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REMOVAL OF CONGO RED DYE FROM AQUEOUS SOLUTION BY DATE PALM LEAF BASE

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ABSTRACT

Removal of dyes from wastewater is important for industry and environmental protection. The adsorption technique, using biomass is attractive method for environmental and economical reasons. This study studies removal of Congo Red dye (CR) from aqueous solutions by adsorption using date palm Leaf Base (LB). The adsorption of congo red dye CR onto LB has been examined in aqueous solution by considering the influence of temperature up to 60°C and pH on the percentage removal of CR. The results showed that the percentage removal of CR increased with increasing temperature and decreased with increasing pH. The Langmuir and Freundlich models have been applied to describe the equilibrium data and the thermodynamic parameters, Gibbs free energy ΔG°, enthalpy change ΔH° and entropy ΔS°, have been determined. The negative value of ΔH suggests that adsorption of CR by the date palm leaf base is exothermic. The positive values of ΔG° at all studied temperatures indicate that CR adsorption is a unspontaneous process. LB is a promising adsorbent for the removal of CR from aqueous solution over a range of concentrations.

Keywords: Adsorption, Date Palm Leaf Base, Congo Red, Thermodynamic Parameters

1. INTRODUCTION

Dyes are used extensively in textile industries. The wastewater from dyeing and finishing operations in the textile industry is generally high in both color and organic content. Exposure to Cong Red dye (CR) can cause allergic reactions. CR contains aromatic amine groups, which are suspected carcinogens (Mozumder and Islam, 2010). A cost-effective dye removal technique is therefore important for industry and environmental protection. The adsorption technique, using different types of adsorbents, is superior to other techniques because of its efficacy, economy, ability to separate a wide range of chemical compounds and easy operational procedures. Recently, researchers have focused on the use of biomaterials as adsorbents for environmental and economical reasons (Khaled *et al*., 2009; Dávila-Jiménez *et al*., 2009; Hameed *et al*., 2009; Tunc *et al*., 2009; Hameed *et al*., 2008; Hameed and El-Khaiary, 2008). Considering that date palm is one of the most cultivated palms around the world, especially in Arab and Middle Eastern countries, utilizing date palm waste to develop new adsorbents for wastewater treatment by adsorption is quite attractive. Thus, this study studies CR removal from aqueous solutions by adsorption using date palm Leaf Base (LB). Removal of day as a function of temperature and pH are investigated and the thermodynamic parameters are calculated.

2. EXPERIMENTAL

2.1. Materials

Date palm Leaf Base (LB) was obtained locally from a farm in the southern region of Riyadh city in Saudi Arabia. It was collected, sorted, cut, ground and sieved to obtain a fine powder. The powder was then kept dry in a closed container until use. No chemical or physical treatments

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were performed prior to the adsorption experiments. The Congo Red (CR) used as an adsorbate was supplied by Techno Pharmchem (Bahadurgarh, India).

2.2. Methods

For the adsorption study, distilled water was used to prepare various solutions at the desired concentrations from the stock solution. For each individual test, 0.5 g of the adsorbent was placed into a screw-capped Erlenmeyer flask containing 25 mL of different concentrations of CR, from 5×10^{-5} to 4×10^{-4} mol/L. The flasks were shaken for a sufficient period to achieve equilibrium at the unadjusted solution pH. The mixture was filtered and the dye uptake was monitored spectrophotometrically (Jenway model 6800 UV/VIS spectrophotometer) by measuring the absorbance at the λ_{max} of 530 nm. The 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 the dry adsorbent (g). The equilibrium data were then fitted using the Langmuir and Freundlich isotherm models.

The effect of pH on the dye adsorption process was investigated by batch equilibrium studies at different pH values in the range of 3-10.

The effect of temperature was studied by calculating the percentage removal of 4×10^{-4} mol L^{-1} dye solution at temperatures up to 60°C.

