراءات روتينية وكانت الزيادة بنسبة (25%)، فهي تشير الى ضعف كبير في مجال السيطرة أو المحافظة على نظافة وخلو صالة الولادة من الكائنات المجهرية المختلفة الجدولان (1 و 2) يوضحان ذلك . تضمنت هذه الدراسة عزل للبكتريا الملوثة لخمسة مواقع مختلفة في صالة الولادة الطبيعية ووجد في كل منها نسبة معينة من التلوث أكثرها في أسرة صالة الولادة يليها الاغطية وملابس الكادر الطبي المشرف على عمليات الولادة في حين كانت المعدات الطبية خالية تماما من التلوث البكتيري ، مما يدل على أن عمليات تنظيف هذه الملابس والمفروشات لاتجري بشكل كامل لتصبح (خاصة أسرة صالة الولادة) كمستودعات للعديد من انواع البكتريا الملوثة لها وأن عملية تعقيمها غير منتظمة بسبب توافد حالات ولادة متوالية وبشكل كثيف مع ضيق للوقت لأجراء التعقيم بشكل كامل فتزداد نسب التلوث . علما أن أغلب البكتريا المعزولة من الصالة بعد التعقيم كانت من جنس المكورات العنقودية الموجبة لصبغة كرام كونها تتحمل الجفاف وتكثر في تيارات الهواء المصاحبة للسعال والعطاس وكذلك في الغبار العالق بالهواء (14). وقد لوحظ اثناء اجراء هذه الدراسة بأن الكادر المشرف على عملية التعقيم هو كادر غير متخصص وذو كفاءة متدنية وغير مناسبة ، فضلا عن استعماله للمطهرات والمعقمات بتركيز عشوائية ، مما يؤدي الى زيادة في مقاومة هذه الجراثيم لها وهي الأكثر انتشارا في بيئة المستشفيات في صالات الولادة ووحدات العناية المركزة (15) . وقد أشار (16)

الى ظاهرة ترك ابواب الصالة مفتوحة بعد اجراءات التعقيم مما يساعد على دخول تيارات هوائية من الصالات المجاورة ليكون عاملا اضافيا في تلوث بيئة صالة الولادة , علما أن المكورات العنقودية تستطيع البقاء حية ولعدة اسابيع في الجو الجاف كالأقمشة والاسرة والادوات الجافة (17) . ومما يساعد في حصول تلوث الصالة بالبكتريا دخول المريضة بملابسها الاعتيادية مع مرافقها ويساعد ذلك عدم التزام الكادر الطبي في وضع الكمادات وقلة استخدام القفازات اليدوية داخل الصالة مع كثرة التكلم اثناء عمليات الولادة .

أن التلوث المهبلية بأنواع من البكتريا المتعايشة طبيعيا يعتبر ظاهرة طبيعية (8) , حيث تكون هذه البكتريا مستفيدة من الوسط الرطب والتميز بوجود مصادر الغذاء العضوي المتمثل بالافرازات المهبلية مع توفر عوامل بيئية اخرى مناسبة لنموها مثل pH والحرارة المناسبة (7) ومتأثرة ايضا بعوامل اضافية في مقدمتها عمر وصحة المرأة . في هذه البيئة المايكروبية تنتهز العديد من الانواع المرضية للنمو والتكاثر فيها مستفيدة من المؤثرات البيئية المختلفة الملزمة لنموها وتكاثرها وبالتالي احداث الاصابة المرضية للمرأة حيث عندها تحتاج الى مداخلات طبية للمعالجة (4). أما الحالة الصحية للمرأة الحامل وهي من العوامل الرئيسية المؤثرة على التغيرات الحاصلة في البيئة المهبلية من حيث انواع واعداد البكتريا الملوثة لها , فقد اظهرت نتائج الفحوصات السريرية للنساء المشمولات بهذه الدراسة أن معظمهن (70%) كانوا سليمات من الناحية الصحية يقابلهن (30%) فقط كان عندهن اصابات مرضية مختلفة مما يدل على سلامة معظمهن من الاصابات المهبلية .

تباينت العزلات البكتيرية المعزولة من البيئة المهبلية للنساء الحوامل والنساء غير الحوامل من حيث انواعها واعدادها , مما يشير الى وجود امكانية واضحة لدخول انواع بكتريا اضافية الى صالة الولادة وبطرق مختلفة , بواسطة المرأة الحامل أو الكادر الطبي أو تيارات الهواء أو المواد المنقولة الى الصالة بعد تعقيمها , في حين كانت عينات السيطرة قليلة في محتواها البكتيري أو خالية لبعض منها , جدول (3) .

عند مقارنة نتائج هذه الدراسة بين ظروف تعقيم الصالة وحالة المريضات عند دخولهن لاجراء عمليات الولادة هو حصول تلوث بنسب عالية عند انتهاء عمليات الولادة, جدول (4) يظهر انواع العزلات البكتيرية الملوثة لمحتويات صالة الولادة قبل وبعد عمليات الولادة ومصدر كل منها , حيث يشير الى أن النساء الحوامل هن المصدر الاول في حصول التلوث البكتيري لصالة الولادة لذلك نوصي بمراجعة كافة اجراءات التنظيف والتعقيم المتخذة في صالات الولادة بتقديمها الاهتمام بملابس المرأة الحامل وضرورة ابدالها بملابس معقمة أو نبيدة كما في صالات العمليات الجراحية الاخرى , مع منع دخول المرافق مع المرأة الحامل, يليها استخدام أغطية نبيدة وزيادة اجراءات تنظيف الصديريات للكادر الطبي .

التلوث البكتيري للافرازات المهبلية عند المرأة الحامل اثناء الولادة وعلاقتها مع مكونات صالات الولادة

نزار وايمان وثريا

جدول-1: مصادر جمع المسحات واعداد وانواع البكتريا الملوثة لصالة الولادة المعقمة

قبل استخدامها

ت	مصدر المسحات	عدد المسحات	نمو المستعمرات البكتيرية	نسبة التلوث %	البكتريا النامية عدد نوع العزلات العزلات
1	الادوات	30	+	8,3	<i>Staphylococcus epidermidis</i> 1
2	أسرة صالة الولادة	15	+	33,3	<i>Staphylococcus epidermidis</i> 2 <i>Staphylococcus aureus</i> 2
3	الأغطية	15	+	25	<i>Staphylococcus epidermidis</i> 1 <i>Staphylococcus aureus</i> 2
4	المعدات الطبية	30	-	0	-
5	ملابس الكادر الطبي	22	+	33,4	<i>Staphylococcus epidermidis</i> 4
	المجموع	112			12

جدول -2: مصادر جمع المسحات واعداد وانواع البكتريا الملوثة لصالة الولادة المعقمة

بعد استخدامها

ت	مصدر المسحات	عدد المسحات	نمو المستعمرات البكتيرية	نسبة التلوث %	البكتريا النامية عدد نوع العزلات العزلات
1	الادوات	30	+	12,5	<i>Staph. epidermidis</i> 4 <i>Staph. aureus</i> 1
2	أسرة صالة الولادة	15	+	42,5	<i>Staph. aureus</i> 7 <i>Escherichia coli</i> 5 <i>Staph. epidermidis</i> 3 <i>Salmonella spp.</i> 2
3	الأغطية	15	+	20	<i>Staph. aureus</i> 7 <i>Staph. epidermidis</i> 1
4	المعدات الطبية	30	+	5	<i>Staph. epidermidis</i> 2
5	ملابس الكادر الطبي	22	+	20	<i>Staph. aureus</i> 4 <i>Staph. epidermidis</i> 4
	المجموع	112			40

جدول-3: العزلات البكتيرية الملوثة لمسحات المهبل عند النساء الحوامل وغير الحوامل
(مسحات السيطرة)

ت	العزلات البكتيرية	عدد عزلات البكتريا المعزولة من مسحات مهبليّة من نساء حوامل غير حوامل (عينات سيطرة) عدد %	عدد عزلات البكتريا المعزولة من مسحات مهبليّة من نساء حوامل عدد %
1	<i>Staph. epidermidis</i>	31	12
2	<i>Staph. aureus</i>	16	7
3	<i>Staph. saprophyticus</i>	6	4
4	<i>Escherichia coli</i>	28	12
5	<i>Streptococcus viridans</i>	29	12
6	<i>Strep. agalactiae</i>	6	2
7	<i>Strep. Pyogenes</i>		2
8	<i>Citrobacter spp.</i>	3	2
9	<i>Lactob. acidophilus</i>	28	7
10	<i>Lactob. casei</i>	6	2
11	<i>Lactob. Jensenii</i>	2	
12	<i>Klebsiella pneumoniae</i>	3	1
13	<i>Klebsiella oxytoca</i>	2	
14	<i>Pseudo. aeruginosa</i>	2	
15	<i>Pseudo. luteola</i>	1	
16	<i>Clostridium perfringens</i>	1	3
		164	54
		%100	%100

التلوث البكتيري للافرازات المهبلية عند المرأة الحامل اثناء الولادة وعلاقتها مع مكونات صالات الولادة

نزار وايمان وثريا

جدول-4: اعداد العزلات البكتيرية النامية وانواعها في المسحات المهبلية وغير المهبلية في

صالة الولادة قيد الدراسة

ت	العزلات البكتيرية	عدد العزلات النقية في صالة الولادة بعد التعقيم	عدد العزلات النقية في صالة الولادة بعد الولادة	عدد العزلات النقية من نساء حوامل	عدد العزلات النقية من نساء غير حوامل*	مصدر التلوث
1	<i>Staphylococcus epidermidis</i>	8	14	31	12	تلوث من الحامل وصالة الولادة
2	<i>Staphylococcus aureus</i>	4	19	16	7	تلوث من الحامل وصالة الولادة
3	<i>Salmonella sp.</i>	-	2	-	-	يهمل
4	<i>Escherichia coli</i>	-	5	28	4	تلوث من الحامل
5	<i>Staphylococcus saprophyticus</i>	-	-	6	-	تلوث من الحامل
6	<i>Streptococcus viridans</i>	-	-	29	12	تلوث من الحامل
7	<i>Streptococcus agalactiae</i>	-	-	6	2	تلوث من الحامل
8	<i>Streptococcus pyogenes</i>	-	-	-	2	يهمل
9	<i>Citrobacter sp.</i>	-	-	3	2	تلوث من الحامل
10	<i>Clostridium perfringens</i>	-	-	1	3	تلوث من الحامل أو غير الحامل
11	<i>Lactobacillus acidophilus</i>	-	-	28	7	تلوث من الحامل
12	<i>Lactobacillus casei</i>	-	-	6	2	تلوث من الحامل
13	<i>Lactobacillus jensenii</i>	-	-	2	-	تلوث من الحامل
14	<i>K. pneumoniae</i>	-	-	3	1	تلوث من الحامل
15	<i>K. oxytoca</i>	-	-	2	-	تلوث من الحامل
16	<i>Pseudomonas aeruginosa</i>	-	-	2	-	تلوث من الحامل
17	<i>Pseudomonas luteola</i>	-	-	2	-	تلوث من الحامل
	المجموع	12	40	164	54	270
	نسبة التلوث من العينات	4%	13,6%	55,8%	18,3%	91,8%**

* عينات سيطرة .

** نسبة التلوث الكلية في المسحات المدروسة (294 مسحة)

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استخدام العواكس البصرية مع الألواح الشمسية لزيادة قدرتها الخارجة

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مصطفى

وزارة العلوم والتكنولوجيا-دائرة بحوث وتكنولوجيا الطاقات المتجددة-مركز بحوث الطاقة الشمسية

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ABSTRACT

In this paper used optical reflector flat mirror type which has high reflectivity to increase electrical output power from solar panel with suitable angles in Iraqi conditions and this angles it was (110° , 115° , 120°).

