

Removal of Crystal Violet dye from aqueous solutions onto date palm leaf without the sharp spines: Adsorption and kinetic studies

Rasmiah Almufarij

Princess Nora Bint Abdulrahman University, Science College, Chemistry Department

Email: dr.rasmia@yahoo.com

Abstract: The adsorption of crystal violet (CV) onto date palm leaf without the sharp spines (DPL) was examined in aqueous solution by considering the influence of pH on dye removal. Langmuir, Freundlich, and Elovich models were applied to describe the equilibrium isotherms. The kinetic data were fitted to a pseudo-second-order model.

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1. Introduction

Adsorption using different adsorbents is superior to the other separation techniques because of its efficacy, economy, ability to separate a wide range of chemical compounds and simple procedure. Research in the past few years has focused on utilizing waste materials from agricultural products because they are inexpensive, eco-friendly and renewable. Several materials have been studied as potential adsorbents[1-6]. Wastewater from dyeing and finishing operations in the textile industry is generally high in both color and organic content. Effluents discharged from dyeing industries are highly colored and can be toxic to aquatic life in the receiving waters [7,8]. Color removal from textile effluents has received attention due to its visibility even more than its potential toxicity[9,10]. Saudi Arabia is among the developing countries with a need to establish new industries based on utilizing natural resources in various sectors. Date palm is an important fruit crop of Saudi Arabia and occupies a large percentage of the cultivated land. Thus, using date palm waste to develop new adsorbents for the wastewater treatment by adsorption is quite attractive.

This work studies the removal of crystal violet dye by adsorption using date palm leaf without the sharp spines. The effect of pH is also evaluated. Finally, the adsorption kinetics are investigated.

2. Materials and Methods

The date palm leaf without the sharp spines (DPL) used for the preparation of the adsorbent was obtained locally from a farm in southern region of Riyadh city in Saudi Arabia. The material was sorted, cut, crushed, grinded and sieved to obtain fine particles. Crystal violet (CV) was supplied by Techno Pharmchem (India). The dye content is at least 88%. Distilled water was used to prepare solutions at the desired concentrations by diluting the stock solution. For

each individual test, 0.25 g samples of the adsorbent were placed into screw-capped Erlenmeyer flasks containing 25 mL of CV solution at different concentrations (mol/l). The flasks were shaken for a sufficient period to achieve equilibrium using an orbital shaker (J.P. Selecta, Spain) at 100 rpm and 35°C. The mixture solution was filtered using Whatmann filter paper (125 mm Ø, Cat. No. 1001 125). The dye uptake was monitored spectrophotometrically by measuring the absorbance at λ_{\max} , which was 584 nm. The amount of adsorption at equilibrium, q_e (mol/g) was calculated by

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where C_0 and C_e (mol/L) are the liquid-phase dye concentrations initially and at equilibrium, respectively. V is the volume of the solution (L), and m is the mass of dry adsorbent (g). The equilibrium data were then fitted using four different isotherm models, namely, the Langmuir, Freundlich, and Elovich models.

The percentage removal was studied as a function of pH. The effect of pH on the adsorption process was studied by preparing adsorbent-adsorbate solutions with fixed adsorbent dose and dye concentration but different pH by adding NaOH (1 M) or HCl (1 M) solutions and shaking until equilibrium.

The kinetic study was also performed at 25°C with a flask shaken only for the desired time period.

3. Results and Discussion

3.1. Adsorption isotherms

The adsorption isotherm indicates how the adsorption molecules are distributed between the liquid phase and the solid phase when the adsorption process is at equilibrium[11]. The adsorption isotherm of CV onto DPL is illustrated in Fig. 1. This isotherm is classified as type S according to the Giles *et al.* classification, indicating that adsorption becomes easier for increasing concentration. The S curve of the

adsorption isotherm generally reflects strong competition between the solvent and the adsorbed species for the adsorbent surface sites[12]. From Fig. 1, the experimental maximum adsorption capacity for the dye onto DPL at 35°C is approximately 1.95×10^{-5} mole g^{-1} .

