Study on Adsorption of Malachite Green by Date Palm Fiber

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ABSTRACT

In this study, the adsorption of malachite green (MG) onto date palm fibers (DPF) was examined in aqueous solutions. The Langmuir and Freundlich adsorption isotherm models were employed to describe the equilibrium adsorption data. The Freundlich isotherm model was found to fit the adsorption data The removal percentage of MG dye from aqueous solutions via adsorption onto DPF adsorbent varied with pH and temperature, showing that these factors play a key role in the adsorption process. The removal percentage was found to increase with decrease in the solution temperature and in alkaline media. The adsorption kinetic data were fitted with a pseudo-second-order model.

Keywords: Malachite green, Date palm fibers, Percentage removal, Adsorption.

INTRODUCTION

Color removal from industrial effluents has been a subject of investigation because of its potential toxicity. Malachite green (MG) is one of the dyes that is extensively used in the textile industry. It exhibits toxic properties that are known to cause carcinogenesis, mutagenesis, teratogenesis and respiratory toxicity[1, 2]. In recent times, adsorption-techniques for wastewater-treatment have become very popular because of to their improved efficiency in the removal of pollutants too stable for biological methods[3]. Research in the past few years has been focused on using agricultural wastes as adsorbent materials because they are inexpensive, eco-friendly and renewable. For instance, pumpkin seeds[4], the husk of mango seeds[5], cotton plant[6], coconut bunch wastes[7], orange peels[8], and pineapple stem[9] have been studied as potential adsorbents. Date palm is an important fruit crop in Saudi Arabia as well as around the world. It is estimated that the annual date palm agricultural wastes comprise more than 20 kg of dry leaves and fibers for each date palm tree[10]. Thus, utilizing the date palm waste as a potential adsorbent for wastewater treatment via adsorption is of considerable interest. In this study, the adsorption of MG from aqueous solutions was studied using the brownish fibrous sheath that surrounds the trunk of the date palm (known as leef) as an adsorbent. In addition, we studied the process kinetics. The removal percentage was calculated to determine the influence of pH and temperature on the adsorption.

MATERIALS AND METHOD

The date palm fibers (DPF) wastes were obtained a local from a farm in the southern region of Riyadh city in Saudi Arabia. They were cut, ground and sieved to a size $\leq 63\ \mu m$. A typical date palm fiber can be seen in Fig.1[10]. MG was received from Techno Pharmchem (India) was used as an adsorbate. The dye content is at least 90%. Test solutions of desired concentrations are prepared from the stock solution using distilled water.

Adsorption tests were carried out by using batch experiments. For each test, 0.5 g of the adsorbent was placed in screw-capped Erlenmeyer flasks containing 25 mL of MG solution. The flasks were shaken constantly for a sufficient period to achieve equilibrium using an orbital shaker (J.P. Selecta, Spain) at 100 rpm and 25°C. Then the solution was filtered using Whatman filter paper (125 mm Ø, cat. No. 1001 125). The dye uptake was monitored with a spectrophotometer (Jenway model 6800 UV/VIS) by measuring the absorbance at λ_{max} = 616 nm. The adsorption at the equilibrium, q_e (mol/g), was calculated using the following equation:

$$q_e = (C_0 - C_e)V/m \qquad \qquad ...(1)$$

where C_o and C_e (mol/L) are the initial and the equilibrium liquid-phase concentrations of the dye, respectively. V is the volume of the solution (in liters), and m is the mass of the dry adsorbent (in grams). The equilibrium adsorption data were fitted with two isotherm models, the Langmuir and Freundlich models.

The effect of pH was studied by preparing suitable adsorbent–adsorbate solutions at room temperature with fixed adsorbent dosage and initial dye concentration at different pH. The pH was adjusted by adding NaOH (1 M) or HCl (1 M) solutions. The temperature effect on the adsorption process was studied by varying the adsorption temperature with a constant initial concentration of the solution. The removal percentage was calculated using Eq. (2).

$$Removal\ (\%) = [(C_o - C_e) /C_o] \times 100 \qquad ...(2)$$

The kinetic study was also performed at room temperature with a flask that was identical to the one used for batch equilibrium tests. The flask was shaken constantly to achieve equilibrium and the aqueous samples were collected at preset-time intervals, and concentrations of MG were measuresed.

