

Research Article

# Equilibrium and Kinetics Studies of Gentian Violet Dye Adsorption on to Activated Carbon Prepared From Aldhnan Hull

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## Abstract

The present study investigated the key parameters and mechanism affecting the removal of Gentian Violet (GV) dye from aqueous medium, using Activated Carbon (AC) produced from hull of Aldhnan. The AC characterized by FTIR spectra to indicate the surface Characteristic groups of adsorbent affect the adsorption. The pH at point of zero charge showed the anionic nature of adsorbent surface and by using batch mode, the study considering the typical condition for adsorption of GV dye by the AC such as; effect of initial dye concentration, pH and contact time. The adsorption kinetics and equilibrium constants was achieved at 305K and the Langmuir isotherm model fit for the equilibrium data better than Freundlich model. Kinetics of adsorption was studied by testing the data in the pseudo first order (Lagergren Equation) and pseudo second order model and the adsorption of GV dye onto AC obeyed pseudo second order model. Thermodynamic studies exhibit that the adsorption reaction is endothermic in nature and spontaneous.

**Keywords:** kinetics, equilibrium, Adsorption, Aldhnan hull.

## الخلاصة

تم دراسة ميكانيكية امتزاز صبغة الجنتيان البنفسجي على الكربون المنشط المحضر من قشور بذور الدهنان عند درجة حرارة 305 كلفن بطريقة الوجبة. المادة المازة شخصت من خلال قياس طيف الأشعة تحت الحمراء والدالة الحامضية عند الشحنة صفر. كما وتم دراسة تأثير كل من الدالة الحامضية، زمن التماس و التركيز الابتدائي للمادة الممتزة للوصول الى الظروف المثلى للامتزاز. تم اختبار القياسات عند الاتزان باستخدام معادلة لانكماير و فروندليج و اظهرت النتائج انطباقا مع معادلة لانكماير اما القياسات الحركية فقد اختبرت بمعادلة المرتبة الاولى الكاذبة، المرتبة الثانية الكاذبة و اظهرت ان تفاعل الامتزاز من المرتبة الثانية الكاذبة. المتغيرات الترمودينمكية مثل الطاقة الحرة، الانتالبي والانتروبي اظهرت ان التفاعل تلقائي و ماص للحرارة.

## Introduction

The dyes are organic compounds having complex structures, which make them stable to light, oxidation, and resistant to degradation [1]. The wide use of dyes in the food, paper, cosmetic, textile, plastic, and pharmaceutical industries leads to increase the concentration of dyes in wastewater and reduce light penetration which affect photosynthetic activity in aquatic life. Moreover, The toxic and carcinogenic nature for most of the dyes [2]. Therefore, there is great deal of research to find efficient and cost-effective technologies for removing dyes from wastewater. The conventional methods for

removal of dyes from industries effluent are coagulation, filtration, floatation, ion exchange, chemical oxidation, photo degradation, solvent extraction and membrane separation etc. These methods have some drawback such as high cost, operating required sensitive conditions, and less efficiency [3]. The powerful technology started in last decades is adsorption of dyes by activated carbon and it is widely used to remove dyes and other pollutants from wastewater. Due to the commercially available activated carbon is costly special attention take place to prepare activated carbon from agriculture by-products [4].



This study tend to estimate the efficiency of activated carbon prepare from Aldhnan hull for adsorption of Gentian violet dye. Aldhnan is one of the wild grass normally grows with rice paddy, Alfalfa field and along with other summer plant that is requires humid in Iraq.

## Materials and Methods

### Gentian Violet

Gentian violet was supplied by CDH New Delhi, used directly without purification. 0.5 gram of dye is dissolved in (1 liter) of double distilled water to prepared stock solution and diluting to different concentration. The IUPAC name of the dye is Tris(4-(dimethylamino)phenyl) methylum chloride and  $\lambda_{\max}$ =590nm.