الخلاصة

تم في هذا البحث استخدام عواكس بصرية على شكل مرايا مستوية وذات انعكاسية عالية بزوايا مناسبة لتطبيقات الطاقة الشمسية مع اللوح الشمسي وفي الاجواء العراقية لزيادة قدرته في إنتاج الطاقة الكهربائية وكانت هذه الزوايا هي 110 و 115 و 120 درجة

المقدمة

يقوم اللوح الشمسي بتحويل الطاقة الشمسية إلى طاقة كهربائية عبر امتصاص الأشعة الشمسية بمادة اللوح الشبه موصلة والتي يتم امتصاصها من قبل الكترونات المادة في مستوى حزمة التكافؤ لطاقة الضوء الشمسي وانتقالها إلى حزمة التوصيل ليتولد تيار ينتقل عبر طرفي المادة الشبه موصلة يتم استهلاكه بواسطة الحمل الكهربائي [1]

والاشعاع الشمسي الواصل من الشمس يكون على شكل ضوء وحرارة والذي يتألف من حزمة عريضة من الأطوال الموجية ويكون على شكل طيف عريض يمكن تقسيمه الى ثلاث حزم وهي حزمة الأطوال فوق البنفسجية ($\lambda > 380 \text{ nm}$) ونسبتها من طيف الإشعاع الشمسي تقريبا 7 % وحزمة الأطوال الموجية المرئية ($380 \text{ nm} < \lambda < 780 \text{ nm}$) ونسبتها من طيف الإشعاع الشمسي تقريبا 47% و حزمة الأطوال الموجية تحت الحمراء ($\lambda > 780 \text{ nm}$) ونسبتها من طيف الإشعاع الشمسي تقريبا 45 % [2].

استجابية مواد الألواح الشمسية غالبا ما تكون محصورة بحزمة طيفية تمتد ما بين المنطقة المرئية ومنطقة تحت الحمراء القريبة مثل مادة السليكون الشائعة الاستخدام في تصنيع الألواح الشمسية التقليدية والتي تكون استجابتها إلى الإشعاع الشمسي محصور ما بين (400 nm - 1100 nm) [1,2].

استخدام العواكس البصرية مع الألواح الشمسية لزيادة قدرتها الخارجة

عماد وعلي وعادل وسرمد وعمار واسماء وفاضل وعماد ومروج وفلاح

ان معدل الإشعاع الشمسي اليومي لمدينة بغداد (5400) كيلو واط . ساعة لكل متر مربع وبحسب كفاءة اللوح الشمسي المستخدم كمثال 12 % فانه من الممكن تحويل طاقة الإشعاع الشمسي إلى طاقة كهربائية بحدود (648) كيلو واط . ساعة لكل متر مربع .

هناك مؤثر مهم يؤثر على مقدار الطاقة الكهربائية المستحصلة من اللوح الشمسي هو كيفية تحديد اتجاهية اللوح الشمسي حيث يجب أن تكون باتجاه الجنوب الجغرافي لمدينة بغداد وكذلك هنالك مؤثر آخر هو تحديد زاوية ميل اللوح الشمسي عن الأفق حيث انها تحدد مقدار تعامد اللوح الشمسي مع موقع الشمس ومقدار الأشعة الساقطة على اللوح [3].

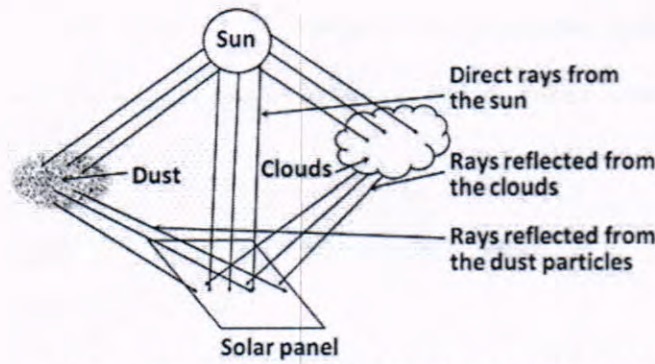
ويمكن زيادة طاقة الإشعاع الشمسي على اللوح الشمسي بعدة تقنيات منها:

• **تقنية التتبع الشمسي :-** وهي عبارة عن تتبع مستمر إلى تغير موقع الشمس من الشروق إلى الغروب حيث يكون مقدار التغير لزاوية موقع الشمس درجة واحدة كل أربع دقائق من الزمن ، و يكون اللوح في حالة تعامد تقريبا مع موقع الشمس والتتبع يكون بتقنيات مختلفة منها تقنية التتبع الشمسي (الفعال) ويتم باستخدام منظومات كهروبصرية للتتبع أو تقنية التتبع الشمسي المبرمج زمنيا (غير فعال) ويتم باستخدام برنامج زمني محسوب فيه وقت الشروق والغروب لكل يوم من أيام السنة وكلا التقنيتان أما يكونان بمحورين أو بمحور واحد، وكل هذه التقنيات لها ايجابيات في زيادة قدرة اللوح الشمسي الناتجة بنسب معينة لكن الجانب السلبي فيها بأنها تستهلك جزء من قدرة الطاقة الكهربائية المتولدة من اللوح الشمسي وذلك لوجود (المحركات الكهربائية) في هذه الأنظمة وقد يكون الفارق في إنتاج الطاقة الكهربائية ملحوظ

• **تقنية استخدام المراكز الشمسية والعاكسة مع الخلايا الشمسية:** تساهم هذه التقنية في زيادة نسبة التحويل الاكبر من قدرة الإشعاع الشمسي إلى الطاقة الكهربائية وبالرغم من الجانب الايجابي في الزيادة الملحوظة في الطاقة الكهربائية لكن تحتاج هذه الأنظمة إلى التبريد المستمر للخلايا الشمسية وذلك نتيجة تركيز الأشعة الشمسية بنسبة كبيرة على الخلايا بالإضافة إلى حاجتها إلى نظام تتبع شمسي وكل هذا على حساب الطاقة الكهربائية المتولدة .

• **تقنية العواكس البصرية المستوية والمستخدمة مع تقنيات الألواح الشمسية الثابتة أو المتحركة** والتي تساهم في زيادة نسبة شدة الإشعاع الشمسي الساقط على اللوح الشمسي وبالتالي الحصول على زيادة نسبة التيار الكهربائي المتولد من اللوح. [2,3,4]

الإشعاع الشمسي الواصل إلى الأرض فمنه ما يصل مباشرة إلى الأرض مباشرة بدون أي مؤثر لتغيير مساره حيث تسمى هذه بالأشعة المباشرة وبعض الآخر منه ينكسر وينعكس معتمدا على حالة الجو المتمثلة في مواقع الغيوم أو نسبة بخار الماء و ذرات الغبار وتسمى هذه بالأشعة المشتتة والشكل (1) يوضح الأشعة الشمسية المشتتة [3,5]



شكل 1: تشتت الأشعة الشمسية من قبل الغيوم والغبار

وكذلك تختلف شدة الإشعاع الشمسي في بداية شروق الشمس عن وقت منتصف النهار وعن وقت الغروب وهذا يعني إن مسار الشمس من الشروق إلى الغروب له تأثير على شدة الإشعاع الشمسي الساقط على اللوح الشمسي مع تغير الزمن [3,4,5,6]
 إن شدة الإشعاع الشمسي يمكن زيادتها بتقنية استخدام العواكس البصرية مع الألواح الشمسية وفي هذه التقنية إن نسبة الأشعة الساقطة على اللوح الشمسي إلى نسبة الأشعة المنعكسة من العواكس البصرية وكما موضح في الشكل (2) يمكن أن تمثل بعامل التركيز الهندسي والموضح في العلاقة التالية :- [4,6,7]

(1).....

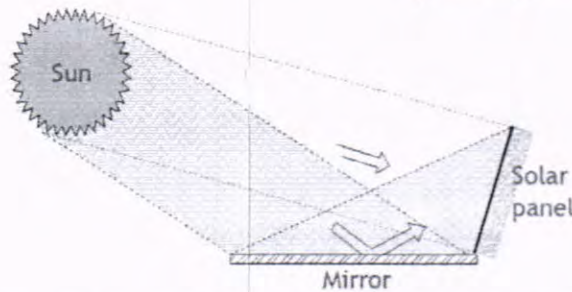
حيث إن :-

$C =$ عامل التركيز الهندسي

$A_{eff} =$ تمثل المساحة الفعالة

$A_{mirror} =$ تمثل مساحة اللوح العاكس البصري

$A_{module} =$ تمثل مساحة اللوح الشمسي



شكل 2: المساحة الفعالة لكل من مساحة اللوح والعاكس البصري

إن المتغير لنسبة الإشعاع الساقط على اللوح الشمسي والإشعاع المنعكس من العاكس البصري هي قيمة الزاوية ما بين اللوح الشمسي والعاكس البصري وكذلك متغير آخر هو طبيعة مادة العاكس البصري المستخدم فالمادة العاكسة للمرايا المطلية بطلاء مركبات الفضة تختلف نسبة

استخدام العواكس البصرية مع الألواح الشمسية لزيادة قدرتها الخارجية

عماد وعلي وعادل وسريد وعمار واسماء وفاضل وعماد ومروج وفلاح

انعكاسها للإشعاع الشمسي عن مادة العواكس من الحديد المقاوم للصدأ والألمنيوم وشرائح أغشية الألمنيوم العاكسة [3,6,7,8,9]

المواد وطرائق العمل

•الأجهزة والمعدات المستخدمة :-

•تم بناء هياكل حديدية عدد/ 2 لاستخدامها في حمل الألواح الشمسية نوع احادية التبلور والعواكس البصرية حيث تم استخدام احدهما لحمل اللوح الشمسي المقارن فقط والثاني لحمل اللوح شمسي وعواكس بصرية على جانبي اللوح الشمسي ولكلا الهيكلين قابلية التغير في الزوايا مع الأفق . وتغير حوامل العواكس البصرية بزوايا مختلفة مع اللوح الشمسي لاختيار عدة زوايا للعاكس البصري مع اللوح الشمسي

•ألواح شمسية عدد / 2 بقدرة 80 واط أحادي البلورة وذلك لغرض المقارنة بين لوح مستخدم مع عاكس بصري واللوح الثاني بدون عاكس ليكون مرجعية في المقارنة بين قيمتي قدرتي اللوحين والشكل (3) يوضح اللوح الشمسي مع العاكس البصري واللوح الشمسي المقارن .



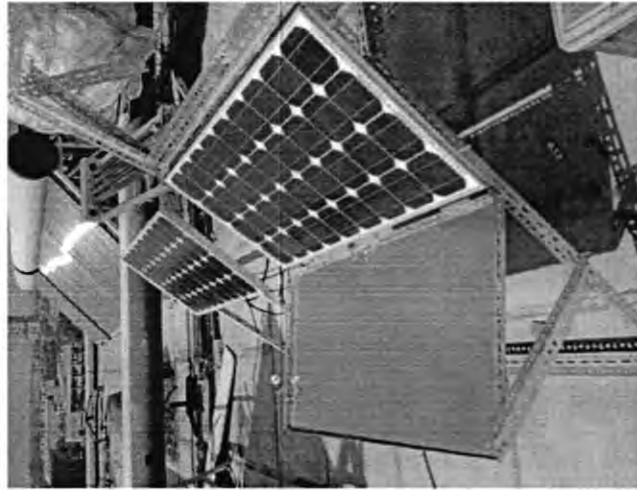
شكل 3 : اللوح الشمسي مع العاكس البصري واللوح الشمسي المقارن

- استخدام جهاز متعدد القراءات لقراءة الفولتية والتيار الخارجة من اللوحين
- عواكس بصرية زجاجية (نوع المرايا الزجاجية) ذات انعكاسية عالية تصل تقريبا الى 95% وهي مطلية بمواد الفضة .
- عدة لقياس الزوايا (منقلة) لقياس زوايا ميل اللوح الشمسي مع الافق وقياس الزوايا الحاصلة ما بين اللوح الشمسي والعاكس البصري .
- استخدام منظومة الانواء الجوية لقياس قدرة الاشعاع الشمسي الساقط على سطح الارض مع تغير ساعات النهار والمقارنة مع نسبة قدرة اللوح الشمسي الخارجة حيث ان منظومة الانواء الجوية تحتوي على متحسس سليكوني معايير لقياس قدرة الاشعاع الشمسي , منظومة الانواء الجوية نوع watch dog

النتائج والمناقشة

في هذه المرحلة تم استخدام عدة زوايا بين العاكس البصري واللوح الشمسي بغرض الوصول الى افضل زاوية يمكن استخدامها ما بين اللوح الشمسي الثابت والعاكس البصري ويمكن اعتمادها على مدار ايام السنة وتم اعتماد هذه الزوايا التالية وذلك لمناسبتها في مثل هذه التطبيقات :-