The thermodynamic parameters calculated to describe the adsorption process onto LB include the changes in standard enthalpy (ΔHº), standard entropy (ΔSº) and standard free energy (ΔGº).

3. RESULTS

3.1. Adsorption Isotherms

The adsorption isotherms indicate how the adsorption molecules are distributed between the liquid phase and the solid phase when the adsorption process reaches equilibrium (Tan *et al*., 2008). **Figure 1** shows the adsorption isotherm of CR onto LB at 25°C.

To find a suitable model for design purposes, the isotherm data analysis includes fitting to different isotherm models. This step has been achieved by applying the linear forms of the Langmuir (Equation 1) and Freundlich (Equation 2) adsorption isotherm models (Sivaramakrishna *et al*., 2014). The applicability of the isotherm equations to describe the adsorption process was judged based on the correlation coefficients R^2 and the maximum value of adsorption:

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

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

where, C_e is the equilibrium concentration, q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mol/g) at equilibriu m and Q_o and b are Langmuir constants related to the adsorption capacity and rate of adsorption, respectively. K_f and n are Freundlich constants related to the adsorption capacity and adsorption intensity, respectively. The constants for all of the adsorption isotherms are listed in **Table 1** and the theoretical plots of these isotherms are shown in **Fig. 2 and 3**.

For the Langmuir model, which suggests monolayer coverage of the dye on the solid surface, plotting $\frac{1}{q_e}$ against $\frac{1}{C_e}$, as represented in **Fig. 2**, yields a straight line, confirming its applicability for describing the adsorption of CR over LB. The correlation coefficient (R^2) for the Langmuir model is 0.976 and the value of Q_o is 0.20×10^{-4} mol g^{-1}. Thus, the experimental adsorption data fit this model fairly well.

To confirm the favorability of the process, the dimensionless constant separation factor or equilibrium parameter (R_L) was calculated as follows (Alshabanat *et al*., 2013):

$$r = \frac{1}{1 + bC_0} \quad (4)$$

where, the value of b was obtained from the Langmuir isotherm. In general, R_L indicates the isotherm type: Irreversible (r = 0), favorable (0<r<1), linear (r = 1) and unfavorable (r<1). The value of (r) in this study is 0.12716, indicating a favorable isotherm.

The equilibrium data are described according to the Freundlich model in **Fig. 3**. The correlation coefficient

(R^2) of the Freundlich model is below 0.90 and the value of the Freundlich constant K_f, which is related to the adsorption capacity, which is presented in **Table 1**, are much higher than the experimental value.

3.2. Effect of Temperature

Figure 4 shows the percentage removal of the dye by the proposed adsorbent. When the temperature is increased from 25 to 60°C, the removal of CR by adsorption increases. An increase in temperature is expected to increase adsorption by decreasing the viscosity of the solution and increasing the mobility of the adsorbate.

3.3. Effect of pH

The effect of pH on CR adsorption onto LB was studied through tests carried out on solutions of various pH as shown in **Fig. 5**, the dye adsorption increased as the pH of the solution decreased, whereas the further increase of pH in alkaline solutions hindered the dye adsorption.

3.4. Thermodynamic Parameters

The thermodynamic parameters for the adsorption of CR onto LB were calculated using the equilibrium constant for CR adsorption, K_d, at different temperatures. The values of this constant were calculated at 25, 40, 50, 60 and 70°C using the following equation (Alshabanat *et al*., 2013):

$$K_d = \frac{\text{dye concentration in adsorbent at equilibriun}}{\text{dye concentration in solution at equilibrium}} \quad (5)$$

The thermodynamic parameters, i.e., the changes in standard free energy (ΔG°), standard enthalpy (ΔH°) and standard entropy (ΔS°), were determined using different equations. ΔG° wascalculated by:

$$\Delta G = -RT \ln K_d \quad (6)$$

The standard enthalpy ΔH° and the entropy change were calculated by the Van't Hoff equation:

$$ln K_d = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \quad (7)$$

As shown in **Fig. 6**, was obtained from the slope of the linear plot of *ln* K_d versus $1/T$, whereas $\Delta S°$ was calculated from the intercept.