### Adsorbent Preparation & Characterization

The hull of Aldhnan was washed several times by distilled water, dried at (378K) for 24h, crushed and grinded to small particle by food processor. The powdered hull then impregnated with concentrated  $H_2SO_4$  (1:1 weight to volume) washed with distilled water until the filtrate reached a sTable pH of 6-7. The sample were Heated at 633K in microwave oven for half an hour and then cooling to room temperature. The prepared activated carbon was grinded, sieved and dried at (378K) for 24hours, and kept for further studies. The AC characterized by FTIR and pH at zero point charge ( $pH_{pzc}$ ) was determined by batch method. Initial pH of 25ml (0.1M)  $KNO_3$  adjusted in pH range from 2 to 8 by using 0.1M NaOH and HCl. Then, same amount of AC 0.1g added to each solution. Shake in thermo-stated magnetic shaker for 3hours at 305 K. The final pH determined after filtering the dispersions and point of zero charge calculated from plot of ( $pH_i - pH_f$ ) against  $pH_i$  [5].

### Adsorption Isotherm

The adsorption isotherm for GV dye solutions were performed in eight glass-stopper 250ml where volume of solution was 50ml with concentration ranged from 20 to 160mg/L, 0.1g of AC added for each solution and left in isothermal shaker for 120 min at 305K and pH 8. The final concentration at equilibrium determined after centrifuged at 590nm and the removal efficiency calculated by the following Equation [6]:

$$\% \text{Removal} = \frac{C_o - C_e}{C_o} 100 \% \quad (1)$$

Where  $C_o$ (mg/L) and  $C_e$ (mg/L) are initial concentration and equilibrium concentration, respectively.

The amount of GV dye adsorbed on one gram of AC at time t is  $q_t$ (mg/g) and at equilibrium  $q_e$ (mg/g) was represented by following Equations [7]:

$$q_t = \frac{C_o - C_t}{M} \times V \quad (2)$$

$$q_e = \frac{C_o - C_e}{M} \times V \quad (3)$$

Where  $C_t$  (mg/L) the dye concentration at time t and  $C_o$ (mg/L),  $C_e$ (mg/L) are beginning concentration and equilibrium concentration respectively. M (g) is the mass of AC used, and V(L) volume of dye solution.

## Results and Discussion

### Characterization of Adsorbent

The FTIR spectrum of AC prepared from Aldhnan hull before and after adsorption of GV dye (Figure 1), shows the bands related to the functional groups present on AC and listed in Table 1. The most abundant and responsible functional groups suggest to adsorb GV dye are N-H amine, C-H aromatic, O-H carboxylic acid, C=O carbonyl and C-N aromatic amine. Figure 2 shows  $pH_{pzc}$  of AC prepared from Aldhnan hull, it was 4. The measurement indicated that the adsorption of cationic dye suiTable at pH above point of zero charge. The adsorption of anion will be more suitable below  $pH_{pzc}$  [9]. This investigate that GV is (cationic dye) adsorption more favorable at pH greater than 4 that is due to the strong electrostatic attraction between positive charge of dye molecule and negative charge of AC surface [10].