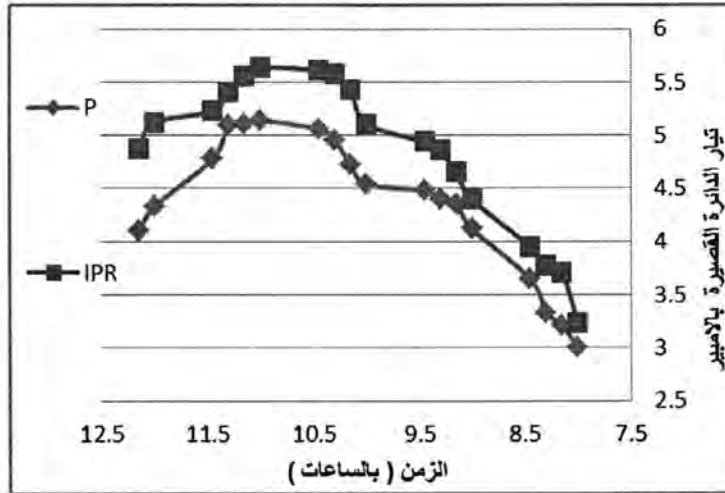
1-2 استخدام العاكس مع اللوح الشمسي في يوم مشمس وزاوية 110 درجة ومن جهة واحدة من اللوح الشمسي وهي الجهة السفلى وكما موضح في الشكل (4) وتم تسجيل التيار الناتج من اللوح الشمسي بدون عاكس بصري ومن لوح شمسي مستخدم معه عاكس بصري والقراءات المسجلة مع تغير الزمن لساعات النهار لمعرفة الساعات التي يكون فيها العاكس البصري اكثر فعالية من الساعات الاخرى وكما موضح في الشكل (5) الذي يوضح قراءات التيار المسجلة من اللوح الشمسي مع ساعات النهار وتم اخذ قراءات الاشعاع الشمسي من منظومة الانواء الجوية مع تغير ساعات النهار وكما موضح في الشكل (6) بغرض معرفة مقدار التغير في قدرة الاشعاع الشمسي الساقطة على اللوح الشمسي واللوح الشمسي وتختلف نسبة الاشعاع الشمسي على اللوح الشمسي عن نسبة قدرة الاشعاع الشمسي على العاكس البصري وذلك لاختلاف زاوية السقوط على كل من اللوح الشمسي والعاكس البصري . هذه القراءات تمت في يوم مشمس وسماء صافية



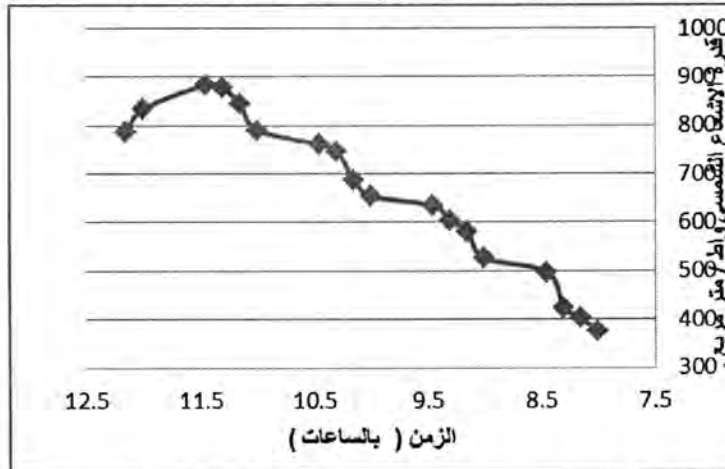
شكل 4: اللوح الشمسي مع العاكس البصري بزاوية 110 درجة واللوح الشمسي المقارن في القراءات وكلما التوحيين مع الأفق بزاوية 35 درجة

استخدام العواكس البصرية مع الألواح الشمسية لزيادة قدرتها الخارجة

عماد وعلي وعادل وسرمند وعمار واسماء وفاضل وعماد ومروج وفلاح

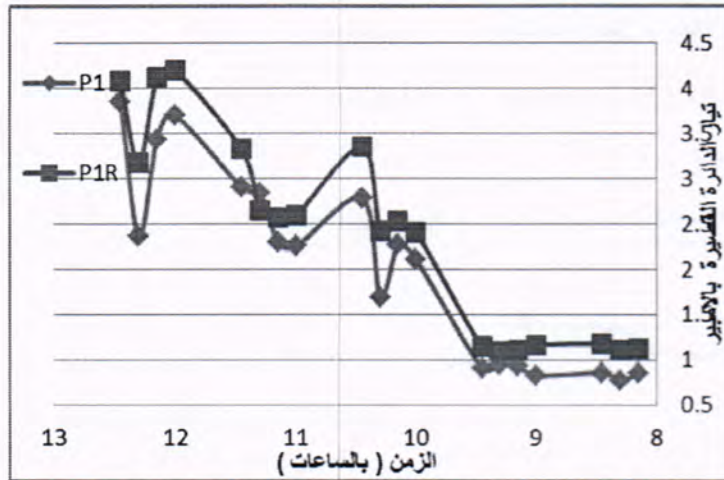


شكل 5: - قيمتي التيار الناتجة من اللوحين مع تغير ساعات النهار (اللوح الشمسي مع العاكس البصري من جهة واحدة (الجهة السفلى) IPR واللوح الشمسي المقارن P)

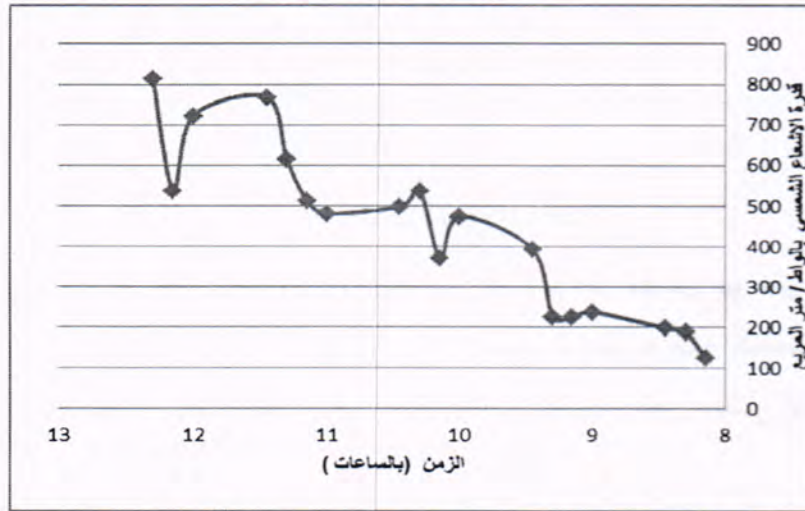


شكل 6: - قراءات قدرة الإشعاع الشمسي مع ساعات النهار

ومن الشكل (5) نلاحظ تغير وزيادة في قيمة القدرة الخارجة من اللوح الشمسي باستخدام العاكس البصري مع اللوح الشمسي وهذا يشير إلى التأثير الإيجابي للعاكس البصري في هذه التطبيقات 2-2- تم إعادة التجربة السابقة ولكن في جو يوم مغبر لغرض معرفة تأثير حالة الجو في حالة الغبار على أداء اللوح الشمسي والعاكس البصري ومقدار انعكاسية العاكس البصري في مثل هكذا أجواء والشكل (7) يوضح قراءات تيار الدائرة القصيرة لكل من اللوح الشمسي ذو العاكس البصري واللوح الشمسي المقارن والشكل (8) يوضح قراءات قدرة الإشعاع الشمسي مع تغير ساعات النهار في يوم مغبر



شكل 7- قراءات تيار الدائرة القصيرة مع الزمن لكل من اللوح الشمسي ذو العاكس البصري واللوحة الشمسي المقارن



شكل 8- قراءات قدرة الإشعاع الشمسي مع الزمن في يوم مغبر

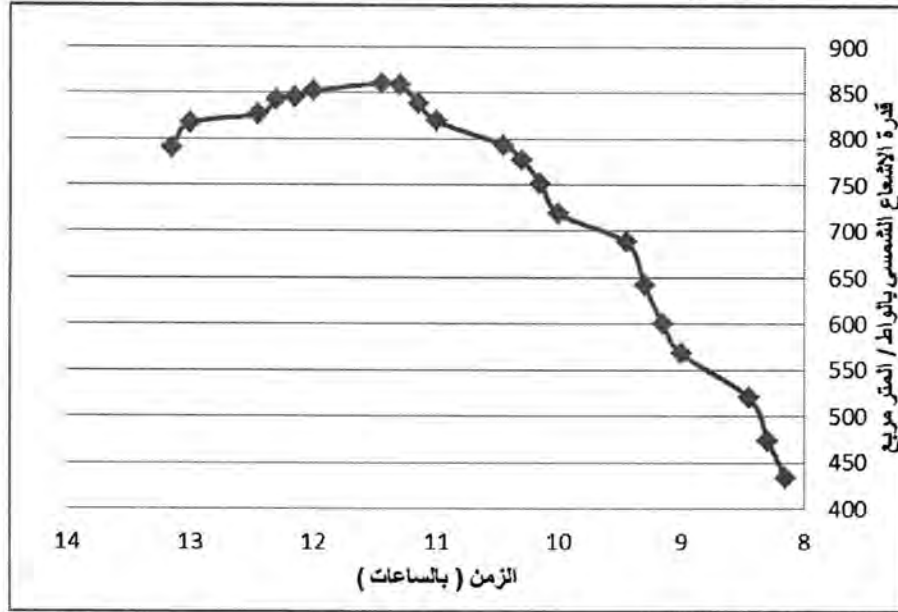
ومن الشكليين (7) (8) يلاحظ تأثير الغبار على توهين قدرة الإشعاع الشمسي الواصلة إلى سطح الأرض وبالتالي التأثير على قدرة اللوح الشمسي الخارجة ومن الشكل (7) يلاحظ وبالرغم من التوهين الحاصل بسبب الغبار لكن هناك تأثير للعاكس البصري على قدرة اللوح الشمسي المستخدم معه عاكس بصري وبالرغم من أن نسبة الغبار المتراكمة على العاكس البصري أكبر من ما هو متراكم على اللوح الشمسي لأنه يكون بوضع شبه أفقي بينما اللوح الشمسي يكون بزاوية 35 درجة فان هناك تأثير لا بأس به على قدرة اللوح الشمسي الخارجة وان كان طفيف .

2-3- استخدام العاكس البصري مع اللوح الشمسي وعلى جانبي اللوح الشمسي وتم ترتيب العاكس البصري بزاوية 115 درجة مع جانبي اللوح الشمسي

استخدام العواكس البصرية مع الألواح الشمسية لزيادة قدرتها الخارجة

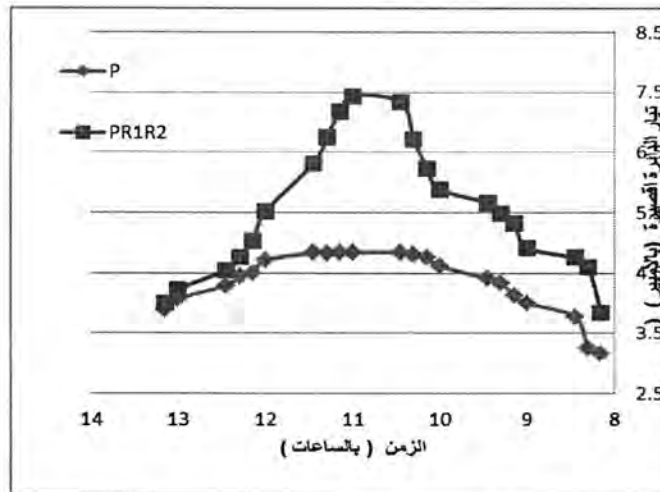
عماد وعلي وعادل وسرمد وعمار واسماء وفاضل وعماد ومروج وفلاح

تم تسجيل القدرة الإشعاع الشمسي الساقطة على الأرض من خلال محطة الانواء الجوية وعلى طول ساعات النهار ومن الشكل (9) يلاحظ مقدار تغير قدرة الإشعاع الشمسي مع تغير ساعات النهار ومن بداية الشروق الى منتصف النهار ويبدأ بالنزول بعد منتصف النهار



شكل - 9:- تغير قدرة الإشعاع الشمسي الساقط على الأرض مع تغير ساعات النهار

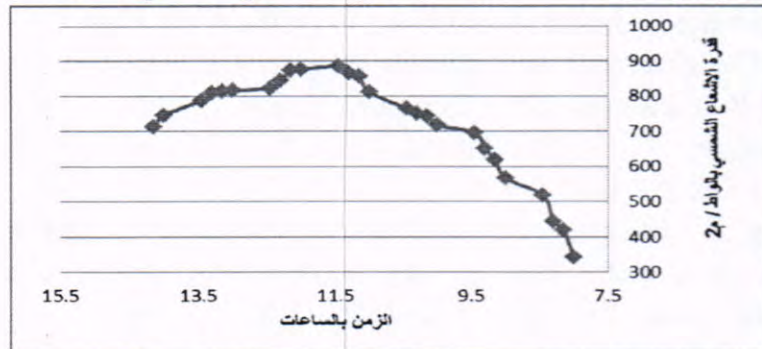
تم تسجيل قيمة التيار الدائرة القصيرة للوح الشمسي المستخدم معه العاكسين البصريين والتيار الخارج من اللوح الشمسي المقارن ومن الشكل (10) يلاحظ التغير لقيمتي التيار مع تغير ساعات النهار .



