

Kinetic and Thermodynamic Studies of Biosynthesis of Silver Oxide Nanoparticles

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ABSTRACT

The present study was carried out by the formation of silver oxide nanoparticles (Ag₂O NPs) using a plant extract from the seeds of *Coriandrum sativum* for the biosynthesis of Ag₂O NPs from silver nitrate solution. Data was characterized using Fourier transform infrared radiation FTIR, X-ray diffraction XRD, atomic force microscopy (AFM), and scanning electron microscopy (SEM). Results indicated a successful creation of nanoparticles of Ag₂O. FTIR spectra showed a band around (501.49 cm⁻¹), corresponding to the double bond of oxygen of Ag₂O and XRD pattern identified the appearance of Ag₂O nanoparticles, where six strong peaks were observed at 2θ (32, 38, 46, 56, 65 and 75°) related to Ag₂O compared with the reference [11], and that indicated to the formation of these particles. Images of AFM showed Ag₂O NPs with an average diameter of (57.31 nm) and SEM indicated a distribution of cubic shape of Ag₂O NPs. In addition, the order of reaction was pseudo-first-order. The value of activation energy, enthalpy, the change in entropy and Gibbs free energy has calculated. The value of activation energy was (+1.37 J/mol), the value of enthalpy (-1.371 J/mol), the negative value of enthalpy was heat emission. The value of entropy was (+56.53 J/mol) and the value of Gibbs free energy was (-3.957 J/mol). In this study, silver oxide nanoparticles were prepared by the bio-synthesis method. The diameter of this particles was (57.31) nm. The kinetics and thermodynamic of this reaction were studied and proved by a chemical equation.

KEYWORDS: *coriandrum sativum*, silver oxide nanoparticles, FTIR.

الخلاصة

تضمنت الدراسة الحالية تكوين الجزيئات النانوية لأكسيد الفضة (Ag₂O NPs) باستخدام مستخلصات نباتية من بذور الكزبرة (*coriandrum sativum*) للتخليق البايولوجي من محلول نترات الفضة. تم تشخيص الجزيئات النانوية الناتجة بتقنية مطياف الأشعة تحت الحمراء (FTIR)، وجهاز حيود الأشعة XRD، مجهر القوة الذرية (AFM)، المسح المجهر الإلكتروني (SEM). بينت النتائج ان عملية تخليق الجزيئات النانوية كانت ناجحة. أذ أظهرت أطياف الأشعة تحت الحمراء قمم في المنطقة (501.49 سم⁻¹) المقابلة للرابطة المزدوجة للأكسجين دليل على تكون جزيئات أكسيد الفضة النانوي، وتبينت هوية أكسيد الفضة النانوي بجهاز حيود الأشعة (XRD) بظهور ستة قمم قوية عند 2θ (32, 38, 46, 56, 65 and 75°) والتي تمثل أكسيد الفضة النانوي بالمقارنة مع المصدر (11) والذي يؤكد تكون هذه الجزيئات. أظهر مجهر القوة الذرية (AFM) أشكال أكسيد الفضة النانوي بمعدل نصف قطر (57.31 نانومتر)، كما أشارت صور المسح المجهر الإلكتروني (SEM) شكل المكعب لأكسيد الفضة النانوي. بينت النتائج أيضا ان مرتبة التفاعل هي المرتبة الأولى الكاذبة، وتم حساب قيمة طاقة التنشيط، الانثالبي والتغير في الانتروبيا. وطاقة جيبس الحرة، وكانت قيمة حساب طاقة التنشيط (+1.37 J/mol) وقيمة الانثالبي السالبة (-1.37 J/mol) تدل على ان التفاعل باعثا للحرارة، اما قيمة الانتروبيا فكانت (+56.53 J/mol) وقيمة طاقة جيبس الحرة تساوي (-3.957 J/mol). في هذه الدراسة تم تحضير جزيئات الفضة النانوية بطريقة التخليق البايولوجي. نصف قطر هذه الجزيئات (57.31 nm). ومن ثم تم دراسة الحركية والثرموديناميكية لهذا التفاعل واثبتت حسابيا بواسطة معادلات كيميائية.