RESULTS AND DISCUSSION

Adsorption study

Adsorption isotherms indicate how adsorbates are distributed between the liquid phase and the solid phase when the adsorption process reaches equilibrium[11]. The adsorption isotherm is important for understanding how the adsorbate interacts with the adsorbent, gieving an idea of the adsorption capacity of the adsorbent[12]. Fig. 2 illustrates the adsorption isotherm of MG onto DPF. The maximum experimental adsorption capacity for the dye onto DPF is approximately 0.2136 mol g^{-1}. From the figure, we can be see that the adsorption isotherm is an S type (based on Giles *et al.* classification), ndicating that the adsorption becomes easier as the concentration increases[13]. In practice, the S curve of the adsorption isotherm indicates a strong competition between the solvent and the adsorbed species for the adsorbent surface sites[13]. Analyzing the isotherm data by fitting it to different isotherm models is important for identifying a suitable

Fig. 1: Date palm fi bers (a) on the tree, (b) separated[10]

model that can be used for design purposes[14]. The adsorption isotherm models of Langmuir (Eq. (3)) and Freundlich (Eq. (4)) were applied to describe the sorption data. The applicability of the isotherm equation to describe the adsorption process was judged in terms of the correlation coefficients (R^2) and the maximum adsorption capacities.

$$(1/q_e) = (1/Q_o) + (1/bQ_o)(1/C_o) \qquad ...(3)$$

where C_e is the equilibrium concentration, q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (in mol/g), and Q_o and b are the Langmuir constants related to the adsorption capacity and rate of adsorption, respectively. In the Langmuir model, a plot of $1/C_e$ against $1/q_e$ yields a straight line with a slope of $(1/bQ_o)$ and an intercept of $(1/Q_0)$, as shown in Fig. 3.

$$\log q_e = \log K_f + (1/n) \log C_e \qquad ...(4)$$

where K_f and n are Freundlich constants related to the adsorption capacity and adsorption intensity, respectively. The n value indicates the degree of nonlinearity between solution concentration and adsorption as follows: if n=1, then the adsorption is linear; if n > 1, then the adsorption is a physical process; and if n < 1, then the adsorption is a chemical process[15]. In the Freundlich model, a plot of log q_e against log C_e yields a straight line with a slope of 1/n and an intercept of log K_f, as shown Fig. 4. The slope 1/n ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity[16]. It becomes more heterogeneous as its value gets closer to zero; a value of 1/n below one indicates a normal Langmuir isotherm while that above one is indicative of cooperative adsorption[16].

The constants in these models, i.e., Q_o, b, K_f, and n, and the correlation coefficients,R^2 are given in Table 1. According to the R^2 values, both models seemed to represent the equilibrium adsorption data. However, Langmuir isotherm is difficult to interpret because it is characterized with a negative q_e value. Therefore, the adsorption of MG onto the adsorbent could be described by the Freundlich model. It was found that the n value in Freundlich equation is <1, indicating that the process is cooperative because the value of the slope 1/n is above unity.

Effect of pH

Fig. 5 illustrates the effect of pH on the removal of MG dye by DPF in the pH range 4-10. It is noticeable from the figure that the maximum removal is 95.725% at pH = 10 and the removal of dye increases with increasing pH. This result could be explained by the attraction forces between different charges; the adsorbent surface becomes negatively

Table 1. Isotherm model constants for the adsorption of MG onto DPF

Temperature	Isotherm	Constants			R^2
25°C (298K)	Langmuir	Q_o (mol g^{-1})	b (L mol^{-1})		0.9547
		-3.3336	-0.18692		
	Freundlich	K_f (L/g)	n	1/n	0.9507
		6.74	0.73	1.369	
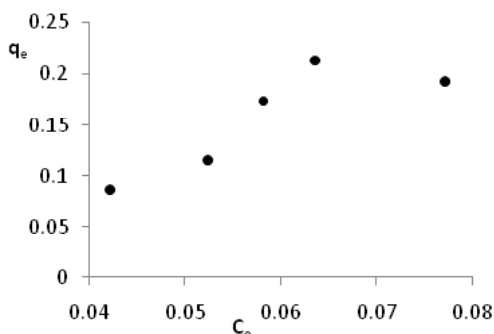
Fig. 2: Adsorption isotherm of MG onto DPF
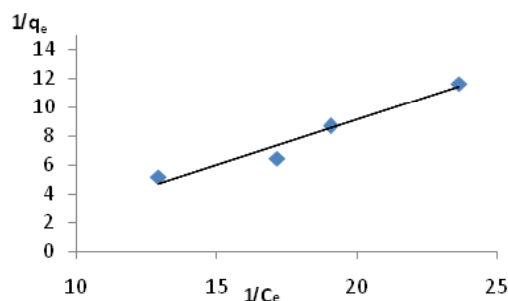
Fig. 3: Langmuir plot of MG onto DPF

charged in alkaline media, resulting in an attraction between the positively charged dye molecule and the negatively charged adsorbent. In acidic media, the presence of excess H^+ ions competing with the positive charge of dye for the adsorption sites, and therefore the removal of dye slows down.