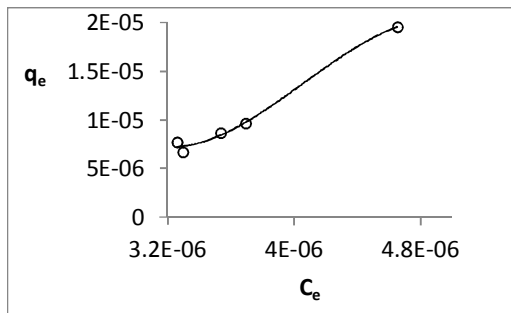


Figure1. Adsorption isotherm of CV onto DPL

The fitting of the isotherm data to different models is an important step for finding a suitable model that can be used for design purposes[13]. Linear forms of the Langmuir, Freundlich, and Elovich adsorption isotherm models (Eq. (2), (3), and (4), respectively) were used to verify the sorption data.

$$\frac{1}{q_e} = \frac{1}{Q_0} + \left(\frac{1}{bQ_0}\right)\left(\frac{1}{C_e}\right) \quad (2)$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (3)$$

$$\ln \frac{q_e}{C_e} = \ln K_E Q_0 - \frac{q_e}{Q_0} \quad (4)$$

where C_e is the equilibrium concentration. q_e is the amount of adsorbate adsorbed per unit mass of adsorbent. Q_0 is the maximum adsorption capacity. b is the Langmuir constant related to the adsorption rate. K_f is the Freundlich isotherm constant related to adsorption capacity (indicating the quantity of dye adsorbed onto the adsorbent). n is the Freundlich isotherm constant related to adsorption intensity (indicating the favorability of the adsorption process). K_E is the Elovich equilibrium constant. The Langmuir model [14] assumes uniform energies of adsorption onto the surface and no transmigration of the adsorbate along the plane of the surface. A linear fit to the Langmuir equation yields b and Q_0 from the slopes and the intercepts of the fit equation (see Fig. 2). The Freundlich model assumes that as the adsorbate concentration increases, the concentration of adsorbate on the adsorbent surface also increases. The linear form of the Freundlich isotherm model yields a straight line. The values of n and K_f are obtained from slope and intercept of the line (see Fig. 3). The Elovich model [15] is based on a kinetic principle assuming that the adsorption sites increase exponentially with adsorption, which implies a multilayer adsorption. The Elovich maximum adsorption capacity and Elovich constant can be calculated from the slopes and the intercepts of the

plot of $\ln(q_e/C_e)$ versus q_e (see Fig. 4). Correlation coefficients (R^2), which are a measure of goodness-of-fit, show a good linearity for this model relative to other models. The calculated values of all constants of these models with values of R^2 are given in Table 1.

For Langmuir, R^2 show a good linearity with value equal 0.951. The maximum adsorption capacity determined using the model, which is defined as the amount of adsorbate per gram of adsorbent required for monolayer coverage, is higher than the experimental value. In addition, the negative value for the Langmuir isotherm constant reflects the inadequacy of the isotherm model for explaining the adsorption process.

Freundlich isotherm model also yields a straight line with $R^2 = 0.967$, showing good linearity. The value of exponent n indicates the favorability of adsorption. In general, values of n in the range 2-10 represent good, 1-2 is moderately difficult, and >1 is poor adsorption characteristics [16]. In this study, the calculated value of n is less than one, indicating poor adsorption. The maximum adsorption capacity obtained using the equation is very higher than the experimental value.

For Elovich model, the adsorption capacity determined using the linear transformation of the Elovich equation ($=1.908 \times 10^{-5}$ mol g^{-1}) is approximately equal to the experimental measurements at equilibrium, corresponding to the plateau of the adsorption isotherms ($=1.95 \times 10^{-5}$ mol g^{-1}). Thus, the assumption of exponential covering of adsorption sites, which implies multilayer adsorption, is in agreement with the experimental results in the studied concentration range. Regarding the applicability of the isotherm equation to describe the adsorption process, this model also shows good linearity, with R^2 is close to unity ($= 0.977$).