INTRODUCTION

Nanotechnology operates with nanometer sized matter (1-100 nm) and can therefore be used for a wide range of applications and for the development of various types of nano materials

and nano devices. It is also inevitable that due to their small size, these materials should have different properties such as chemical reactivity and electrical conductance, magnetism, optical effects and physical strength [1].

There are a wide range of nanomaterial synthesis techniques available through which we can manufacture nanomaterials in the form of colloids, clusters, powders, tubes, rods, wires, thin films, etc. [2].

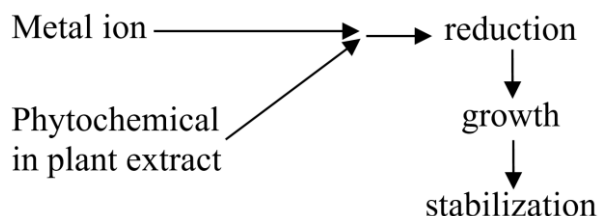
Nanoparticles are under rapid growth in recent times due to their greener route and easier formation of nanoparticles. Recently, they have improved significantly over bulk metal, A great deal of interest has been found in the synthesis of nanoparticles by green methods. Such nanoparticles are gradually being introduced into consumer products [3].

In 1991, in a special program developed by the U.S., Anastas first coined the word "green chemistry." Environmental Protection Agency (EPA) to encourage major chemical and technological growth [4].

Biosynthesis of silver nanoparticles (AgNPs) from plant extract and silver nitrate solution is costing less and eco-friendly. This reaction includes a bio reduction of the Ag ion to AgNPs as a phytochemical compound in the plant extract. Terpenoid, flavones, ketone, aldehyde, amid and carboxylic acid are the primary phytochemical involved [5].

Plants appear to be the best candidates among these organisms are suitable for large scale nanoparticles biosynthesis. Plant produced nanoparticles are more stable and the synthesis rate is faster than for microorganisms [6]. The advantages of using plant and plant-derived materials for metal nanoparticles biosynthesis have interested researchers in investigating mechanisms of plant-based metal ion uptake and bio-reduction and in understanding the possible mechanisms of metal nanoparticles formation in plants [6].

It is possible to divide the preparation of plant-mediated green nanoparticles into three levels: activation phase, growth step, and termination phase. The main stage is the activation phase in which metal ions are retrieved from their salt precursors through the action of plant metabolites.; Biomolecules can be reduced. Therefore, the metal ions are altered from their mono- or divalent oxidation states to zero-valent states and the nucleation of the reduced metal atoms takes place [7].



Scheme 1. Bio-synthesis mechanism.

The nanostructure, such as nanoparticles or nanocrystal must be capped to make a functional and stable biocompatible aggregation in the biological system [8].

Capping agent is a biological or chemical component that naturally restricts the nanoparticles synthesis reaction and particle development [9].

Because of the tiny size of nanoparticle, they tend to have a great surface compared to the bulk material, which can lead to instability and require a capping agent to help stabilize the structure [8].

Silver nanoparticles are the most widely used nanoparticles in wound dressings, antimicrobial coatings, anti-cancer chemotherapy and cosmetics, with unique physical, chemical and biological properties [9].

Silver oxide is a semi-conductive p-type with a 1.2eV. The oxygen vacancies appear to play a dominant position in the silver oxide conductive system [10].

EXPERIMENTAL

Preparation of Plant Extract from the Seed of (*Coiandrum Sativum*)

The extract was prepared by weighting (0.4g) of the seeds (*Coiandrum Sativum*), washing with distilled water to clear impurities. Then, 200mL of distilled water was added to the seeds, heated with stirring up to 70 °C, and centrifuged for 10 minutes. The supernatant was then filtered twice and stored at 4 °C, for further use.

Bio-Synthesis of Silver Oxide Nanoparticles

Silver nitrate (0.6 g) was dissolved in 150mL of distilled water. To prepare a sample of silver ion solution from the seed of (*Coiandrum Sativum*), (0.4g) was dissolved in 200 mL of distilled water. Ag₂O NPs were prepared at a temperature about 70 °C and the required time

was about 25 minutes. The color of the reaction mixture was changed every 5 minutes from yellow to dark brown which indicated the formation of silver oxide nanoparticles.