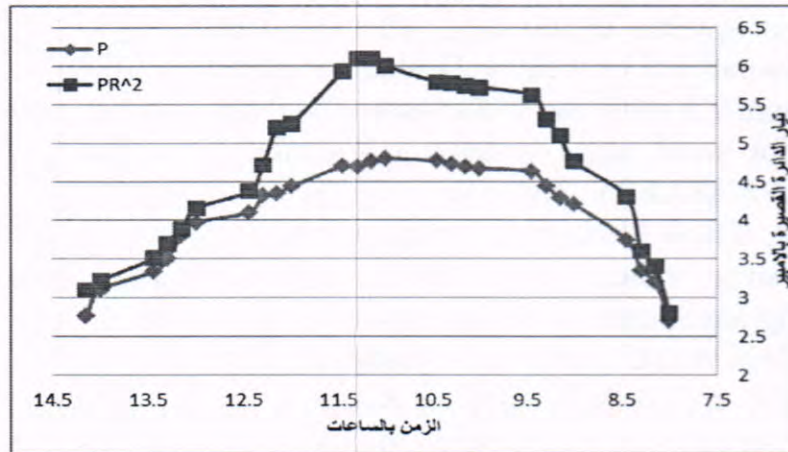
الشكل - 10 :- مقدار تيار الدائرة القصيرة لكل من اللوحين الشمسيين مع تغير ساعات النهار ومن خلال الشكل (10) يلاحظ مقدار التأثير الواضح للعاكسين البصريين المستخدمين مع اللوح الشمسي على قدرة اللوح الشمسي الخارجة المستخدم معه العواكس البصرية ومن قيمة تيار

الدائرة القصيرة فان قيمة التيار كانت اكبر من القيمة القصوى للوح الشمسي وهي 5.4 أمبير ووصولها إلى 7.5 أمبير وهذا يوضح مقدار التأثير للعواكس البصرية على قدرة اللوح الخارجة لكن هذه الزيادة قد يكون لها تأثير سلبي على اللوح الشمسي بارتفاع درجة حرارة اللوح الشمسي وبالتالي انخفاض فولتية الدائرة المفتوحة وهذا يؤثر على عملية الشحن للبطاريات حيث سوف تكون فولتية اللوح الشمسي اقل من فولتية البطارية وبالتالي سوف لا يكون انسياب لتيار الشحن .

2-5- في هذه الخطوة تم صنع زاوية بين اللوح الشمسي والعواكس البصرية بمقدار 120 درجة ومن الإشكال (11) و (12) يلاحظ مقدار التغير في قدرة اللوح الشمسي الخارجة



شكل 11: قراءة قدرة الإشعاع الشمسي من منظومة الأنواء الجوية



الشكل 12: قراءتين للقيمتي القدرة الخارجة من اللوحين الشمسيين مع العاكس البصري ويدونه

من خلال خطوات العمل المتوالية للبحث نستنتج بان هناك زوايا محددة في حالة استخدام العواكس البصرية مع اللوح الشمسي في غرض زيادة كفاءة اللوح الشمسي في إنتاج قدرة اكبر وان الزوايا التي يتم اعتمادها في مثل هذه الأنظمة وفي الأجواء العراقية التي تعتمد على نصب الألواح الشمسية بزاوية 35 درجة مع الأفق وعلى مدار السنة فان الزوايا التي يمكن اعتمادها في أنظمة استخدام العواكس البصرية مع اللوح الشمسي هي 110 و 115 و 120 درجة وان لكل زاوية تأثير يختلف كل واحدة عن الأخرى تبعا إلى الموسم الشمسي لأيام السنة واختلاف موقع الشمس مع مدار

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علاقة *Mycoplasma pneumoniae* بالحساسية في مدينة الموصل : العراق

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تاريخ التقديم: 2011/ 4/ 5

تاريخ القبول: 2011/ 5/29

ABSTRACT

Background: To clarify the correlation between *Mycoplasma pneumoniae* infections and allergic airways in Mosul-Iraq.

Patients and Methods : Throat and nasopharyngeal swabs were collected, the total IgE level and specific IgM of *Mycoplasma pneumoniae* were carried out in a group of 90 patients who registered at Allergy department in Al-Jumhory Teaching hospital in Mosul in period Feb.2009-Feb.2010.

Results: Overall 8 (8.89 %) were culture positive (seronegative) for *Mycoplasma pneumoniae* and 7 (7.79 %) were seropositive (culture negative) , all patients 15 (16.67 %) had elevated serum total IgE level.

Conclusions: *Mycoplasma pneumoniae* infection caused significant increasing in total serum IgE level in allergic patients in comparison to non-allergic patients, suggested it may be allergens.

الخلاصة

انتخب (90) من المراجعين لشعبة الحساسية في استشارية المستشفى الجمهوري التعليمي في الموصل للفترة من شباط 2009 إلى شباط 2010، تراوحت اعمارهم بين (6-69) سنة، وابدوا جميعا استجابة موجبة لاختبار الجلد جمعت منهم (90) مسحة من التجويف الانفي البلعومي والبلعوم لغرض عزل وتشخيص *Mycoplasma pneumoniae* ودراسة علاقتها بفرط التحسس كما قدر تركيز الكلوبولين المناعي الكلي Total IgE وتركيز الكلوبولين المناعي IgM الخاص بجراثومة *Mycoplasma pneumoniae* في مصولهم.

بلغ المعدل الهندسي لتركيز الكلوبولين المناعي الكلي Total IgE (140.56 ± 107.671) وحدة دولية/سم³ وتم الحصول على (8) عزلات فقط لأفراد النوع *Mycoplasma pneumoniae* بينما أظهرت نتائج التشخيص المصلي لها وجود (7) افراد مصابين بها (كان معدل الكلوبولين

باسمة ويونس

المناعي IgM لديهم أعلى من قيمة Cut off والتي تبلغ 10 وحدة دولية /سم³ ابدوا جميعا زرعاً سالبا.

وُجِدَ فرق معنوي عند مستوى احتمالية (5%) في تركيز الكلوبولين المناعي الكلي Total IgE لدى المكتسبين لهذه البكتريا من المصابين بالحساسية مقارنة مع المتحسسين غير المصابين بها.

المقدمة

يشكل الربو مشكلة كبيرة في السنوات الأخيرة، وهو مرض التهابي يصيب الرئتين ويختلف في شدته باختلاف العمر والآلية المسببة له وينتج عن التأثير المتداخل لعوامل عديدة وراثية وبيئية تلعب دوراً في تطوره [1-2].

الربو إما أن يكون خارجي المنشأ Extrinsic Asthma الذي يعتبر مثالا على الحساسية المتماحطة ، أو داخلي المنشأ Intrinsic Asthma الذي يسمى Non Atopic Asthma ويحدث في البالغين عادة وتكون أعراضه اشد من أعراض المتماحل ولا يرتبط بالتاريخ العائلي ويتم التفريق بين النوعين عن طريق قياس مستوى ألد IgE الكلي في المصل إذ يرتفع في حالة الربو المتماحل [3-2].

يكون الربو أكثر شيوعاً في الأطفال خصوصاً عند تواجدهم في أماكن تتواجد فيها محسسات الربو مثل حلم الغبار المنزلي وحبوب الطلع و ابواغ الفطريات والريش وفضلات الحيوانات وبعض الأغذية والأدوية ، أعراض الربو : أزيز وضيق في التنفس وسعال وزيادة إفراز المخاط في المجاري التنفسية [4].

يشير مصطلح الحساسية Allergy إلى النوع الأول من تفاعلات فرط التحسس والذي يلعب الكلوبولين المناعي IgE دوراً مهماً في إحداثه وتطوره، بينما يشير مصطلح Atopic Allergy إلى أعراض قوية تحدث لدى الأفراد الذين لديهم تاريخ عائلي Family History وميل وراثي للإصابة بأمراض الحساسية، حيث يميل هؤلاء الأفراد إلى إنتاج ألد IgE عند التعرض للمستضدات البيئية أو ما يسمى بالمحسسات Allergens، كما أن لديهم مستوى مرتفعاً من الكلوبولين المناعي الكلي Total IgE [5].

تؤثر الحساسية الآتية في حوالي ثلث سكان العالم وتعتبر مشكلة كبرى في العالم الغربي خصوصاً في السنوات الأخيرة، إذ لوحظ أن هناك ارتفاعاً ملحوظاً في حدوثها مثل الربو المتماحل وحساسية الجلد والأنف والعيون والحساسية الغذائية [6]، كما لوحظ في العقود الأخيرة ارتباط بعض أمراض الحساسية الآتية وخاصة التنفسية منها مثل الربو وحساسية القصبات الهوائية ببعض أنواع البكتيريا وأصبحت العلاقة بين أمراض الحساسية التنفسية وإصابات الجهاز التنفسي بالبكتيريا غير النموذجية Atypical Bacteria مثل *Chlamydia pneumoniae* و *Mycoplasma pneumoniae* مكاناً خصباً لإجراء البحوث وأخذت حيزاً كبيراً من انتباه الباحثين إذ أشارت العديد من الدراسات والبحوث إلى أن 40% من مرضى الربو المزمن لديهم إصابات نشطة ببكتيريا *Mycoplasma pneumoniae* حيث تحدث هذه البكتيريا حالة تفاقم الربو، ولوحظ أيضاً أن إعطاء هؤلاء المرضى مضادات حيوية مؤثرة في هذه البكتيريا أدى إلى انخفاض معنوي في حدة أعراض الربو مما يشير إلى وجود علاقة قوية بين البكتيريا والربو [7].

تعتبر هذه البكتيريا إحدى أهم ممرضات الجهاز التنفسي العلوي والسفلي في الأطفال والبالغين وتسبب أمراضاً عديدة أهمها ذات الرئة المكتسب من المجتمع (CAP) Community Acquired Pneumonia أو Atypical Pneumonia أو Walking pneumonia حيث أن 20-30% من إصابات ذات الرئة في المجتمعات الحساسة تعود إلى هذه البكتيريا [8-9].

تنتمي *Mycoplasma pneumoniae* إلى قسم Mollicutes التي تضم أنواعاً بكتيرية صغيرة الحجم وعديمة الجدار الخلوي وتمتلك أصغر جينوم في بدائية النواة وغشائها ثلاثي الطبقات يحتوي على المستيرولات وحجم الجينوم حوالي 816.394 bp وتستعمر الجهاز التنفسي وتمتلك تراكيب سطحية تساعد على الالتصاق والحركة والانقسام وأهمها عضبة الالتصاق Attachment Organelle [10].