Table 2 provides the obtained thermodynamic parameters.

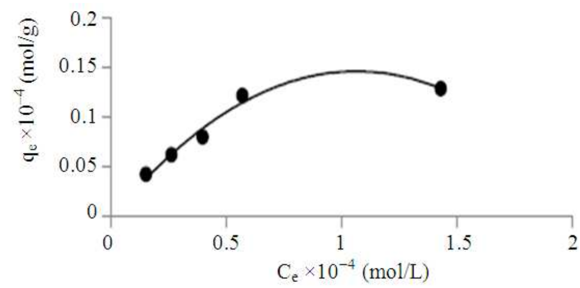

Fig. 1. Adsorption isotherms of CR on LB

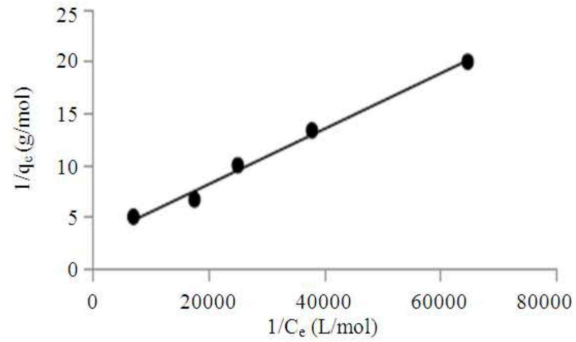

Fig. 2. Langmuir plot for CR adsorption onto LB

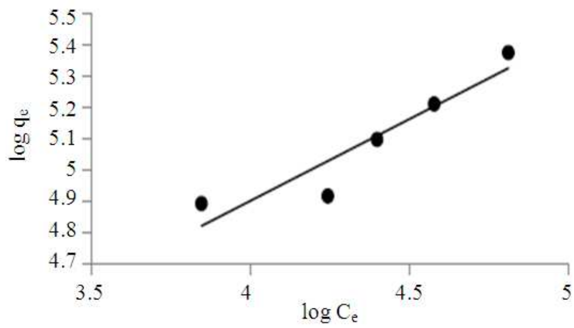

Fig. 3. Freundlich plot for CR adsorption onto LB

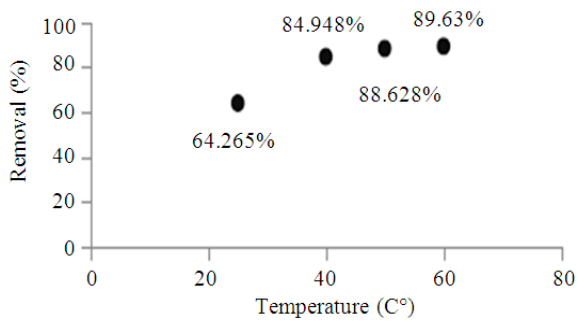

Fig. 4. Effect of temperature on CR adsorption onto LB

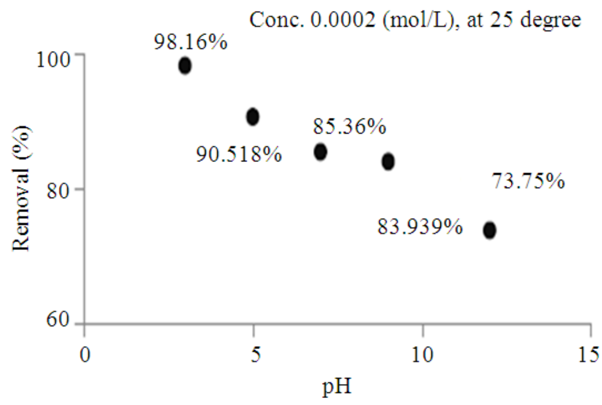

Fig. 5. Effect of pH on CR adsorption onto LB

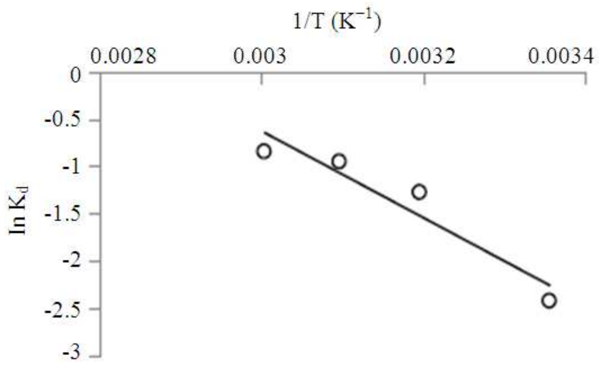

Fig. 6. ln Kd versus 1/T according to the Van't Hoffe equation

Table 1. Values of the constants in the different adsorption models

Langmuir	R^2	Q_e (mol/g)	b (L/mol)
	0.976	0.20×10^{-4}	0.1716×10^5
Frindulish	R^2	K_f	n
	0.876	6.516×10^2	1.919

Table 2. Thermodynamic parameters

T (K)	ΔG° (KJ/mol)	ΔH° (KJ/mol)	ΔS° (J/K.mol)
298	5.968		
313	3.290		
323	2.530		
333	2.320	-11272.95	108.248

4. DISCUSSION

4.1. Adsorption Isotherms

The isotherm is clearly type *L* according to the Giles classification, which indicates that as more sites in the substrate are filled, it becomes increasingly difficult for a bombarding solute molecule to find a vacant site. This finding implies that there is no strong competition from the solvent (Giles *et al*., 1960). Regardless of mechanism, the maximum value is 0.13×10^{-4} mol g^{-1}.

Regression analysis reveals that the Langmuir model fits the experimental data well with correlation factor higher than 0.97 for adsorbent. This indicates that the adsorption mechanism of CR onto LB can be assumed as monolayer coverage and the adsorption is homogeneous, where the adsorption of each adsorbate molecule onto the surface has equal sorption activation energy.

It is pertinent to mention that the Langmuir model is better fitted than Fraundlich model in this study and indicates the formation of the monolayers of the dye on the adsorbent.