Figure 1. The color change of the Ag₂ONPs solution.

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Figure 2. Formation of Ag₂ONPs due to change in the color to dark brown..

RESULTS AND DISCUSSION

UV-Visible analysis

The spectra of UV –visible were used to determine the maximum absorption of Ag₂O NPs. Figure 3 shows that the maximum absorbance was around 437 nm, which indicated the Plasmon resonance (SPR) of Ag₂O NPs.

FTIR Analysis

The FTIR technique was used to determine the functional groups exist and responsible for forming Ag₂O NPs. Several peaks were appeared in the region 3429, 2962, 1786, 1635, 1122 and 501 cm⁻¹. The absorbance of 3429 cm⁻¹ referred to OH broad bands, 2962 cm⁻¹ referred to the presence of CH₃, CH₂ and CH.

The peak at 1786 cm⁻¹ referred to the presence of carboxylic acids and derivatives of (C=O) and the peak in 1635cm⁻¹ referred to C=C, the peak in 1122 cm⁻¹ referred to O-C (2-bands) of carboxylic acids and derivative.

A spectrum of around 501.49 cm⁻¹ was corresponding to the double bond of oxygen of Ag₂O NPs. These results could be an evidence of successful creation of Ag₂O NPs.

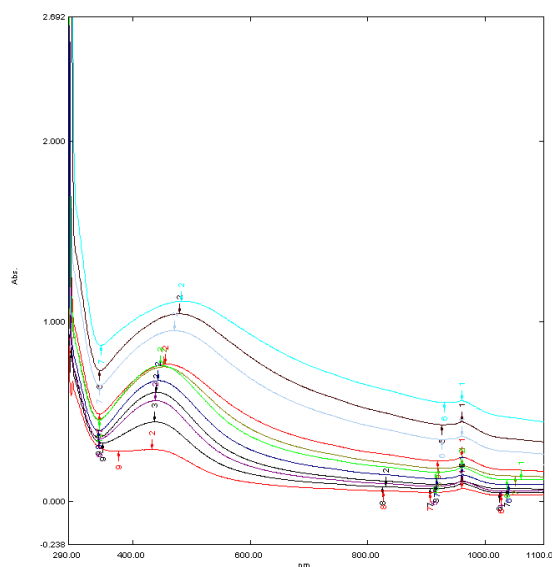


Figure 3. UV-Vis spectra of Ag₂O NPs.

X-Ray Diffraction (XRD)

The XRD technique was used to determine the structure of Ag₂O NPs.

Structural and shape identification of Ag₂O nanoparticles were measured with X-ray diffraction in the range of angle 2θ between 20° to 80°. The X-ray pattern confirmed the appearance of six strong peaks at 2θ (32,38, 46, 56, 65 and 75°), as which compared with the article [11] were related to Ag₂O Nps formation.

Atomic Force Microscopy (AFM)

Biosynthesis of Ag₂O NPs was also characterized using AFM. Figure 5 shows the surface structure of Ag₂O NPs and Figure 6 shows the statistical analysis of the diameter. The average diameter of the nanoparticles was (57.31nm), which could indicate the presence of Ag₂O NPs.

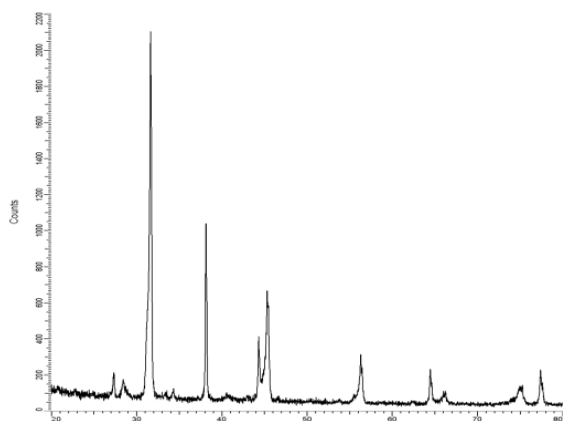


Figure 4. The XRD analysis of Ag₂O NPs.