إن الارتفاع الملحوظ في أمراض الحساسية في الآونة الأخيرة في العراق إضافة إلى شحة الدراسات التي تركز على العلاقة بين البكتيريا غير النموذجية وأمراض الحساسية دعتنا إلى إجراء الدراسة الحالية التي تهدف إلى ما يأتي :

- 1- عزل وتشخيص النوع البكتيري *Mycoplasma pneumoniae* من مرضى الربو وحساسية الجهاز التنفسي وتوضيح علاقتها بإحداث حالة تفاقم الربو.
- 2- التحري عن حساسية ومقاومة هذه البكتيريا للمضادات الحيوية المؤثرة فيها.

3- المقارنة بين التشخيص المصلي (قياس IgM) والطرائق الزرعية في إعطاء نتائج الإصابة بهذه البكتيريا.

المواد وطرائق العمل

جُمِعَت العينات من مراجعي شعبة الحساسية في استشارية المستشفى الجمهوري التعليمي في الموصل والمُشخصين بإصابتهم بفرط التحسس من قبل الطبيب المختص وبعد خضوعهم لاختبار الجلد ، وتراوح أعمارهم ما بين (6-69) سنة ودونت معلومات عنهم في استمارة الاستبيان في الملحق (1) وشملت عينات الدراسة ما يأتي:-

1-مسحات البلعوم وتجويف البلعوم الأنفي Throat and Nasopharyngeal swabs

جُمِعَت 90 مسحة شملت (82) من البلعوم الأنفي و(8) من بلعوم المصابين بحساسية القصبات والربو وحساسية الأنف ونقلت المسحات إلى المختبر بعد وضعها في البيئة الناقلة المحورة في المختبر بإضافة مصل البيض Modified PPLO Broth.

2- عينات المصل

سحب الدم الوريدي لـ (90) شخصاً قيد الدراسة، ووضع في أنابيب خالية من المواد المانعة للتخثر ونبذ بسرعة 3000 دورة/دقيقة لمدة 5 دقائق وحفظ المصل بالتجميد لحين الاستخدام. الأوساط الزرعية

1- وسط أگار الدم Blood agar medium

2- وسط أگار المايكوبلازما المحور في المختبر Modified PPLO agar

حضر الوسط حسب ما جاء في [13-12-11] وحُوِّر الوسط بإضافة مصل البيض (بياض البيض) بدلا من مصل دم الخيول، إذ أُضيف 20 سم³ من بياض البيض إلى كل 140 سم³ من الوسط بعد إضافة خلاصة الخميرة ومزج جيدا، وأخيرا أُضيف إليه 1 سم³ من محلول المضاد Ampiclox بتركيز 100 ملغم / سم³ و0.5 سم³ من محلول خلاصة الثاليوم بتركيز 10% وحفظ الوسط في الثلاجة لحين الاستخدام.

3- وسط مرق المايكوبلازما المحور Modified PPLO Broth

حُضِرَ من نفس مكونات PPLO agar عدا الأغار.

4- وسط ازرق الميثيلين _ الكلوكون ثنائي الطور

Methylene blue _ Glucose Diphasic medium (MB_GD)

حضر الوسط حسب ما جاء في [11-12-13] وحُوِّز الوسط بإضافة مصل البيض (بياض البيض) بدلا من مصل دم الخيول.

التشخيص المصلي لبكتريا *Mycoplasma pneumoniae*

أُستخدِمت عدة عمل (Kit) خاصة مُجهَّزة من شركة Demeditec في التشخيص المصلي لهذه البكتريا باختبار ELISA واجري الاختبار حسب توصيات الشركة المنتجة للكت.

قياس مستوى الكلوبولين المناعي IgE الكلي

أُستخدِمت عدة عمل (Kit) مجهزة من شركة BioCheck واعتمد في تقدير المستوى الكلي للـ IgE في المصل على اختبار ELISA واجري ذلك حسب توصيات الشركة المنتجة للكت.

عزل وتشخيص *Mycoplasma pneumoniae*

لقح 0.2 سم³ من الوسط الناقل الحاوي على العينة مباشرة في وسط PPLO agar المحضّر مختبريا والمحور بإضافة مصل البيض (بياض البيض) وحُصِنَت الأطباق لاهوائيا في درجة حرارة 37 م° لمدة 4-7 أيام ولوحظ تكون مستعمرات شبيهة بالبيض المقلي [13].

اختبارات التشخيص

اجري عزل وتشخيص بكتريا *Mycoplasma pneumoniae* على الاختبارات الآتية والتي اجريت حسب ما جاء في [13]:

- 1- الفحص المجهرى
 - 2- اختبار صبغة دينس
 - 3- اختبار تخمر الكاربوهيدرات
 - 4- اختبار قدرتها على تحليل دم الإنسان
 - 6- اختبار أنزيم Catalase و اختبار أنزيم Cytocrome Oxidase
- اختبار حساسيتها للمضادات الحيوية

اجري بالاعتماد على طريقة Kirby-Bauer المحورة والمعتمدة من قبل منظمة الصحة العالمية [14]، وقد أُستخدِمت أقراص المضادات الموضحة في الجدول (1) والمجهزة من قبل شركة Bioanalyse .

الجدول 1: أنواع المضادات الحياتية المستخدمة في اختبار حساسية *Mycoplasma pneumoniae*

الرمز	التركيز	المضاد	الرمز	التركيز مايكروغرام/ قرص	المضاد
B	10	Bacitracin	ME	30	Methicillin
CLR	15	Clarithromycin	TE	30	Tetracyclin
NA	30	Nalidixic acid	AZM	15	Azithromycin
AK	30	Amikacin	C	30	Chloramphenicol
DA	2	Clindamycin	SXT	25	Tri+sulfanoxazol
S10	10	Streptomycin	CIP	5	Ciprofloxacin
P	10	Penicillin	DO	30	Doxycycline
VA	30	Vancomycin	ENR	5	Enrofloxacin
AM	30	Ampicillin	CRO	30	Cefotriaxone
AK	30	Amikacin	E	15	Erythromycin

التحليل الاحصائي

اعتمدت النسبة المئوية واستخدم اختبار Simple T test في تحليل النتائج المعتمدة في الدراسة.

النتائج والمناقشة

التقدير الكمي للكلوبيولين المناعي IgE الكلي:

أجري قياس مستوى الكلوبيولين المناعي IgE الكلي لـ 90 من المستجيبين لاختبار الجلد وأظهرت النتائج أن المعدل الهندسي لتركيز IgE لديهم بلغ (140.56 ± 107.67) وحدة دولية/سم³ كما موضح في الجدول (2) كما درست مستويات الـ IgE الكلي ولوحظ أن المستجيبين لاختبار الجلد والذين كان لديهم تركيز IgE أعلى من 100 وحدة دولية/سم³ شكلوا نسبة (57.77%) فيما شكل الذين كان لديهم تركيز IgE أقل من 20 وحدة دولية/سم³ نسبة (6.68%) وكما موضح في الجدول (3).

الجدول 2: المعدل والمعدل الهندسي لتركيز IgE الكلي وحدة عالمية/سم³ في مصول بعض

المستجيبين لاختبار الجلد

الانحراف المعياري	المعدل الهندسي لتركيز IgE وحدة عالمية/سم ³	معدل تركيز IgE وحدة عالمية/سم ³	العدد الكلي للعينات
112.91±	105.89	147.50	90

الجدول 3: توزيع مستويات تركيز IgE الكلي للمستجيبين لاختبار الجلد

تركيز IgE وحدة دولية/سم ³	العدد	(%)	المعدل	المعدل الهندسي وحدة دولية/سم ³	الانحراف المعياري
< 20	6	6.68	6.66	6.00	4.08±
20-100	32	35.55	72.34	66.93	23.43±
> 100	52	57.77	208.20	179.90	149.38±

وبالاستناد إلى ما أقرته منظمة الصحة العالمية فإن تركيز IgE 20 وحدة دولية/سم³ لا تعد عامل خطورة للحساسية و إذا كانت قيمته 20-100 وحدة دولية/سم³ فهناك احتمال الإصابة بالحساسية وإذا ارتفع مستواه عن 100 وحدة دولية/سم³ فيشير إلى وجود إصابة مؤكدة بالحساسية حسب ما جاء في تعليمات الشركة المنتجة للعدة المستخدمة في القياس [15].

يلعب الكلوبولين المناعي IgE دورا محوريا في تطور أمراض الحساسية الآتية والربو وأشار عدد من الباحثين إلى وجود علاقة معنوية بين المستوى المرتفع له والاستجابة لاختبار الجلد، وتؤثر عدة عوامل على تركيزه في المصل في الأصحاء والبالغين مثل الجنس والسكن والعمر والتدخين والتلوث الهوائي والمنطقة الجغرافية ونوع الغذاء كما يرتفع مستواه في حالة الإصابة بالطفيليات والايذز والحروق الشديدة [16-17].

ذكر الباحث [17] أن مستوى الـ IgE الكلي يرتفع خلال الإصابة بالحساسية الآتية والربو ويرافق الارتفاع في مستواه شدة أعراض المرض ويدل المستوى العالي له على وجود استجابة فعالة لخلايا Th-2 وإنتاج مستويات عالية من IL-4 و IL-3 (السايبتوكينات المسؤولة عن تخصص خلايا B لإنتاج IgE).

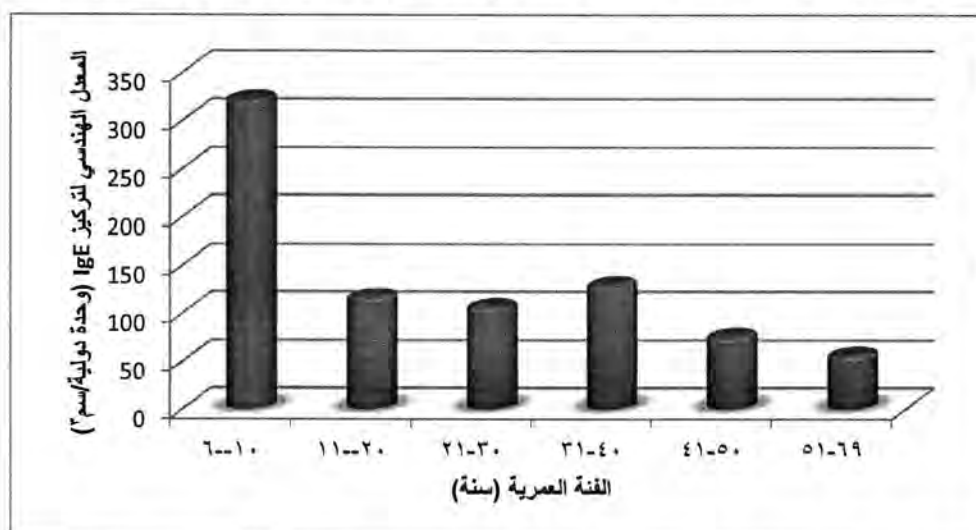
أوضح [18] أن ارتفاع مستوى IgE يرافق الإصابة بالطفيليات ومستوى التلوث الهوائي ويرتفع مستواه في الأصحاء المعرضين لملوثات الهواء بدرجة كبيرة.

أكد [19] أن مستوى IgE ارتفع مرافقا للارتفاع في عدد الحمضات في الدم وأضاف [20] أن إنتاج IgE يعتمد على سلسلة من التفاعلات بين خلايا B و T والخلايا الحمضة والبدينة وتساهم

الجزئيات السطحية و الساييتوكينات وخاصة IL-4 و IL-13 في ارتفاع مستواه في المصل كما تلعب العوامل الجينية والبيئية دوراً مهماً في ذلك.

أوضحت نتائج الشكل (1) أن المعدل الهندسي لتركيز IgE الكلي كان أعلى عند الفئة العمرية (10-6) سنة تليها الفئة العمرية (40-31) سنة ثم الفئة (20-11) سنة.

أوضح [21] Ly وآخرون سنة 2005 أن إفراز IL-13 والـ IgE يرتفع في الأطفال في عمر 2-5 سنوات ويتغير حسب مقدار تعرضهم للمحسسات واستنتج أن تخصص خلايا Th-2 للمحسس يتم في عمر 5 سنوات فيما ذكر [22] أن معدل الـ IgE في الأطفال أعلى من البالغين ويقل بزيادة العمر ويتغير حسب نوع الإصابة التحسسية وأكد [17] أن تركيز IgE يصل ذروته عند عمر 8-12 سنة وينخفض بعد ذلك وتؤثر العوامل الجينية والتاريخ العائلي في معدل المصل وأضاف [23] أن أعلى تركيز للـ IgE كان عند الفئة العمرية (7-10) سنة ويلعب التلوث الهوائي دوراً في ذلك.