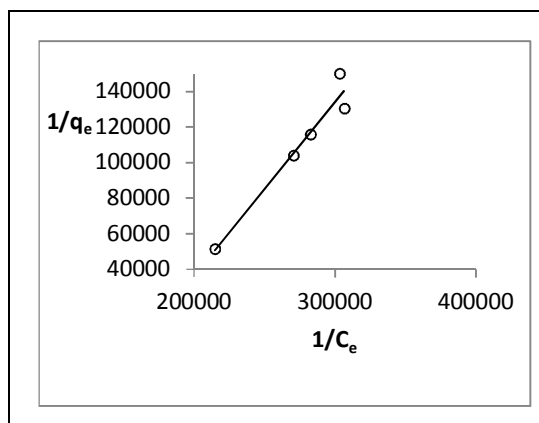


Figure 2. Langmuir plot of CV onto DPL

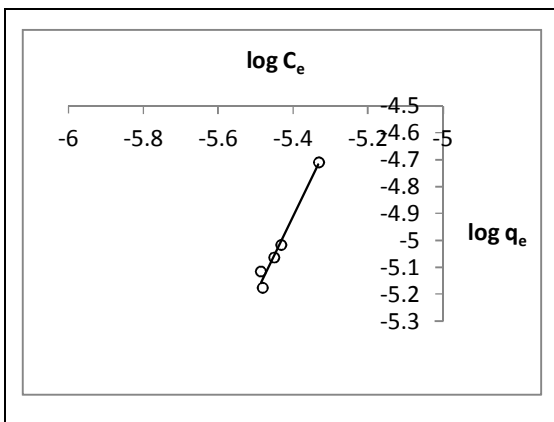


Figure 3. Freundlich plot of CV onto DPL

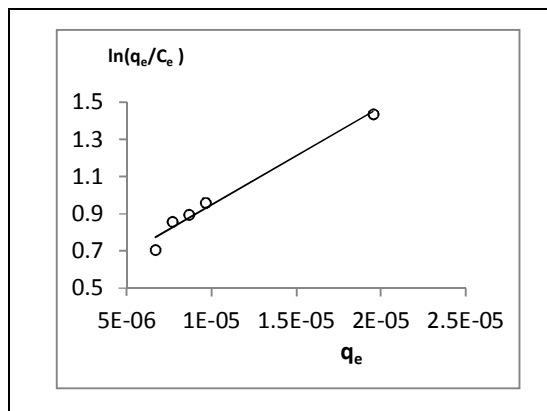


Figure 4. Elovich plot of CV onto DPL

Table 1. Isotherm model constants for the adsorption of CV onto DPL

Isotherm	Constants		R^2	$Q_{Experimental}$ $mol\ g^{-1}$
	Q_s ($mol\ g^{-1}$)	b ($L\ mol^{-1}$)		
Langmuir	-6.277×10^{-5}	0.16306×10^5	0.951	1.95×10^{-5}
Freundlich	n	K_f (L/g)	0.967	
	0.095057	0.33×10^{10}		
Elovich	Q_s ($mol\ g^{-1}$)	K_E ($Lmol^{-1}$)	0.977	
	1.908×10^{-5}	0.80007×10^5		

3.2. Effect of pH

Acidity is very important in the adsorption process, especially for dye adsorption. The pH of a medium will control the magnitude of the electrostatic charges imparted by the ionized dye molecules. Both the adsorbent and adsorbate may have functional groups that can be protonated or deprotonated to produce different surface charges in solutions at different pH, resulting in electrostatic attraction or repulsion between the charged adsorbates and adsorbents[17]. Therefore, the effect of pH on the adsorption behavior of the dye on the adsorbent was studied by observing the percentage of dye removal over a pH range of acidity, natural and basicity. The variation in the removal of CV with pH is shown in Fig. 5. As presented in the figure, the obtained results show that the percentage removal of dye decreases slightly with increasing basicity up to pH 7.0, after which it increase. This behavior may be due to the adsorbent becoming negatively charged at acidic and basic pH, resulting in an attraction between the positively charged dye molecule and adsorbent, compared to the surface charge density on the adsorbent at natural pH where it becomes positively charged, resulting in electrostatic repulsion from the positive charge of the dye molecule.

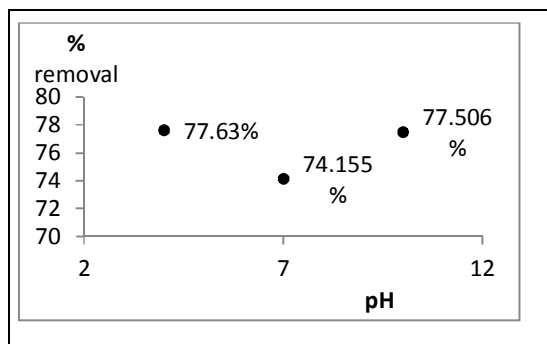


Figure5. Percentage removal of CV dye onto DPL at different pH values

3.5. Kinetic Study

The study of adsorption kinetics describes the solute uptake rate, which controls the residence time of the adsorbate at the solid/ solution interface. The kinetics of CV adsorption onto DPL were analyzed at 25°C using pseudo-first-order and pseudo-second-order kinetic models. The linear pseudo-first-order equation [18] is given as follows:

$$\ln(q_e - q_t) = \ln q_e - K_1 t$$

where q_e and q_t are the adsorption capacity at equilibrium and at time t , respectively, and k_1 is the rate constant of the pseudo-first-order adsorption. A plot of $\ln(q_e - q_t)$ versus t (see Fig. 6) should be linear, and k_1 and q_e can be determined from the slope and intercept of the plot, respectively. The shape of the lines and the correlation coefficient (R^2) is 0.482, indicating that the first-order Lagergren equation did not fit the complete range of the adsorption process well.

The linear pseudo-second-order equation [19] is given as follows:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t$$

where k_2 is the pseudo-second-order rate constant. The slope of the plot of t/q_t versus t gives the value of q_e , and the intercept can be used to calculate k_2 . The plot of t/q_t versus t (see Fig. 7) yields a very straight line. The value of R^2 is 0.996 for the pseudo-second-order model, and the value of q_e is very close to the q_e (experimental) at 25°C. The calculated q_e value, the rate constant, K_2 for second order, and the value of the q_e (experimental) are given in Table 2. Comparing the values of q_e and R^2 between the models gives indicator that the pseudo-second-order is a better fit for the former.

Table 2. Rate constants and adsorption capacity at equilibrium for the adsorption of CV onto DPL

The order	Constants		R^2	q_e (mol g ⁻¹) (Experimental, at 25°C)
2nd	K_2 (g mol ⁻¹ min ⁻¹)	q_e (mol g ⁻¹)	0.996	2.699×10^{-5}
	1.6263×10^3	2.479×10^{-5}		

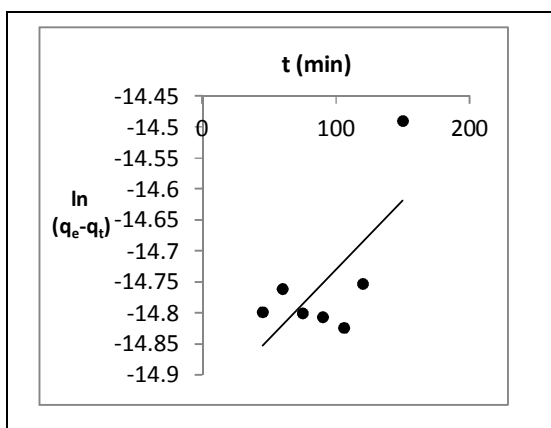


Figure 6. $\ln(q_e - q_t)$ versus time for the adsorption of CV onto DPL

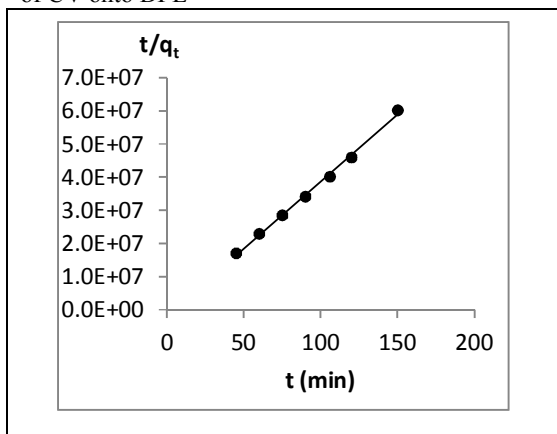


Figure 7. t/q_t versus time for the adsorption of CV onto DPL

4. Conclusions

This study indicates that date palm leaf without the sharp spines (DPL) is a promising adsorbent for the removal of crystal violet dye (CV) from aqueous solutions within the concentration range used in this study. Equilibrium data were analyzed according to Langmuir, Freundlich, and Elovich and isotherms. The Elovich model was best able to describe the adsorption isotherm of CV onto DPL because the maximum adsorption capacity obtained from this model was equal to the experimental value and the value of R^2 is close to unity. Percentage removal of dye changes slightly with pH. The kinetics analysis revealed that the pseudo-second-order model was a better fit of the experimental data than the first-order kinetic expressions.

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Corresponding Author:

Dr. Rasmiah Almufarij
Chemistry Department, Science College,
Princess Nora Bint Abdulrahman University,
Riyadh, Saudi Arabia
dr.rasmia@yahoo.com

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