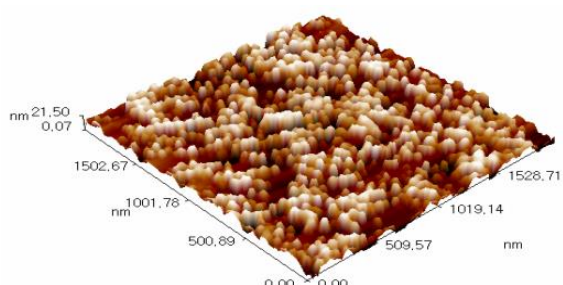


Figure 5. The topographic image of the surface of Ag₂O NPs using AFM.

Scanning Electron Microscopy (SEM)

The average particle size and the shape of Ag₂O NPs was determined and analyzed using (SEM), which indicated a distribution of cubic shape of nanoparticles shown in Figure 7.

Energy Dispersive X-ray Analysis (EDX)

The EDX was used to indicate the elements that present in the sample.

Figure 8 shows the ratio of silver to oxygen molecular Ag₂O NPs, which was (2:1).

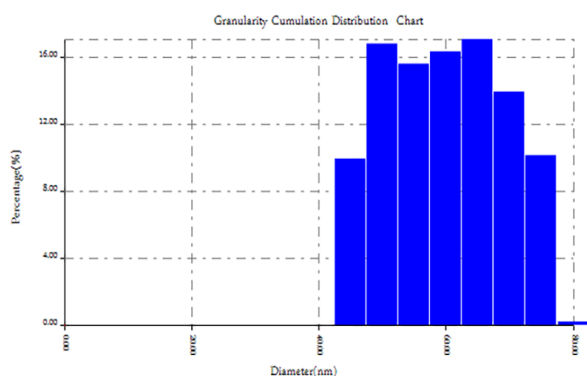


Figure 6. The statistical analysis of Ag₂O NPs using

AFM.

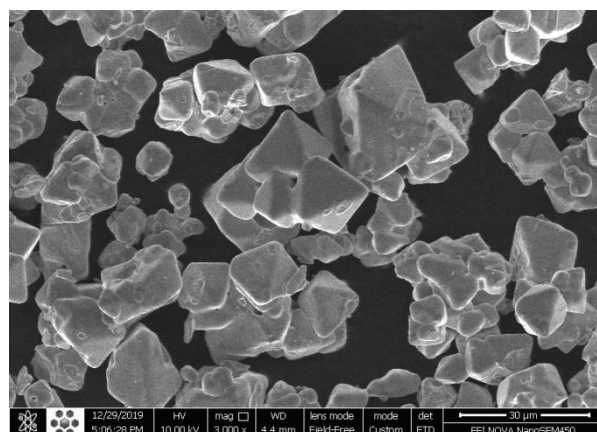


Figure 7. SEM image of Ag₂O NPs

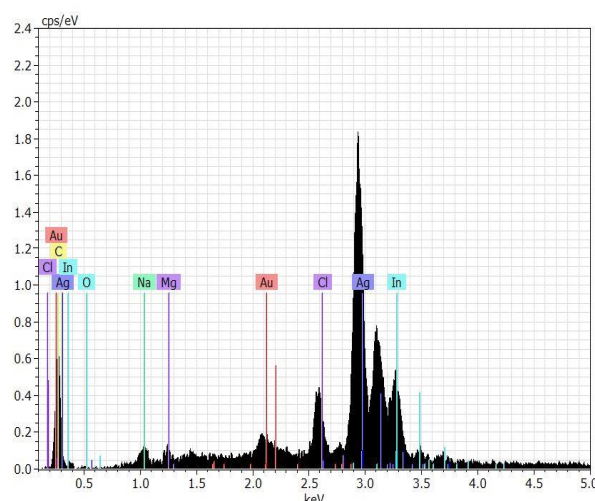


Figure 8. The EDX analysis of Ag₂O NPs, where the molecular ratio of silver: oxygen was 2:1.

