

Research Article

Removal of Crystal Violet Dye from Aqueous Solutions onto Date Palm Fiber by Adsorption Technique

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The adsorption of crystal violet (CV) onto date palm fibers (DPFs) was examined in aqueous solution at 25°C. The experimental maximum adsorption capacity value was 0.66×10^{-6} . Langmuir, Freundlich, Elovich and Temkin models were applied to describe the equilibrium isotherms. The influence of pH and temperature on dye removal was evaluated. The percentage removal of CV dye by adsorption onto DPF at different pH and temperatures showed that these factors play a role in the adsorption process. Thermodynamic analysis was performed, and the Gibbs free energy ΔG° , enthalpy change ΔH° , and entropy ΔS° were calculated. The negative values of ΔG° indicate spontaneous adsorption. The negative value of ΔH° indicates that the interaction between CV and DPF is exothermic, and the positive value of ΔS° indicates good affinity between DPF and CV. The kinetic data were fitted to a pseudo-second-order model.

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, ecofriendly, and renewable. Several materials have been studied as potential adsorbents, such as orange peels [1], mango seed husks [2], pineapple stems [3], coconut bunch waste [4], pumpkin seeds [5], and cotton plant waste [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 CV dye by adsorption using date palm fiber (DPF). The effect of pH and temperature and the thermodynamic parameters are also evaluated. Finally, the adsorption kinetics are investigated.

2. Materials and Methods

The date palm fiber (DPF) used for the preparation of the adsorbent was obtained locally from a farm in the 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 Pharm-Chem, Bahadurgarh (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, from 0.9×10^{-5} to 7×10^{-5} 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 25°C. The mixture solution was filtered using Whatman filter paper (125 mm Ø, Cat. no. 1001 125). The dye uptake was monitored spectrophotometrically by measuring the absorbance at λ_{\max} 584 nm. The amount

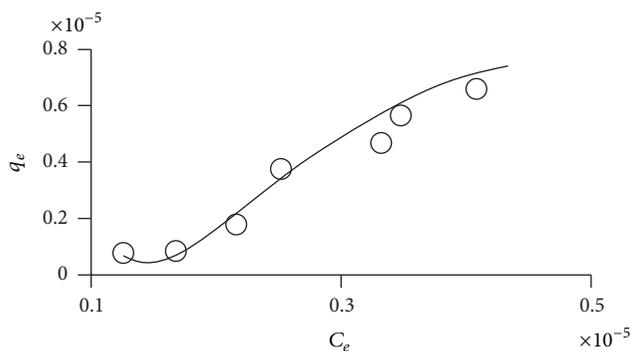


FIGURE 1: Adsorption isotherm of CV onto DPF (experimental conditions: 25°C, 100 rpm, λ_{\max} of absorbance = 584 nm, and adsorbent mass = 0.25 gm per 25 mL of CV solution at different concentrations: 0.9×10^{-5} – 7×10^{-5}).

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, Elovich, and Temkin 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 (0.25 gm) and dye concentration (3×10^{-5}) but different pH by adding NaOH (1 M) or HCl (1 M) solutions and shaking until equilibrium.

The temperature dependence of CV sorption onto DPF was studied with a constant initial concentration at 100 rpm. The percentage removal at 25, 35, 45, and 55°C was recorded. The thermodynamic parameters ΔG° , ΔH° , and ΔS° were calculated.

The kinetic study was also performed 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 DPF is illustrated in Figure 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 Figure 1, the experimental maximum adsorption capacity for the dye onto DPF is approximately 0.66×10^{-6} mol g⁻¹.

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, Elovich, and Temkin adsorption isotherm models ((2), (3), (4), and (5), resp.) were used to verify the sorption data:

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

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

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

$$q_e = B \ln A + B \ln C_e, \quad (5)$$

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, and B and A are constants related to the heat of adsorption and the equilibrium binding constant, respectively, $B = RT/b$, where R is the constant gas, T (K) is the absolute temperature, and b is the Temkin isotherm constant.

The Langmuir [14] model 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 Langmuir constant (b) and the maximum adsorption capacity (Q_0) from the slopes and the intercepts, respectively.

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 slope and intercept of the obtained fit are used to calculate the Freundlich constants n and K_f [15]. The Elovich model [16] 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 . The Temkin [17] isotherm equation assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent-adsorbate interactions and that the adsorption is characterized by a uniform distribution of the binding energies up to some maximum binding energy. The Temkin equilibrium constants can be calculated from the slope and intercept of the plot of q_e versus $\ln C_e$. However, all the constants of these models are given in Table 1.

