

Removal of Disperse 2BLN Dye from Industrial Water onto Activated Carbon Prepared from Sugar Can Stalks

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Abstract: An activated carbon prepared from sugar can stalks by phosphoric acid treatment was tested for its efficiency in removing disperse 2BLN dye. Different parameters affecting dye removal were studied. These parameters include contact time, initial dye concentration, carbon dose, stirring rate, pH and temperature. Langmuir and Freundlich isotherm models were applied to the equilibrium data. The adsorption capacity (Q_0) obtained from the Langmuir isotherm plot was 27.1 mg/g at an initial pH of 1.5. The temperature variation study showed that dye adsorption is endothermic and spontaneous with increased randomness at the solid solution interface.

Key words: disperse 2BLN dye, adsorption, activated carbon, sugar can stalks.

INTRODUCTION

In recent years, the color of the effluent discharged into receiving waters has become a serious environmental problem. The high level of global production and use of dyes generates colored a huge amounts of wastewaters, which give cause of environmental concern. Textile companies, dye manufacturing industries, pulp mills and paper, electroplating factories, distilleries, food companies and a host of other industries discharge colored wastewater¹. The methods of color removal from industrial effluents include physical, chemical and biological methods²⁻⁴. Among these methods, adsorption appears to have considerable potential for

the removal of color from industrial effluents. Various adsorbents have been tried for the removal of different types of synthetic dyes. Activated carbon is perhaps the most widely used adsorbent for the removal of many organic contaminants which are biologically resistant, but activated carbon is prohibitively expensive. The technology to manufacture activated carbon of good quality is not fully developed in developing countries. Moreover, there are many problems connected with the regeneration used activated carbon. Consequently, the high cost of the activated carbon, coupled with the problems associated with regeneration, has necessitated the search for alternate adsorbents. Therefore, there is a need to

produce activated carbon from cheaper and readily available materials, which can be used economically on a large scale. The abundance and availability of agricultural by-products make them good sources of raw materials for activated carbons⁵. Several wastes and residues have been investigated for the adsorption of dye bearing effluents with varying success⁶⁻⁸. However, new economical, easily available and highly effective adsorbents are still needed.

Disperse blue 2BLN (disperse blue 56, C.I. 63285), 1,5-Diamino-2-chloro-4,8-dihydroxy-9,10-anthracenedione (Fig. 1) is an anthraquinone dye its molecular weight is 365.18 and molecular formula (M.F.: C₁₅H₁₃BrN₂O₄). It is one of the disperse dyes used in textile dyeing.

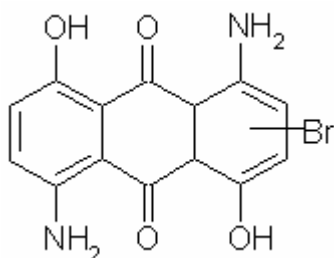


Figure 1. Chemical structure of 2BLN disperse dye

In this work, activated carbon prepared from sugar can stalks by chemical and physical activation was used as an adsorbent to remove 2BLN dye from aqueous solution. The equilibrium and kinetic data on batch adsorption studies were carried out to evaluate the adsorption process. The effect of adsorption parameters such as pH, contact time, adsorbent dose and initial dye concentration on the removal efficiency were also reported to optimize the method.

EXPERIMENTAL

Materials

All chemical reagents were of analytical degree and were used without further purifications. The dye was obtained from commercial market. The stock solutions of 2BLN disperse dye, contains around 200 mg dye/L, were prepared by dissolving the dye in twice distilled water. The working solutions were obtained by diluting the stock solutions with twice distilled water.

Preparation of activated carbon

Sugar can stalks were washed with distilled water and dried in a drier for 2 h at 105 °C until a

constant weight was reached. It was then ground in a ball mill and sieved to particle sizes ranging from 0.3 to 0.5mm. The sieved raw material was then activated by chemical treatment. The activation was carried out by pyrolysis in a muffle furnace in absence of air at 500°C for 2 h and then the sample was soaked in the acid (2 carbon:1 acid) for 24 h. After decantation, the sample was washed with distilled water several times and then dried in an oven at temperature of 110 °C overnight. The activated carbon was kept in a closed container till use.