The Kinetics of the Bio-Synthesis Reaction of Ag₂O NPs

The order of the reaction

This study implied the order of reaction, which was preside first order. and that was proved by Trail method.

Table 1 shows the concentration of Ag₂O NPs and the time of formation.

Table 1. The concentration of Ag₂O NPs and the required time.

[Ag ₂ O]	Time (min)
0	0
0.011	10
0.022	15
0.032	20
0.042	25

Figure 9 illustrates the relationship between the concentration and the time of reaction of Ag_2O NPs.

Synthesis of Ag_2O under different temperatures.

In this study, Ag_2O was bio-synthesized under different temperatures to provide the best quantity and properties of NPs. Table 2 and Figure 10 shows the concentration of Ag_2O produced under the corresponding temperature (60-90 °C). Tables 3-6 and Figures 11-14 show the concentration of Ag_2O produced under 60, 70, 80 and 90 °C, respectively.

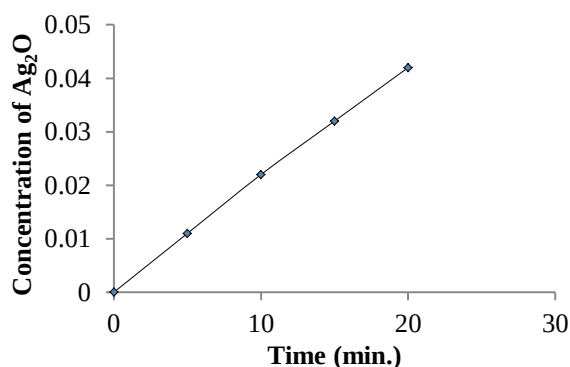


Figure 9. The relationship between concentration and time of reaction.

Studies in all temperatures

Table 2. The concentration Ag_2O under the corresponding temperature used for synthesis.

Concentration (%)	Temperature (°C)
0.041	60
0.057	70
0.032	80
0.026	90

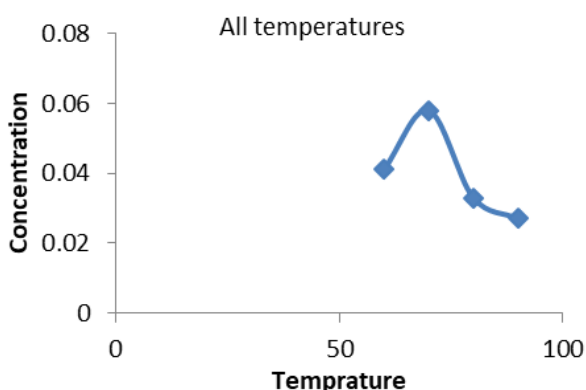


Figure 10. The synthesis Ag_2O in all temperatures.

Synthesis under 60 °C

Table 3 and Figure 11 show the concentration of the synthesized Ag_2O under 60 °C.

Table 3. The synthesis of Ag_2O under 60°C.

Time (min)	Concentration (%)
0	0
5	0.018
10	0.031
15	0.041
20	0.047

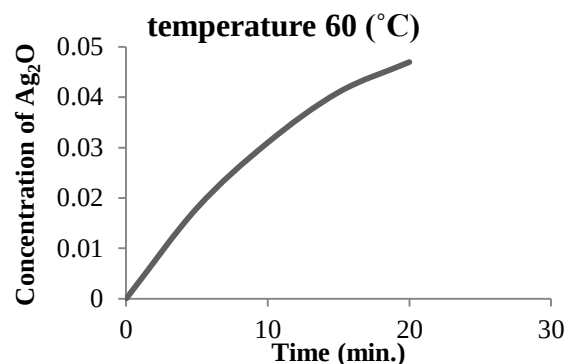


Figure 11. The synthesis of Ag_2O under 60 °C.

Synthesis under 70 °C

Table 4 and Figure 12 show the concentration of the synthesized Ag_2O under 70°C.

Table 4. The synthesis of Ag_2O under 70 °C.