The applicability of the isotherm equations to describe the adsorption process was judged based on the maximum value of adsorption and correlation coefficients (R^2), which are a measure of goodness of fit.

For Langmuir, the maximum value of adsorption (Q_0) is negative and this observation reflects the inadequacy of this model for explaining the adsorption process, although

TABLE 1: Isotherm model constants for the adsorption of CV onto DPF.

Isotherm	Constants		R^2	$Q_{\text{Experimental}} \times 10^{-6} \text{ mol g}^{-1}$
Langmuir	$Q_0 \times 10^{-4} (\text{mol g}^{-1})$ -0.2396	$b \times 10^{-5} (\text{L mol}^{-1})$ 1.1137	0.996	
Freundlich	n 0.524	$K_f \times 10^4 (\text{L/g})$ 13.1825	0.989	
Elovich	$Q_0 \times 10^{-6} (\text{mol g}^{-1})$ 0.579	$K_E \times 10^4 (\text{L mol}^{-1})$ 2.9845	0.961	0.66
Temkin	$A \times 10^5 (\text{mol g}^{-1})$ 12.02604	$B \times 10^{-5}$ 0.5	0.916	

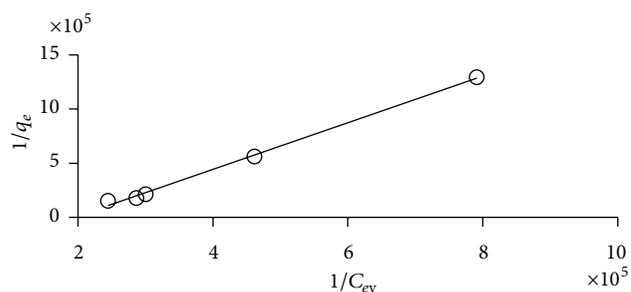


FIGURE 2: Langmuir plot of CV onto DPF (experimental conditions: 25°C, 100 rpm, λ_{max} of absorbance =584 nm, and adsorbent mass =0.25 gm per 25 mL of CV solution at different concentrations: 0.9×10^{-5} – 7×10^{-5}).

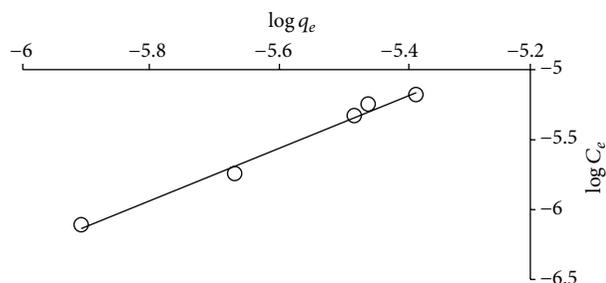


FIGURE 3: Freundlich plot of CV onto DPF (experimental conditions: 25°C, 100 rpm, λ_{max} of absorbance =584 nm, and adsorbent mass =0.25 gm per 25 mL of CV solution at different concentrations: 0.9×10^{-5} – 7×10^{-5}).

it shows a good linearity compared to other models (see Figure 2 and Table 1).

For Freundlich model, the maximum adsorption capacity obtained using the equation is higher than the experimental value, indicating that the experimental adsorption data does not fit this model, although the high R^2 value it takes (see Figure 3 and Table 1).

The adsorption capacity determined using the linear transformation of the Elovich equation ($=0.579 \times 10^{-6}$) is approximately equal to the experimental measurements at equilibrium, corresponding to the plateau of the adsorption isotherms ($=0.66 \times 10^{-6}$). Thus, the assumption of exponential covering of adsorption sites, which implies multilayer

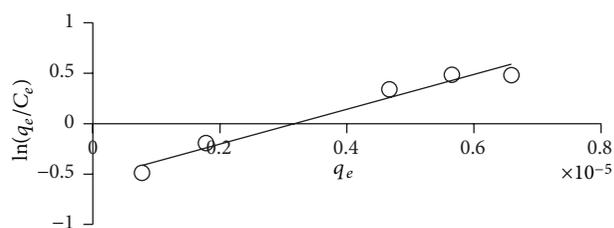


FIGURE 4: Elovich plot of CV onto DPF (experimental conditions: 25°C, 100 rpm, λ_{max} of absorbance =584 nm, and adsorbent mass =0.25 gm per 25 mL of CV solution at different concentrations: 0.9×10^{-5} – 7×10^{-5}).