شكل 1: المعدل الهندسي لتركيز الكلوبولين المناعي الكلي IgE في مصل بعض المستجيبين لاختبار الجلد حسب الفئات العمرية (سنة)

توضح نتائج الجدول (4) أن المعدل الهندسي لتركيز الـ IgE كان أعلى في الذكور مقارنة مع المعدل الهندسي للـ IgE في الإناث إذ بلغ (116.60 ± 111.98) وحدة دولية/سم³ في الذكور و في الإناث كان (170.37 ± 102.65) وحدة دولية/سم³.

درست العلاقة بين مستوى الـ IgE الكلي والجنس ووجدت فروقات معنوية وغير معنوية حسب الدراسات ولاحظ [24] أن مستوى الـ IgE أعلى في الذكور المصابين بالحساسية الأنفية مع وجود

فروق معنوية وأوضح أن السبب هو وجود جينات مسؤولة عن إنتاج آل IgE مختلفة بين الجنسين إضافة إلى وجود مواقع جينية إضافية لإنتاجه على الكروموسوم 20 في الذكور فيما أضاف [23] أن ارتفاع IgE في الذكور قد يعود إلى كثرة تعرضهم للمحسسات والملوثات بينما أكد [19] أن لنوع الغذاء والعمر دوراً مهماً في ذلك.

الجدول 4: تركيز IgE الكلية (وحدة دولية/سم³) للمستجيبين لاختبار الجلد من كلا الجنسين حسب السكن والمهنة

	الجنس		السكن		المهنة	
	ذكر	أنثى	مدينة	ريف	موظف	غير موظف
المعدل الهندسي G.M	111.89	102.65	104.38	147.64	152.21	100.51
الانحراف المعياري	116.60±	170.37±	142.98±	131.48±	81.89±	148.93±

أظهرت نتائج الجدول (4) أيضاً أن المعدل الهندسي لتركيز آل IgE لدى سكان الريف بلغ (131.48±147.64) وحدة دولية / سم³ وهو أعلى من سكان المدينة إذ بلغ (142.98±104.38) وحدة دولية / سم³، و بينت النتائج أيضاً أن المعدل الهندسي لتركيز آل IgE الكلي لدى الموظفين كان أعلى إذ بلغ (81.89±152.21) وحدة دولية/سم³ مقارنة مع غير الموظفين (148.93±100.51) وحدة دولية/سم³ كما موضح في الجدول (4) وقد اختلفت هذه النتائج عن نتائج دراسة العاني سنة 2002 الذي أكد أن معدل IgE الهندسي كان أعلى لدى غير الموظفين وبلغ (699±263) وحدة دولية/سم³ مقارنة مع الموظفين (784±67.34) وحدة دولية/سم³ مع وجود فرق معنوي، إن سبب الاختلافات في النتائج قد يعود إلى قلة عدد الأفراد قيد الدراسة الحالية إضافة إلى اختلاف الظروف البيئية في الفترة بين الدراستين.

على الرغم من أن سكان الريف أقل تعرضاً للإصابة بالحساسية الآنية إلا أن معدل آل IgE يرتفع لديهم، وقد يكون سبب ارتفاعه هو المستوى المعاشي والحالة الصحية والمستوى العلمي والثقافي لديهم إذ يتعرض سكان القرى إلى إصابات متكررة بالديدان المتطفلة التي ترفع مستوى آل IgE الكلي لديهم وهذا ما أكدته كل من [20-16-23-25].

باسمة ويونس

أكد [26] أن معدل الـ IgE الكلي يكون مرتفعاً لدى العمال بسبب تعرضهم للمحسسات أكثر من غيرهم ولاحظ ارتفاع مستوى الـ IgE لدى المتدربين في المخابز بعد عام من التدريب، وأكد ذلك [27] وأضاف أن التأريخ العائلي له دور في ذلك.

درست العلاقة بين مستوى الـ IgE الكلي وبعض عوامل الخطورة ولاحظ ارتفاع المعدل الهندسي للـ IgE لدى الأفراد ذوي التأريخ العائلي مع أمراض الحساسية وبلغ (69.68 ± 113.29) وحدة دولية/سم³ فيما كان معدله الهندسي لدى الأفراد غير الممتلكين للتأريخ العائلي (181.36 ± 97.67) وحدة دولية/سم³ كما موضح في الجدول (5).

أوضح [25] أن معدل IgE يكون مرتفعاً لدى الأفراد ذوي التأريخ العائلي مع أمراض الحساسية مقارنة مع غيرهم وأضاف أن كلا من [19] و [16] أن الـ IgE يرتفع لدى الأشخاص ذوي التأريخ العائلي حتى وإن تظهر لديهم أعراض الحساسية بسبب الميل الوراثي لهؤلاء على إنتاج الـ IgE ، أوضح [5] أن الأفراد ذوي التأريخ العائلي لأمراض الحساسية لديهم ميل وراثي لإنتاج IgE عند التعرض للمستضدات البيئية ويكونون أكثر عرضة للإصابة بالحساسية ويطلق عليهم مصطلح المتماحلون Atopic person.

الجدول 5: المعدل الهندسي لتركيز IgE الكلي (وحدة دولية/سم³) لبعض المستجيبين لاختبار

الجلد وحسب التأريخ العائلي وعادة التدخين والحساسية الدوائية

	التأريخ العائلي		التدخين		الإصابة بحساسية الأدوية	
	وجوده	عدم وجوده	مدخن	غير مدخن	مصاب	غير مصاب
المعدل الهندسي G.M	113.29	97.67	152.73	95.91	141.60	103.90
الانحراف المعياري	$69.68 \pm$	$181.36 \pm$	$115.17 \pm$	$148.14 \pm$	$70.86 \pm$	$147.98 \pm$

أوضحت نتائج الجدول (5) أن المعدل الهندسي لتركيز IgE لدى المدخنين كان أعلى بلغ (115.17 ± 152.73) وحدة دولية/سم³ وكان لدى غير المدخنين (148.14 ± 95.91) وحدة دولية/سم³ ، كما أظهرت النتائج أيضاً أن المعدل الهندسي لتركيز الـ IgE الكلي كان أعلى لدى المصابين بحساسية الأدوية كما موضح في الجدول (5).

للتدخين آثار جانبية خطيرة على الجهاز التنفسي، والجسم ويعتبر احد عوامل الخطورة للإصابة بالربو وحساسية الأنف ويحور استجابة الجهاز المناعي تجاه استجابة خلايا Th2.

أكد [28] أن التدخين أدى إلى ارتفاع إفراز IL-13 و IL-5 اللذين لهما دور مهم في سلسلة التفاعلات المؤدية إلى إنتاج الكلوبولين المناعي IgE إذ يعمل IL-13 على زيادة إفراز المخاط في القصبات الهوائية ويعمل على تضيقها ويحفز الالتهاب في الرئتين ويعمل بالتعاون مع IL-5 و IL-4 على تعزيز إنتاج IgE كما أوضح ذلك [29] وأضاف [30] أن الـ IgE يرتفع لدى المدخنين لكن ارتفاعه لا يتناسب مع عدد السكاثر المستهلكة وذكر أن السبب في ارتفاع مستوى الـ IgE لدى المدخنين هو احتواء دخان السكاثر على غازات مهيجة تزيد من التشققات في الغشاء المخاطي للأنف والقصبات الهوائية وتسهل وتزيد من دخول المحسسات.

تعمل بعض أنواع المضادات الحيوية وخاصة البنسلينات على تحفيز الحساسية إذ تكون عبارة عن مستضدات ناقصة ترتبط مع بروتينات الجلد أو المصل وتحفز إنتاج الـ IgE وتعتبر عامل خطورة لتطور أمراض الحساسية الانية وتلعب العوامل الجينية دوراً في ذلك [31].

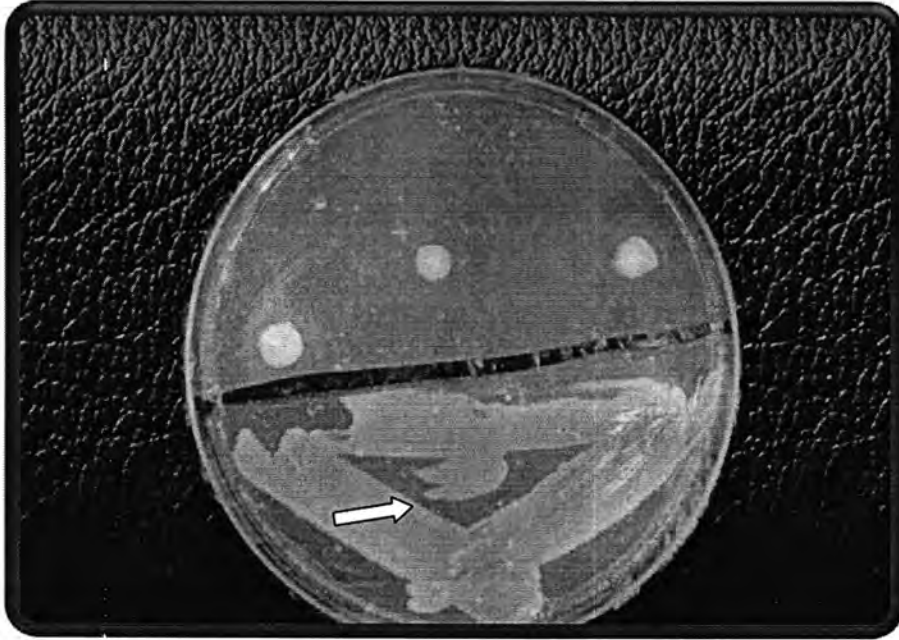
عزل وتشخيص *Mycoplasma pneumoniae*

1- الفحص المجهري

بينت نتائج الفحص المجهري للأغشية المحضرة من وسط اگار PPLO agar المحور ظهور أفراد النوع *Mycoplasma pneumoniae* بشكل كروي وعلى شكل تجمعات لخلايا كروية كما لوحظت ظاهرة تعدد الأشكال Pleomorphism الناتجة عن عدم امتلاكها للجدار الخلوي مما يجعلها مرنة ومطاطية، وأظهرت أفرادها اصطباغاً سالباً ضعيفاً لصبغة غرام ولكنها اصطبغت بصورة أفضل بوساطة صبغة كمزا Giemsa stain [32].

2- شكل المستعمرات

ظهرت مستعمراتها بأشكال كروية محدبة، معتمة، قشطية القوام ذات حواف بيضاء ومركز أصفر اسمك من الحواف شبيهة بالبيض المقلبي إذ تعد هذه من الصفات التفريقية لها، يوضح شكل 2 مستعمرات *Mycoplasma pneumoniae* على وسط Modifid PPLO agar.