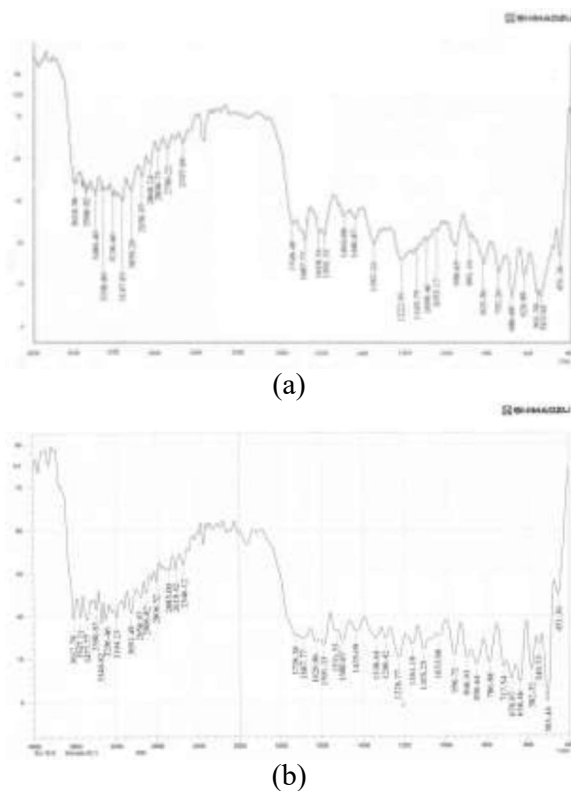


Figure 1: (a) FTIR spectra of AC (b) FTIR spectra of AC after adsorption of GV dye.

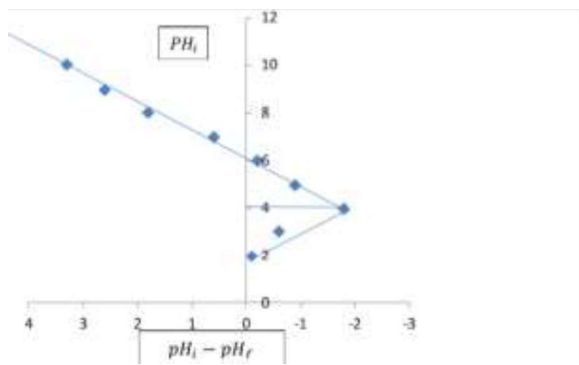


Figure 2:  $[\text{pH}]_{\text{PZC}}$  of AC prepared from Aldhnan hull.

Table 1: Characteristic group in AC by FTIR.

Wavenumber, ( $\text{cm}^{-1}$ )	bond	Characteristic group
3618.58	O-H stretch	Alcohol, phenol
3406.40	N-H stretch	Amine, amides

3147.93	C-H stretch	Aromatic
3059.20	=C-H stretch	Alkenes
2956.97, 2868.24	C-H stretch	Alkanes
2800.73, 2706.22	H-C=O stretch	Aldehydes
1687.77	C=O stretch	Carbonyls
1494.88, 1440.87	C-C stretch	Aromatic
1352.14	C-H rock	Alkanes
1222.91	C-O stretch	Alcohol, ester, ether, carboxylic acid
825.56	=C-H bend	Alkenes
626.89, 561.3, 543.94	C-Br stretch	Alkyl halide

### Factors affecting the adsorption

#### Contact time effect

The effect of contact time between the AC and GV dye on the removal percentage was determined at 50mg/L initial dye concentration with pH 8, 0.1g adsorbent weight, and 305K. Figure 3 shows increasing in the removal percentage with time and after 120 min reaches the equilibrium time, the quantity of dye adsorbed on adsorbent identical to the quantity of dye desorbed from the adsorbent.

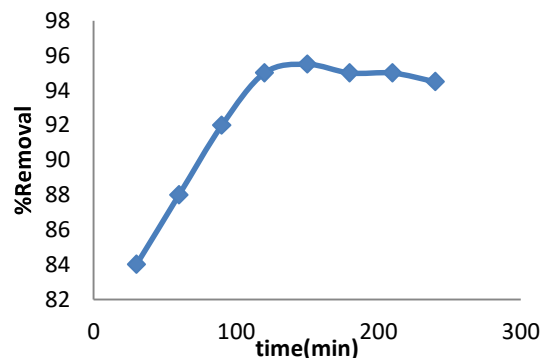


Figure 3: Effect of contact time on percentage removal of GV dye by AC at 305K, adsorbent dose (0.1g) and pH (8).

### pH Effect

The pH of solution is effect on the surface charge of adsorbent and degree of ionization [11]. Therefore, the pH has significant impact on the removal of GV dye from aqueous solution by AC prepared from Aldhnan hull. The result obtained from Figure 4 indicated increasing in uptake of basic dye (GV) at pH above (8).