Effect of temperature

Fig. 6 gives information about the percentage removal of the MG by DPF at different temperatures. As observed, the percentage removal decreases slightly with increase in temperature from 25 to 45 °C and the maximum removal is 94.3% at 25°C. A similar trend was reported by Chandra *et al.*[17] for the adsorption of MB onto activated carbon prepared from durian shell; the researchers suggest that the physical bonding between the organic compound (including the dye) and the active sites on the adsorbent weakens as the temperature increases. In addition, the dye solubility also increases, which causes the interaction between the solute and the solvent to become stronger than that between the solute and adsorbent. Therefore, the solute is less likely to be adsorbed. The highest MG removal of 94.3% was achieved at 25°C.
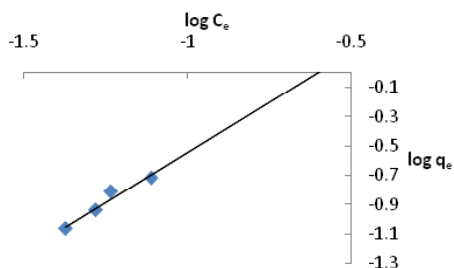

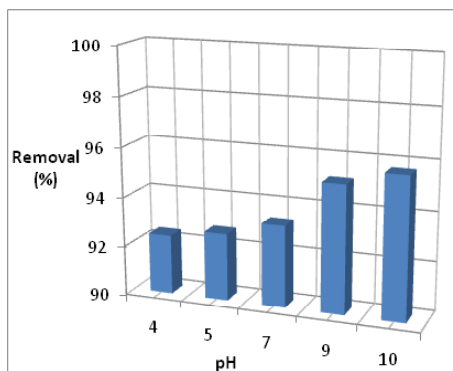**Fig.4: Freundlich plot of MG onto DPF**

Fig.5: Removal (%) of MG dye by DPF at different pH

Kinetic Study

Two models were used to analyze the adsorption kinetics of MG by DPF at 25°C. The first model was pseudo-first-order, and therefore the Lagergren equation was applied. It is given as follows[18]:

$$\ln(q_e - q_t) = \ln q_e - K_1 t \qquad \qquad ...(5)$$

where q_e is the adsorption capacity at equilibrium, q_t is the adsorption capacity at time t and k_1 is the rate constant. A plot of $\ln(q_e - q_t)$ versus t is linear and K_1 could be calculated from the slope while q_e could be determined from the intercept of the plot (the figure is not shown). The adsorption process could not be described using the model because the value of correlation coefficient R^2 was low and the experimental q_e value did not agree with the value calculated using the equation.

Second model was based on the linear pseudo-second-order equation. It is given as follows[19]:

$$(t/q_t) = 1/(K_2 q_e^2) + (1/q_e)t \qquad ...(6)$$

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 yields a straight line, as shown in Fig. 7. The calculated value of q_e for the pseudo-second-order model is 0.080 (mol g^{-1}), which agrees well with the experimental value at 25°C (= 0.0858 mol g^{-1}). Moreover, the R^2 value for this model is 0.999, indicating an excellent fit. The value of K_2 is found to be 454.215 ($gmol^{-1}min^{-1}$).
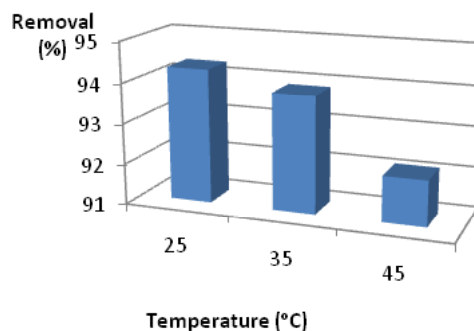

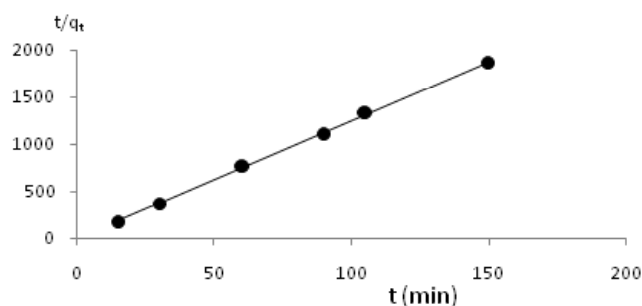**Fig.6: Removal (%) of MG dye by DPF at different temperature**

Fig. 7: pseudo-second-order model of the kinetic adsorption of MG dye by DPF

CONCLUSION

In this work, we studied the adsorption of MG from aqueous solution over a range of MG concentrations on DPF surface. The equilibrium adsorption data was analyzed according to Langmuir and Freundlich isotherms. The effect of temperature and pH were studied by calculating the percentage removal of MG. Better color removal occurred at low temperatures and in basic media. The kinetic studies revealed that the pseudo-second-order was a better fit than the pseudo first-order model.

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