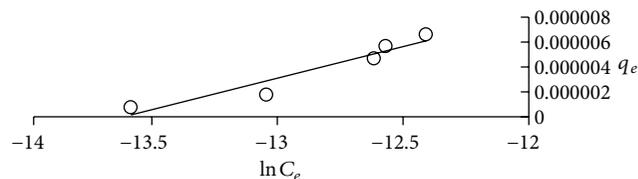


FIGURE 5: Temkin plot of CV onto DPF (experimental conditions: 25°C, 100 rpm, λ_{max} of absorbance =584 nm, and adsorbent mass =0.25 gm per 25 mL of CV solution at different concentrations: 0.9×10^{-5} – 7×10^{-5}).

adsorption, is in agreement with the experimental results in the studied concentration range. Regarding the R^2 value, this model also shows good linearity, with R^2 is close to unity, see Figure 4 and Table 1.

For the Temkin isotherm, The value of R^2 is the lowest of all studied models. Thus, this model describes the adsorption isotherm of CV onto DPF poorly, see Figure 5 and Table 1.

Thus, it can be said that the experimental adsorption data fit the Elovich model was fairly well compared to the other models based on the maximum value of adsorption and correlation coefficients (R^2).

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

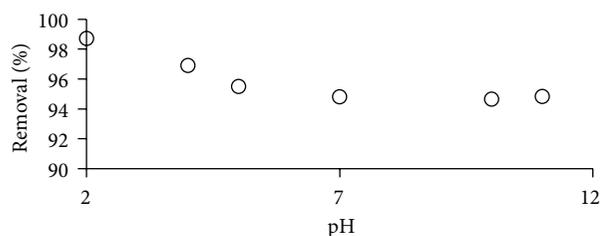


FIGURE 6: Percentage removal of CV dye onto DPF at different pH values (experimental conditions: 25°C, 100 rpm, λ_{\max} of absorbance =584 nm, and adsorbent mass =0.25 gm, and dye concentration = 3×10^{-5}).

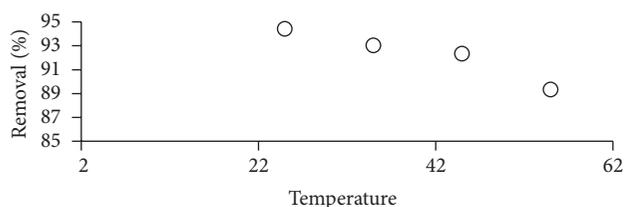


FIGURE 7: Percentage removal of CV dye onto DPF at different temperatures (experimental conditions: 25, 35, 45, and 55°C, 100 rpm, λ_{\max} of absorbance =584 nm, and adsorbent mass =0.25 gm).

attraction or repulsion between the charged adsorbates and adsorbents [18]. 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 wide pH range of 2–11. The variation in the removal of CV with pH is shown in Figure 6. 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 remains almost constant. This behavior may be due to the increase in negative charge density of surface at acidic pH, resulting in a attraction between the positively charged dye molecule and adsorbent. As the pH increases, the surface charge density on the adsorbent decreases, resulting in electrostatic repulsion from the positive charge of the dye molecule.

3.3. Effect of Temperature. The effect of temperature on the sorption of CV by DPF is shown in Figure 7. The percentage of dye removal decreases from 94% to 89% for dye as the solution temperature increases from 25 to 55°C. Because the adsorption decreased as the temperature increased, the system is considered to be exothermic. A similar trend was reported by Chandra et al. [19] for the adsorption of MB on activated carbon prepared from durian shell, who explained that as the temperature increased, the physical bonding between the organic compound (including the dye) and the active sites of the adsorbent weakened. In addition, the dye solubility also increased, which caused the interaction between the solute and solvent to become stronger than that between the solute and adsorbent. Therefore, the solute was more difficult to adsorb.

3.4. Thermodynamic Parameters. The thermodynamic parameters for the adsorption of CV on DPF were calculated using

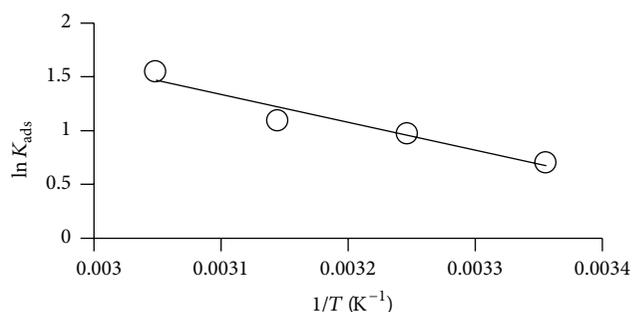


FIGURE 8: $\ln K_{\text{ads}}$ versus $1/T$ according to the van't Hoff equation (7) (experimental conditions: 25, 35, 45, and 55°C, 100 rpm, λ_{\max} of absorbance =584 nm, and adsorbent mass =0.25 gm).