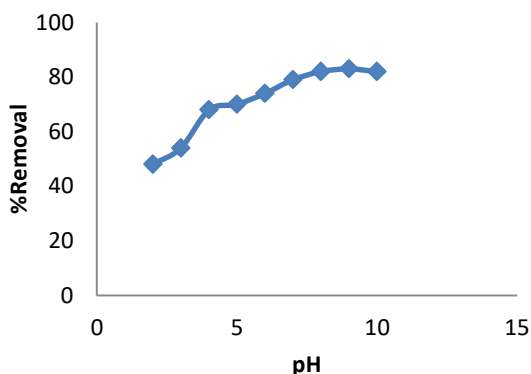
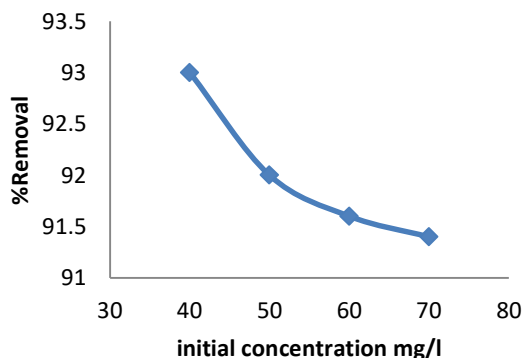


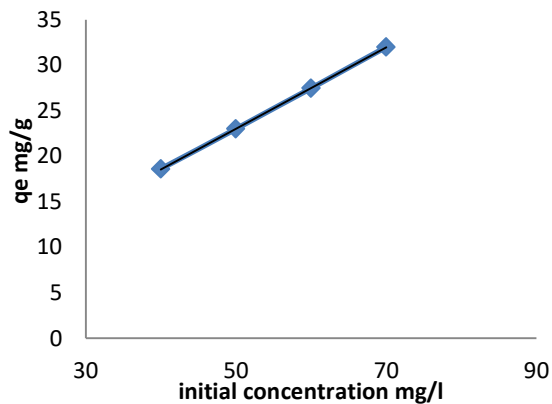
Figure 4: Effect of pH on percentage removal of GV dye by AC at 305K, adsorbent dose (0.1g) and contact time (120min).

### GV Dye Initial Concentration Effect

The influence of initial dye concentration on the rate of GV dye removal was examined by using different initial dye concentration (40, 50, 60 and 70) mg/l. The result shown in Figure 5a and 5b indicate decreasing in percentage removal with rising initial concentration and increasing in adsorption capacity. The removal efficiency of dyes by AC at lower dye concentration is higher due to the free binding sites and with increasing concentration the binding sites will becomes saturated [12]. Therefore, the removal percentage is decreasing with increasing of the concentration.



(a)



(b)

Figure 5: influence of initial concentration on (a) percentage removal (b) adsorption capacity of GV dye by AC at 305K, adsorbent dose (0.1g) and contact time (120min).

### Adsorption Isotherms

The adsorption isotherm is a relationship between the quantity of GV dye adsorbed per unit mass of AC and equilibrium concentration of GV dye at constant temperature. The equilibrium isotherm of adsorption exhibit how the particle of adsorbate distributes between the aqueous solution and the solid surface of adsorbent [13]. The well-known equilibrium model by Langmuir and Freundlich is used in this investigation.

### Langmuir model

The linear form of Langmuir Equation and separation factor defined by weber and chakkravorti are given by following Equations [14]:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (4)$$

$$R_L = \frac{1}{1 + K_L C_o} \quad (5)$$

Where  $C_e$  is the concentration at equilibrium in mg/l,  $q_e$ , the quantity of GV dye adsorbed on one gram of AC (mg/g),  $q_m$  and  $K_L$  are monolayer adsorption constants related to maximum adsorption capacity and affinity of binding sites of adsorbent towards adsorbate, respectively. In Langmuir model plotting of  $\frac{C_e}{q_e}$  versus  $C_e$  gives straight line (Figure 6), and the value of Langmuir constants  $K_L$  and  $C_o$  initial dye concentration are submitted in Equation (5) to calculate the separation constant  $R_L$  the value was

found in favorable range ( $0 < R_L < 1$ ) and that confirmed the AC is favorable for adsorption of GV dye at the optimum condition used in this investigation.