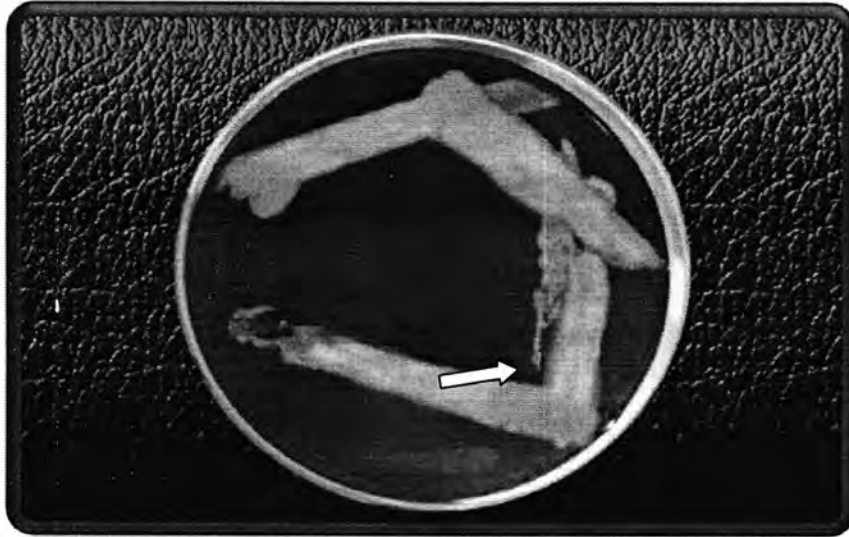


شكل 2: مستعمرات *Mycoplasma pneumoniae* نامية على وسط PPLO المحور

3-اختبار قدرتها على اختزال صبغة دينيس

ظهرت مستعمراتها عديمة اللون نتيجة لاختزالها لازرق المثيلين الموجودة ضمن مكونات

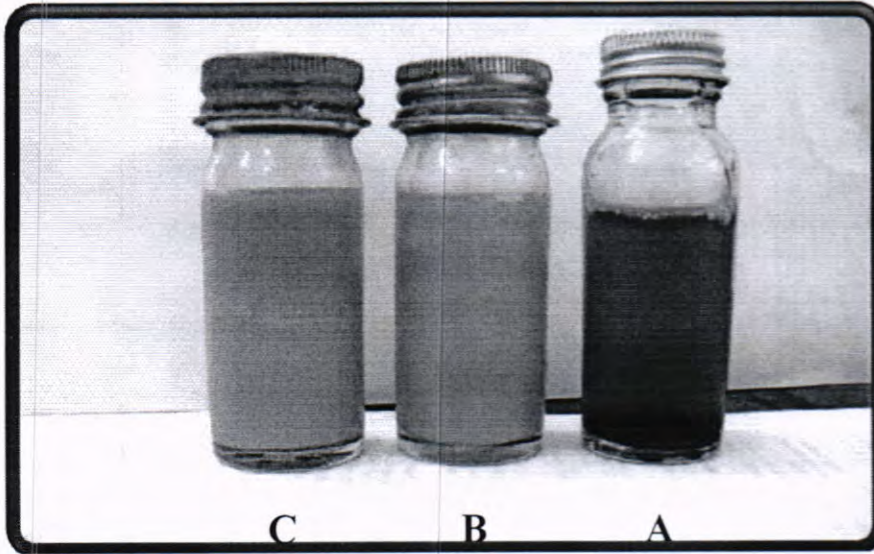
صبغة دينيس كما موضح في الشكل 3.



شكل 3: اختبار اختزال صبغة دينيس

4-اختبار تخمر الكاربوهيدرات

يعتبر اختبارا تشخيصيا مهما لأفراد النوع *Mycoplasma pneumoniae* ويستدل على النتيجة الموجبة من تحول لون الطور السائل للوسط ثنائي الطور من الأرجواني إلى الأصفر فيما يتحول لون الطور الصلب إلى الأخضر المصفر نتيجة تخمر الكلوكوز وإنتاج أحماضاً خفضت الدالة الحامضية للوسط، يوضح الشكل 4 النتيجة الموجبة لهذا الاختبار.

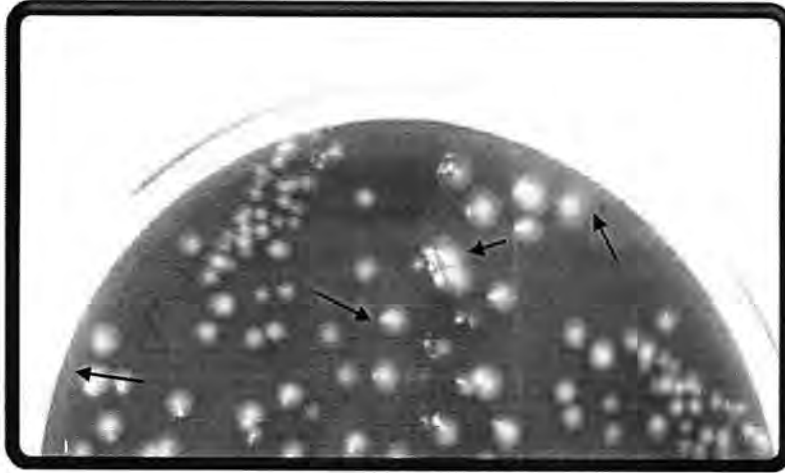


شكل 4: النتيجة الموجبة لهذا الاختبار

A: وسط السيطرة ؛ B: بعد 4 اسابيع من التلقيح ؛ C: بعد 6 اسابيع من التلقيح

5- اختبار قدرتها على تحليل خلايا دم الإنسان الأحمر

يوضح شكل (4) ظهور مستعمرات *Mycoplasma pneumoniae* محاطة بهالة رقيقة من التحلل الدموي دلالة على قدرتها على تحليل كريات الدم الأحمر تحلا كاملا β -haemolysis والذي يعود إلى إنتاجها بيروكسيد الهيدروجين H_2O_2 الذي يحطم الأغشية الخلوية [33].



شكل 5: التحلل الدموي لبكتريا *Mycoplasma pneumoniae*

6- اختبار أنزيم Catalase

كونت مستعمراتها فقاعات بعد إضافة قطرة من بيروكسيد الهيدروجين (3%) إلى جزء من المستعمرات المنقولة على سطح شريحة زجاجية إذ يعمل أنزيم Catalase على تحويل بيروكسيد الهيدروجين إلى أوكسجين وماء [33].

7- اختبار أنزيم Oxidase

لوحظ تغير لون ورقة الترشيح المشبعة بالكاشف etra mythyl-p-pheylen diamine (1%) hydrochloride إلى اللون الأرجواني بعد نقل جزء من مستعمراتها وهذه نتيجة موجبة [33].

حساسية النوع *Mycoplasma pneumoniae* للمضادات الحيوية قيد الدراسة

يوضح الجدول (6) حساسية أفرادها للمضادات الحيوية قيد الدراسة:

الجدول 6: حساسية أفراد النوع *M. pneumoniae* للمضادات الحيوية

النتيجة	التركيز	المضاد الحيوي	النتيجة	التركيز Mg/Disc	المضاد الحيوي
R	10	Bacitracin	R	30	Methicillin
S	30	Tetracyclin	S	15	Clarithromycin
S	30	Chloramphenicol	R	15	Azithromycin
S	5	Ciprofloxacin	R	25	Trimethoprim + Suflaroxasol

S	5	Enrofloxacin	S	30	Doxycyclin
S	30	Amikacin	Ms	30	Nalidixic acid
S	10	Streptomycin	R	2	Clindamycin
R	30	Vancomycin	R	10	Penicillin
Ms	30	Cefotriaxone	R	10	Ampicillin
S	15	Erythromycin	R	10	Gentamycin

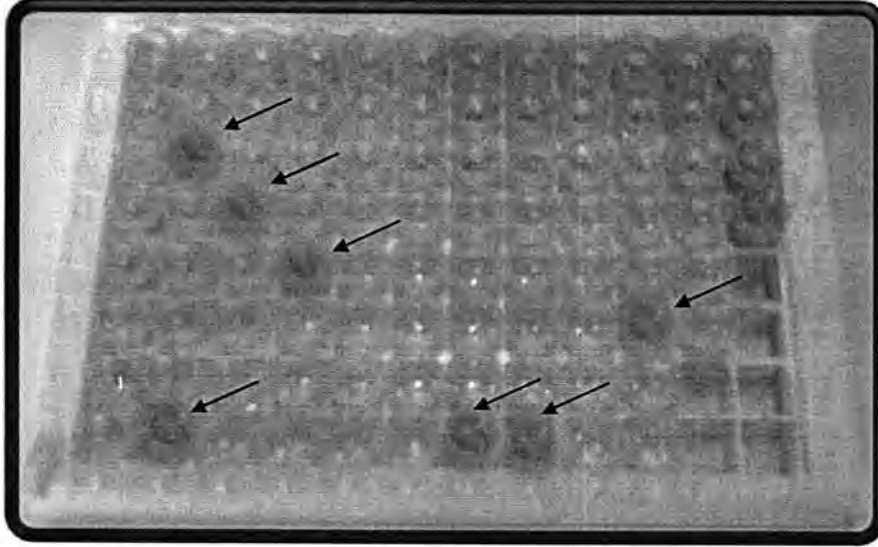
بينت نتائج الجدول (6) أن أفراد *Mycoplasma pneumoniae* كانت مقاومة للبنسلينات كما أنها كانت مقاومة لـ Clindamycin, Azithromycin, Bacitracin, Gentamycin و Vancomycin بينما كانت متوسطة الحساسية لـ Cefotriaxone, Nalidixic acid وكانت حساسة لباقي المضادات قيد الدراسة.

بسبب عدم امتلاكها لجدار خلوي فإن جميع أنواع المايكوبلازما تكون مقاومة للبنسلينات والمضادات الحيوية التي تعمل على الجدار الخلوي كما أن مقاومتها لبعض أنواع مضادات Macrolides قد يعود إلى الطفرات أو التحوير في المناطق التي تعمل عليها هذه المضادات.

أوضح [34] أن أفراد *Mycoplasma pneumoniae* كانت متوسطة الحساسية لـ Azethromycin وحساسة لـ Clarithromycin و Erythromycin ومقاومة لـ Levofloxacin وذكر أن السبب في مقاومتها لبعض أنواع Macrolides هي تحوير الهدف التي تعمل عليها (23S rRNA) بواسطة الطفرة أو الميثلة كما أنها قد تقوم بضخ المضاد الحيوي بنفس سرعة دخوله إلى داخل الخلية وأضاف [35] أن أفراد *Mycoplasma pneumoniae* قاومت مضادات Macrolides عن طريق حدوث طفرة في الجزء 23S rRNA .

التشخيص المصلي لبكتريا *Mycoplasma pneumoniae*

اعتمدت طريقة ELISA وباستخدام عدة عمل مجهزة من شركة Demeditec خاصة بتشخيص الكلوبولين المناعي IgM الخاص بالنوع *Mycoplasma pneumoniae* وأظهرت النتائج وجود (7) مرضى مصابين بها (كما موضح في الشكل 6) إذ كان تركيز IgM لديهم أعلى من قيمة Cutoff وابدوا جميعاً نتائج زرعية سالبة .



شكل 6: التشخيص المصلي لـ *Mycoplasma pneumoniae*

قورنت نتائج التشخيص المصلي مع نتائج التشخيص الزرع كما موضح في الجدول (7) إذ تبين أن الطرائق الزراعية أعطت نسبة أعلى من المصلية.

جدول 7: النسب المئوية لإيجابية اختباري الزرع والمصل المتبعان في تشخيص *Mycoplasma pneumoniae*

طرائق التشخيص	الفحص الموجب	الفحص السالب	المجموع
التشخيص الزرع	8(8.89%)	82(91.11%)	90(100%)
التشخيص المصلي	7(7.78%)	83(92.22%)	90(100%)

قد يعود السبب في إعطاء المرضى المشخصين مصليا بإصاباتهم ببكتريا *Mycoplasma pneumoniae* نتائج سالبة في التشخيص الزرع إلا أن هؤلاء المرضى قد تعاطوا بعض المضادات الحيوية التي تثبتت من نموها كما أن IgM قد يكون تثبط نمو هذه البكتريا مما أعطت نتائج زرعية سالبة.

أكد [36] أن IgM قد ينتج بكميات كبيرة خلال الأسبوع الأول من الإصابة كما أن استجابته تكون ضعيفة جداً في البالغين وتكون البكتريا متواجدة في الممرات التنفسية قبل تكوين الـ IgM وانخفضت أعدادها بعد تكونه وقد تبقى لعدة أسابيع.

أوضح [37] أن طريقة الـ ELISA أفضل طرائق التشخيص المصلي لأفراد *Mycoplasma pneumoniae* وتكون أكثر حساسية من الزرع وتمتلك نسبة حساسية (92%)

وخصوصية (95%) وأضاف أنها من الممكن أن تساوي حساسية الـ PCR إذا مضى الوقت المناسب لتكون الـ IgM أو IgG واعتمادا على سلامة الجهاز المناعي للمريض.

تعد الطرائق المصلية من أفضل الطرائق في تشخيص أفراد النوع *Mycoplasma pneumoniae* وتشخص نسباً أعلى مما تشخصه الطرائق الزراعية وأن السبب في انخفاض نسبتها في دراستنا قد يعود لتحطم الـ IgM في المصل بسبب ظروف الخزن والنقل مع العلم أننا استلمنا عدة التشخيص الحديثة الإنتاج والمدة ونقلت قدر الأماكن تحت الظروف المثلى.