Time (min)	concentration
0	0
5	0.013
10	0.043
15	0.046

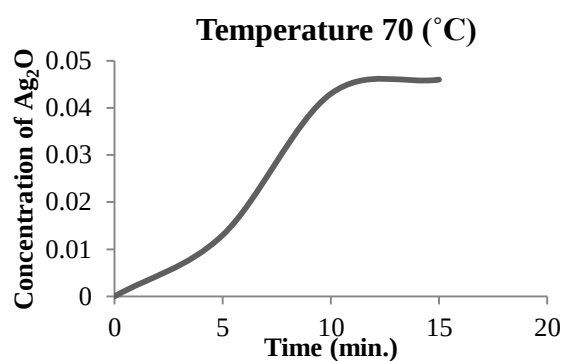


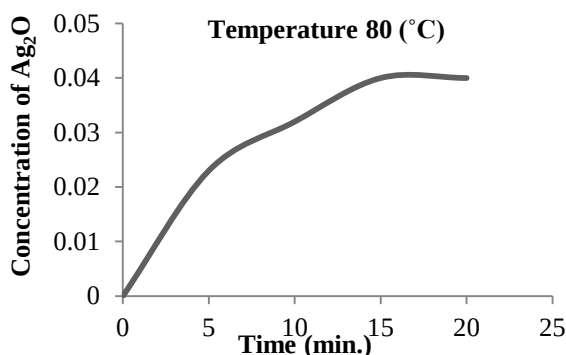
Figure 12. The synthesis Ag_2O under 70 °C.

Synthesis under 80 °C

Table 5 and Figure 13 show the concentration of the synthesized Ag_2O under 80 °C.

Table 5. The synthesis of Ag₂O under 80 °C.

Time (min)	concentration
0	0
5	0.023
10	0.032
15	0.036
20	0.04
25	0.04

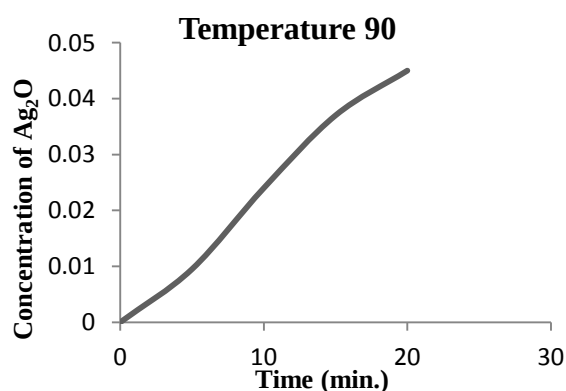
**Figure 13.** The synthesis Ag₂O under 80 °C.

Synthesis under 90 °C

Table 6 and Figure 14 showed the concentration of the synthesized Ag₂O under 90 °C.

Table 6. The synthesis of Ag₂O under 90 °C.

Time (min)	Concentration
0	0
5	0.0095
10	0.024
15	0.037
20	0.045

**Figure 14.** The synthesis of Ag₂O under 90 °C.

These results indicated that the optimum temperature was 70°C due to the highest absorption value. The continuous changing in the concentration of silver oxide nanoparticle

was based on the value of absorbance in each temperature were be used and which be recorded by uv_visible .

Calculations methods of activation energy, entropy, enthalpy and Gipp's free energy for Ag₂O NPs.

The K (rate constant) was calculated from the slope of each temperature used, as shown in Table 7.

Table 7. The slope, the constant rate and lnk-1/T related to the temperature used for synthesis.

Temperature	Slope	k	lnk	1/T
60 °C	277.77	277.77	5.62	0.016
70 °C	384.6	384.6	5.95	0.014
80 °C	555.55	555.55	6.31	0.0125
90 °C	625	625	6.43	0.011

The slope was calculated according to the equation:

$$\text{Slope} = \frac{y_2 - y_1}{x_2 - x_1} \quad \text{Slope} = -165$$

This value of the slope was used to calculate the activation energy as follows:

$$\text{Slope} = \frac{-E_a}{R}$$

Where, R value was 8.314 j/mol and the activation energy was +1.37 j/mol.