4.2. Effect of Temperature

A slight increase in removal of the dye by LB was observed with increasing temperature. This observation revealed that the adsorption process was slightly endothermic. This may be caused by the increased tendency of adsorbate ions mobility with temperature which slightly enhances the removal of CR from the solution by LB (Al-Khatib *et al*., 2012).

4.3. 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 the adsorbate may contain functional groups that can be protonated or deprotonated to produce different surface charges at different pH, resulting in electrostatic attraction or repulsion between the charged adsorbates and adsorbents (Sivaramakrishna *et al*., 2014). The lower adsorption of CR in alkaline media may be due to the presence of excess OH-ions competing with dye anions for the adsorption sites.

4.4. Thermodynamic Parameters

The positive free energy values at all temperatures indicate that the process is unspontaneous. The increase in ΔG° with decreasing temperature suggests greater dye adsorption at high temperatures. The exothermic nature of process was confirmed by the negative value of the enthalpy change ΔH°. Positive values of the entropy change ΔS° indicate the good affinity of the adsorbent towards CR dye.

5. CONCLUSION

Considering the results described above, it can be concluded that CR could be removed onto LB within the used concentration range by adsorption. According to correlation coefficient and experimental and theoretical maximum adsorption capacity, the Langmuir model describes the adsorption process better than the Freundlich model. According to the measurements made in this study, the percentage removal of the dye increases with increasing temperature and decreasing pH.

6. ACKNOWLEGMENT

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