تشخص الطرائق المصلية (60%) من إصابات *Mycoplasma pneumoniae* السريرية وتشمل عدة فحوصات منها التجلط البارد Cold agglutinin وتثبيت المتمم Complement Fixation و Enzyme Immuno assay وتعتبر الأخيرة من أفضلها وهي المستخدمة حالياً في تشخيص *Mycoplasma pneumoniae* [37-43].

علاقة *Mycoplasma pneumoniae* بفرط التحسس

يوضح الجدول (8) أن 15 فرداً أي (16.67%) من (90) من المستجيبين لاختبار الجلد كانت لديهم إصابة فعالة بـ *Mycoplasma pneumoniae* وأن (40%) منهم مصابون بالربو أو حساسية القصبات الهوائية.

درست العلاقة بين الربو وإصابات *Mycoplasma pneumoniae* من قبل العديد من الباحثين وأوضح [39] أن (32%) من مرضى الربو المزمن مصابون بها ، أكد [4] أن هذه البكتريا يمكن أن تعمل كمحسسات أو عوامل تزيد من حدة أعراض الربو في الأطفال والبالغين وأضاف Gross وآخرون سنة 2010 أن (40%) من مرضى الربو المزمن لديهم إصابات فعالة بها وببكتريا *Chlamydia pneumoniae* والتي أدت إلى تفاقم أعراض الربو.

جدول 8: النسب المئوية لاكتساب أفراد النوع *Mycoplasma pneumoniae* من المستجيبين

لاختبار الجلد حسب خصائصهم العامة

الخصائص العامة للمستجيبين لاختبار الجلد		العدد الكلي	
الجنس	المسكن	العدد	(%)
		العدد	(%)
أنثى	ريف	9	60
ذكر	مدينة	6	40
		12	80
		3	20

علاقة *Mycoplasma pneumoniae* بالحساسية في مدينة الموصل : العراق

باسمة ويونس

33.34	5	موظف	المهنة
66.66	10	غير موظف	
-	-	مدخن	التدخين
100	15	غير مدخن	
53.33	8	وجوده	التاريخ العائلي
46.67	7	عدم وجوده	
40	6	مصاب	الإصابة بالربو
60	9	غير مصاب	

أوضحت نتائج الجدول (8) أن (60%) من المستجيبين لاختبار الجلد والمكتسبين لـ *Mycoplasma pneumoniae* كانوا من الإناث وكانت نسبة الذكور (40%)، كما لوحظ أن (80%) من المستجيبين لاختبار الجلد والمكتسبين لجرثومة *Mycoplasma pneumoniae* كانوا من سكان المدينة، وأوضحت النتائج كما مبين في الجدول (8) أن (66.66%) من المستجيبين للاختبار والمكتسبين لجرثومة *Mycoplasma pneumoniae* كانوا من غير الموظفين بينما كانت نسبة الموظفين (33.34%) وأوضحت نتائج الجدول أيضا أن (53.33%) المستجيبين لاختبار الجلد والمكتسبين لهذه الجرثومة لديهم تاريخ عائلي مع أمراض الحساسية.

إن الإناث أكثر عرضة للإصابة بالحساسية كما أوضحنا سابقا لأنهن أكثر بقاءً في المنزل الذي يشكل مجتمعا صغيراً مغلقاً كما أنهن أكثر تعاملًا مع الأطفال والذين هم أكثر عرضة للإصابة بهذه البكتيريا ويمكن انتقالها منهم إلى أمهاتهم، وهذه الأسباب ربما أدت إلى ارتفاع نسبة الإصابة بهذه البكتيريا وزيادة التحسس في الإناث.

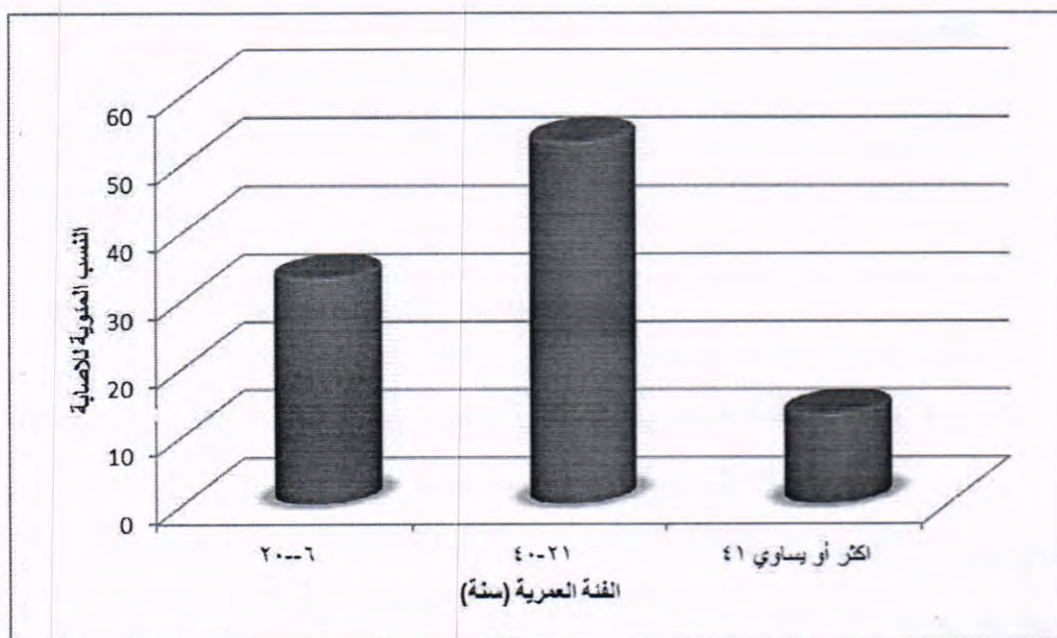
أوضح [40] أن هذه البكتيريا تصيب الذكور والإناث ولا يوجد فرق معنوي بين الجنسين وأكد ذلك [38] أيضاً.

أوضحنا سابقا أن سكان المدينة أكثر عرضة للإصابة بالحساسية الآنية بسبب الظروف البيئية و المحسسات في الموصل، إن ارتفاع نسبة السكان في المدينة إضافة إلى الازدحامات في الشوارع والأسواق التي تسهل من انتشار هذه البكتيريا قد يكون السبب وراء ارتفاع نسبة الإصابة بهذه البكتيريا بين سكان المدينة إذ تنتقل هذه الجراثيم عن طريق التلامس المباشر مع الشخص المصاب أو إفرازاته التنفسية المتطايرة مع العطاس والسعال وتنتشر بسرعة في المناطق المغلقة والمزدحمة وتترافق مع

إصابات الجهاز التنفسي بالفيروسات والبكتريا الأخرى كما أنها معروفة بتسببها لذات الرئة المكتسبة من المجتمع Community acquired pneumonia كما أكد ذلك كلٌّ من [9-42-41].
لم تسجل أية حالة إصابة بهذه البكتريا لدى المدخنين من المستجيبين لاختبار الجلد وقد يعود السبب إلى المعلومات الخاطئة التي أدلى بها المرضى تبعاً للظروف الاجتماعية ومستوى الوعي العلمي والثقافي.

يتميز المرضى الذين لديهم تاريخ عائلي مع أمراض الحساسية الأنفية بميل وراثي لإنتاج الكلوبولين المناعي IgE عند التعرض للمحسسات البيئية وأن إصابة هؤلاء بهذه البكتريا يؤدي إلى زيادة حدة أعراض الربو وحساسية الأنف والقصبات الهوائية إذ قد يتكون IgE خاص بهذه البكتريا وأكد [43] أن الإصابة بهذه البكتريا لدى الأشخاص المصابين بالربو والذين لديهم تاريخ عائلي أدت إلى زيادة حدة الربو لديهم مقارنة مع غير المصابين بالربو.

يوضح الشكل (7) النسب المئوية للمستجيبين لاختبار الجلد والمكتسبين لبكتريا *Mycoplasma pneumoniae* حسب الفئات العمرية قيد الدراسة ولوحظ أن أكثر نسبة للإصابة كانت عند الفئة العمرية (21-40 سنة) تلتها الفئة العمرية (6-20 سنة) ثم الفئة (أكبر أو يساوي 41 سنة).



شكل 7: النسب المئوية لاكتساب أفراد النوع *M.pneumoniae* لدى المستجيبين لاختبار الجلد حسب العمر

باسمة ويونس

دُرست العلاقة بين العمر والإصابة بهذه البكتريا وأوضح العديد من الباحثين أن هذه البكتريا تصيب جميع الأعمار على حد سواء في المجتمعات الحساسة وتكون أكثر إصابة لدى الأطفال في سن المدرسة بسبب التلامس المباشر ما بين المصابين وغير المصابين كما أنها تنتشر في المعسكرات والمستشفيات والمناطق أو المجتمعات المغلقة نتيجة لتدني الظروف الصحية كما لوحظ أن أعلى نسبة إصابة كانت عند الفئات العمرية (2-5) سنة و (7-12) سنة وتختلف هذه النسبة باختلاف الدراسات وطرائق التشخيص والمنطقة الجغرافية والمجتمع قيد الدراسة [44-45].

بلغ المعدل الهندسي للـ IgE الكلي للمستجيبين لاختبار الجلد والمكتسبين لجراثومة *Mycoplasma pneumoniae* (149.28 ± 203.41) وحدة دولية/سم³ بينما كان المعدل الهندسي للـ IgE الكلي لدى غير المصابين بها (137.70 ± 100.15) وحدة دولية/سم³ مع وجود فرق معنوي عند مستوى احتمالية (0.05) كما موضح في الجدول (4-13).

جدول 9: المعدل والمعدل الهندسي لتركيز الكلوبولين المناعي الكلي Total IgE (وحدة

دولية/سم³) لدى المستجيبين لاختبار الجلد من المكتسبين لأفراد

Mycoplasma pneumoniae وغير المكتسبين لها

التركيز وحدة دولية/سم ³	المصابين بالحساسية و بكتريا <i>M.pneumoniae</i>	المصابين بالحساسية فقط
المعدل	*235.16	146.57
المعدل الهندسي	203.41	100.15
الانحراف المعياري	$149.28 \pm$	$137.70 \pm$

* فرق معنوي عند مستوى احتمالية ($P \leq 0.05$)

أكد [3] أن هذه البكتريا من الممكن أن تشترك في الآلية الممرضة للربو في مراحل مختلفة وذلك عن طريق تفاعلها مع عدة عناصر مختلفة في الرئة مثل الخلايا البدينة و الحمضات في مرضى الربو المتماحل وتحفز هذه الخلايا ويترحرر منها Serotonin ومتوسطات أخرى تؤدي إلى ارتفاع مستوى الكلوبولين المناعي الكلي Total IgE وقد يتكون IgE نوعي خاص بها أي تعمل كمحسس كما يرتفع مستوى TNF α ، IL-4، IL-5 وهذا بدوره يعزز من إنتاج IgE ويزيد من حدة أعراض الربو، كما أنها تحفز عملية إعادة بناء القصبات الهوائية Airway Remodeling التي تعتبر إحدى مميزات الربو وتحفز الخلايا الطلائية على إفراز IL-8 وأضاف [46] أن أفراد النوع

Mycoplasma pneumoniae تلتصق على أهداب الخلايا الطلائية للرئتين وتعطل وظائفها وتزيد من إفراز المخاط وتضييق القصبات الهوائية ولاحظ [47] أنها زادت من تعبير IL-6 ومستقبلات TLR-2 مما أدى إلى زيادة حدة أعراض الربو كما أنها زادت من تعبير الجين المشفر للبروتين MUC5AC.

أوضح [37] أن إصابة القصبات الهوائية لمرضى الربو ببكتريا *Mycoplasma pneumoniae* عملية معقدة ومتعددة العوامل وتعتمد على تفاعل معقد معين بين الحساسية الآتية والإصابة بهذه البكتريا إذ تؤدي الإصابة بها لدى الأشخاص المتماحلين إلى تحفيز استجابة خلايا Th-2 في القصبات الهوائية وبالنتيجة تزيد من حدة أعراض الربو ويتكون IgE خاص بهذه البكتريا.

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