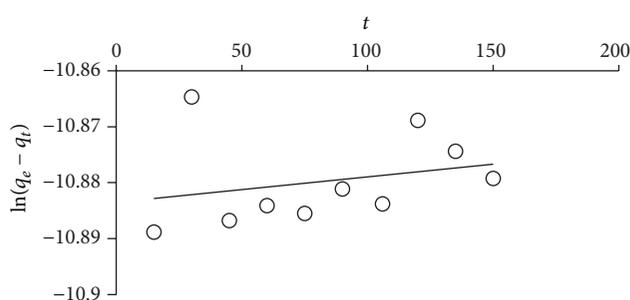


FIGURE 9: $\ln(q_e - q_t)$ versus time (min) for the adsorption of CV onto DPF (experimental conditions: 25°C, 100 rpm, λ_{\max} of absorbance =584 nm, and adsorbent mass =0.25 gm, period time: 15, 30, 45, 60, 75, 90, 106, 120, 135, and 150 min).

the following equations, and the values are given in Table 2 (Figure 8 represents (7));

$$\Delta G^\circ = -RT \ln K_{\text{ads}}, \quad (6)$$

$$\ln K_{\text{ads}} = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}. \quad (7)$$

The equilibrium constants (K_{ads}) were calculated according to the following equation [20]:

$$K_{\text{ads}} = \frac{\text{dye concentration on the solid at equilibrium}}{\text{dye concentration in solution at equilibrium}}, \quad (8)$$

where ΔG° , ΔH° and ΔS° are the changes in Gibb's free energy, enthalpy, and entropy, respectively. The negative free energy value at 25°C indicates the feasibility of the process and its spontaneous nature. The exothermic nature of process was confirmed by the negative value of enthalpy change ΔH° . The positive entropy change ΔS° indicates the good affinity of DPF for CV and the increasing disorder at the solid-solution interface during the adsorption process.

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

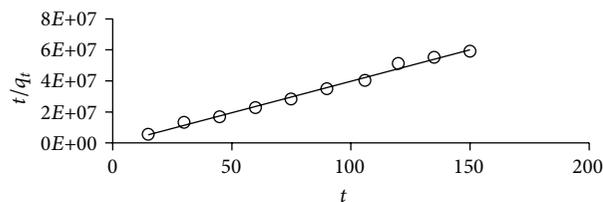


FIGURE 10: t/q_t versus time (min) for the adsorption of CV onto DPF (experimental conditions: 25°C, 100 rpm, λ_{\max} of absorbance =584 nm, and adsorbent mass =0.25 gm, period of time: 15, 30, 45, 60, 75, 90, 106, 120, 135, and 150 min).

TABLE 2: Thermodynamic parameters for the adsorption of CV onto DPF.

25°C (298 K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)
	-1.73926	-21.516632	77.7941

TABLE 3: Rate constant and adsorption capacity at equilibrium for the adsorption of CV onto DPF.

The order	Constants		R^2
	$K_2 \times 10^3$ (g mol ⁻¹ min ⁻¹)	$q_e \times 10^{-6}$ (mol/g)	
2nd	20.132	0.86	0.999

CV adsorption onto DPF were analyzed using pseudo-first-order and pseudo-second-order kinetic models. The linear pseudo-first-order equation [21] is given as follows:

$$\ln(q_e - q_t) = \ln q_e - K_1 t, \quad (9)$$

where q_e and q_t are the amount adsorbed 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 Figure 9) should be linear, and rate constant (K_1) and adsorption capacity at equilibrium (q_e) can be determined from the slope and intercept of the plot, respectively. The value of R^2 (=0.067) indicates that the first-order Lagergren equation did not fit the complete range of the adsorption process well.

The linear pseudo-second-order equation [22] is given as follows:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t, \quad (10)$$

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 Figure 10) yields a very straight line. The correlation coefficient (R^2) for this model is 0.992, indicating a better fit for the former. The calculated and experimental q_e values agreed satisfactorily. However, the calculated, q_e , and the rate constant, (K_2), are given in Table 3.

4. Conclusions

This study indicates that date palm fiber (DPF) is a promising adsorbent for the removal of crystal violet dye (CV) from

aqueous solutions over a range of concentrations. Equilibrium data were analyzed according to Langmuir, Freundlich, Elovich, and Temkin isotherms. Despite the much higher correlation coefficient for the Langmuir and Freundlich models, the Elovich model was best able to describe the adsorption isotherm of CV onto DPF because the maximum adsorption capacity obtained from this model was equal to the experimental value. The temperature and pH play a role in the adsorption process. Greater adsorption occurred at low temperature and pH. The thermodynamic calculations indicated that the process was spontaneous and exothermic. 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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