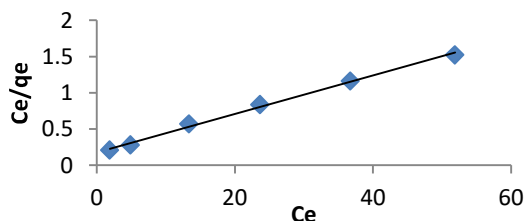


Figure 6: Langmuir equilibrium model of GV dye on AC at 305K.

### Freundlich Model

This is generally used isotherm for describe adsorption on heterogeneous surface. The linear logarithmic form of Freundlich isotherm represented by given Equation [15][16]:

$$\text{Log } q_e = \text{log } K_F + \frac{1}{n} \text{log } C_e \quad (6)$$

Where  $q_e$  is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g),  $C_e$  is the equilibrium concentration of dye (mg/l).  $K_F$  and  $\frac{1}{n}$  are Freundlich constants. The linear plots of  $\text{log } q_e$  against  $\text{log } C_e$  (Figure 7), gives slope value below unity and closer to zero and this implies that adsorption process follows chemisorptions process. The values of correlation coefficient and constants of Langmuir and freundlich model summarized in (Table 2), it shows the adsorption of GV dye on AC follows Langmuir as well as Freundlich model and the Langmuir adsorption model appears better fit ( $R^2=0.996$ ) than the Freundlich model ( $R^2=0.954$ ).

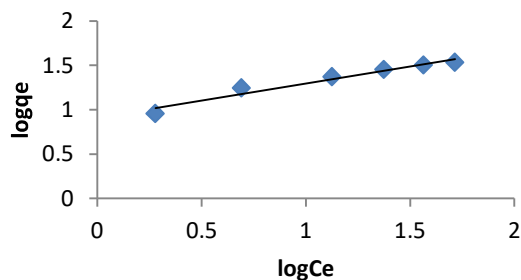


Figure 7: Freundlich equilibrium model of GV dye on AC at 305K.

Table 2: Langmuir and Freundlich model constants.

Langmuir model			Freundlich model		
$q_m$	$K_L$	$R^2$	$K_F$	$\frac{1}{n}$	$R^2$
37.46	0.1469	0.996	8.150	0.3828	0.954

### Adsorption Kinetic

In order to investigated the behavior of adsorption reaction, the experimental data testing by pseudo-first order model (Lagergren Equation), and pseudo-second order model. The linear form of pseudo-first order formulated as the following [17]:

$$\text{Log}(q_e - q_t) = \text{log } q_e - \frac{k_1}{2.303} t \quad (7)$$

Where  $q_e$  and  $q_t$  the quantity of GV dye adsorbed at optimum time and at time  $t$  respectively, and  $k_1$  the adsorption rate constant obtained from plots of  $\text{log}(q_e - q_t)$  against the time  $t$  for 50 and 100mg/l concentration of GV dye. The value of correlation coefficient, rate constant and equilibrium uptake, obtained from Figure 8 and listed in Table 3, exhibit that the adsorption of GV dye on AC prepared from Aldhnan hull follows pseudo-first order model.

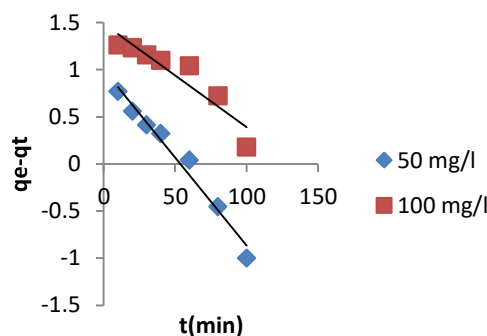


Figure 8: Pseudo-first order model of GV dye on AC prepared from Aldhnan hull at various initial concentrations.