The entropy ΔS was calculated from the intercept of the curve between lnk and 1/T as follows:

$$\text{Intercept} = \frac{\text{change in entropy}}{R}$$

The value of ΔS was +56.53 j/mol. The enthalpy value ΔH was calculated as follows:

$$\text{Slope} = \frac{\text{change in enthalpy}}{R}$$

The value of ΔH was -1.371 j/mol, which indicated a heat emission reaction. The Gipp's free energy ΔG was calculated as following:

$$\Delta G = \Delta H - T * \Delta S$$

$$\Delta G = -1.371 - 70 * 56.53 = -3.957 \text{ J/mol}$$

The relationship between Gibbs free energy and the value of enthalpy and the entropy indicates that reaction was spontaneous in all temperatures.

CONCLUSIONS

Silver oxide nanoparticles have prepared from the extract of (*Coriandrum Sativum*) seeds using biosynthesis reaction. These nanoparticles had a diameter of 57.31 nm and randomly aggregated with unspecific shape, as indicated by AFM and SEM images. The thermodynamic and kinetics of the synthesis of silver oxide nanoparticles have studied under four temperatures (60, 70, 80 and 90 °C).

Silver oxide reaction order was reached and recorded as pseudo first order, by trial method and according to the concentration for both metal salt and plant extract.

Activation energy, enthalpy, entropy and Gibbs free energy were calculated, which proved that the reaction was heat emission.

REFERENCE

- [1] A. P. Nikalje, "Nanotechnology and its Applications in Medicine," vol. 5, pp. 1–3, 2015.
- [2] K. Murugesan, P. Sivakumar, and P. N. Palanisamy, "An Overview on synthesis of metal oxide nanoparticles," vol. 2, no. 14, pp. 58–66, 2016.
- [3] Annu, A. Ali, and S. Ahmed, *Green synthesis of metal, metal oxide nanoparticles, and their various applications*, vol. 4, 2019.
- [4] S. Verma, S. Goyal, and S. Singla, "International Journal of Biotechnology and Bioengineering Green Chemistry: A New Approach to The Synthesis, Processing and Application of Chemical Substances," *Int. J. Biotechnol. Bioeng.*, vol. 4, no. 4, pp. 89–95, 2018.
- [5] N. M. Muchanyereyi *et al.*, "Green Synthesis of Silver Nanoparticles Using Euphorbia Confinalis Stem Extract, Characterization and Evaluation of Antimicrobial Activity," *J. Nanomater. Mol. Nanotechnol.*, vol. 06, no. 03, 2017.
- [6] S. Iravani, "Green synthesis of metal nanoparticles using plants," *Green Chem.*, vol. 13, no. 10, pp. 2638–2650, 2011.
- [7] R. Chokkareddy and G. G. Redhi, "Green synthesis of metal nanoparticles and its reaction mechanisms," *Macabresque Hum. Viol. Hate Genocide, Mass Atrocity Enemy-Making*, no. November, pp. 113–139, 2018.
- [8] V. Vadlapudi, "Novel Capping Agents for Nanomaterials," *Eur. J. Appl. Sci.*, vol. 7, no. 6, pp. 297–301, 2015.
- [9] M. Velu *et al.*, "Production, optimization and characterization of silver oxide nanoparticles using Artocarpus heterophyllus rind extract and their antifungal activity," *African J. Biotechnol.*, vol. 16, no. 36, pp. 1819–1825, 2017.
- [10] U. K. Barik and A. Subrahmanyam, "Electrical and Optical Properties of Silver Oxide (Ag₂O) Thin Films Prepared by Reactive Electron Beam Evaporation Electrical and Optical Properties of Silver Oxide (Ag₂O) Thin Films Prepared by Reactive Electron Beam Evaporation," no. April, pp. 2–6, 2015.
- [11] E. E. Elemike, D. C. Onwudiwe, A. C. Ekennia, C. U. Sonde, and R. C. Ehiri, "Green synthesis of Ag/Ag₂O nanoparticles using aqueous leaf extract of Eupatorium odoratum and its antimicrobial and mosquito larvicidal activities," *Molecules*, vol. 22, no. 5, pp. 1–15, 2017.