The pseudo-second order model (HO and McKay 1999) in the linear form is expressed as the following [18]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (8)$$

Where  $q_e$  and  $q_t$  the quantity of GV dye adsorbed at optimum time (equilibrium) and at any time respectively,  $k_2$  the adsorption rate constant. The plots of  $\frac{t}{q_t}$  against time  $t$  gives a straight line (Figure 9), and from the slope and intercept the value of  $k_2$  and  $q_e$  can be evaluated. The initial adsorption rate  $h_o$  at various initial concentrations is related in the following Equation [19]:

$$h_o = k_2 q_e^2 \quad (9)$$

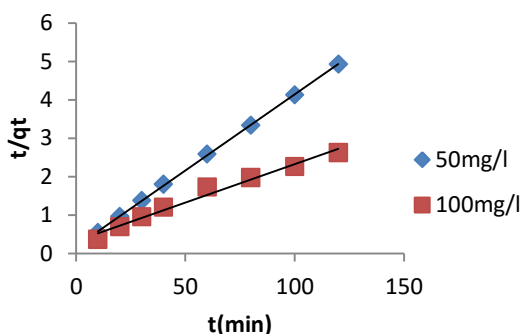


Figure 9: Pseudo-second order model of GV dye on AC prepared from Aldhnan hull at various initial concentration.

Table 3: kinetic parameters for adsorption of Gentian violet dye on activated carbon prepared from Aldhnan hull

$C_o$	$q_{e,exp}$	Pseudo-first order			
		$k_1$	$q_{e,cal}$	$R^2$	
50	24.4	0.043	10.01	0.975	
100	45.8	0.025	30.64	0.866	
$C_o$	$q_{e,exp}$	Pseudo-second order			
		$k_2$	$q_{e,cal}$	$R^2$	$h_o$
50	24.4	0.00874	25.25	0.999	5.5
100	45.8	0.0012	50.25	0.979	3.0

The comparison of kinetic constants and correlation coefficients of kinetic models show better fit with pseudo-second order model as in Table 3. That assumes chemisorptions process and decreases of initial rate with increases of initial dye concentration.

### Thermodynamic Analysis

The thermodynamic parameters such as changes in (free energy, enthalpy and entropy) can be calculated from the following Equations [20]:

$$\Delta G = -RT \ln K \quad (10)$$

$$\Delta H = [RT_1 T_2 / (T_2 - T_1)] \ln \left( \frac{K_2}{K_1} \right) \quad (11)$$

$$\Delta S = (\Delta H - \Delta G) / T \quad (12)$$

Where  $K$  is equilibrium constant calculated from Langmuir Equation,  $R$  gas constant ( $8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ ),  $T_1$  and  $T_2$  are temperature in (K) and  $\Delta G$  ( $\text{kJ} \cdot \text{mol}^{-1}$ ),  $\Delta H$  ( $\text{kJ} \cdot \text{mol}^{-1}$ ) and  $\Delta S$  ( $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ ) are change in Gibbs free energy, enthalpy and entropy respectively. The negative sign of change in Gibbs free energy exhibit the sorption process is spontaneous [21]. The positive value of change in enthalpy shows endothermic reaction of GV dye on AC and the chemisorptions process suggested due to higher enthalpy value more than ( $40 \text{ kJ} \cdot \text{mol}^{-1}$ ) [22]. The change in entropy has positive value and that indicate an increased randomness at the adsorbate-adsorbent interface during the adsorption reaction [23].

### Conclusion

The pigment isolated from *Micrococcus luteus* can absorb UV radiation and may be used in sunscreen cosmetics. The pigment is a carotenoid, which can use as a vitamin source and also a natural dye.

The crude pigment produced from the strain *Micrococcus luteus* was found to contain antimicrobial activity. Further, purification may give better effect.

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