Adsorption studies

Batch adsorption experiments were carried out at room temperature (25°C±1). Exactly 25 ml of dye solution of known initial concentration (50 mg/l) was stirred at a constant stirring rate (200 rpm) with a required dose of adsorbents (2-10 g/l) for a specific period of contact time (5–120 min) using a magnetic stirrer, after noting down the initial pH of the solution to the optimum pH. The pH of the solutions were adjusted to the required value by adding either 1M HCl or 1M NaOH solution. After equilibrium, the final concentration (C_e) were measured using absorbance values with a JascoV-530 (UV-Vis) spectrophotometer (Japan) and compared with the absorbance values of the initial solutions. The absorbance was measured at 542 nm. Experiments were carried out in duplicate and mean values are presented. The percentage removal of dye were calculated using the following relationship:

$$\% \text{ Dye Removal} = \frac{C_0 - C_e}{C_0} \quad (1)$$

where C_0 and C_e are the initial and final (equilibrium) concentrations of dye (mg/l), respectively. Blanks containing second distilled water were used for each series of experiments as controls. The amount of dye adsorption per unit mass of AC at equilibrium, q_e (mg/g) was calculated by the following equation:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (2)$$

where V is the volume of the dye solution (ml) and W is the weight of AC (g) added to volume V .

Results and Discussion

Effect of contact time

The effect of contact time on the percentage removal of the dye was investigated at initial dye concentration 50 mg/l as shown in Fig. 2.

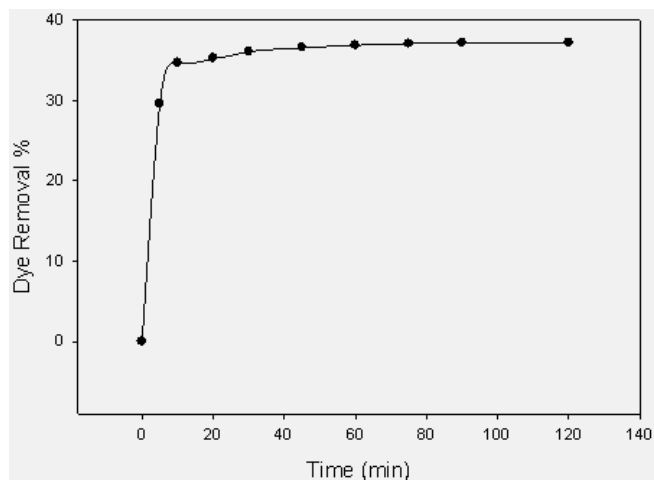


Figure 2. Effect of contact time on the removal of 2BLN disperse dye by AC at pH 1.5, dose of adsorbent 2 g/l and at C_0 50 g/l.

The percentage removal of dye by different activated carbons was rapid in the beginning due to larger surface area available of adsorbent but it gradually decreased with time until it reached equilibrium. The plots reveal that maximum percent removal of the dye after about 1 h of continuous stirring. After adsorption, the rate of dye uptake is controlled by the rate of dye transported from the exterior to the interior sites of the adsorbent particles.

Effect of pH

pH plays an important role in the adsorption capacity. The effect of initial pH of dye solution on the percentage removal of dye was studied by varying the initial pH under constant process parameters. The results are shown in Fig. 3. The dye adsorbed by AC was higher at lower pH, so the optimum pH was attained at highly acidic solution. The same behavior was observed by many authors^{9,10}. Maximum removal of the dye (about 37.4%) was achieved at pH 1.5. As the pH was increased from 1.5 to 7.0 the removal percent decreased to 32.8%. Thereafter, the percent removal remained low up to pH 11.0 (38.6%). It was reported that solution's pH would affect active surface sites of adsorbents¹¹. In acidic condition, the positive charge dominates the surface of the adsorbent. This attractive force increases the adsorption chances of dye species onto the surface of the adsorbent. As the pH

increases, the surface of the adsorbent tends to become negatively charged, which does not favor the adsorption of disperse dyes due to electrostatic repulsion. At the same time, the presence of excess OH^- ions in alkaline conditions will compete with the dye anions for the adsorption sites¹².

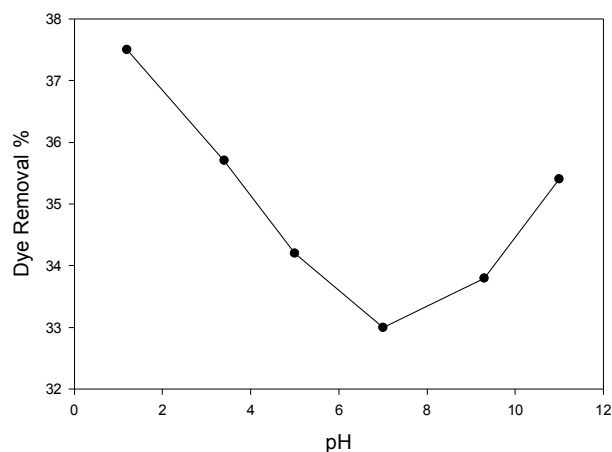


Figure 3. Effect of different pH on the removal of 2BLN disperse dye by AC adsorbent at C_0 50 mg/L dye, 60 min and 2 g/L of adsorbent.

Effect of initial dye concentration

Fig. 4a. shows the effect of contact time on the removal of disperse dye by AC for different initial dye concentrations (50, 100, 150, 200 mg/l). The adsorption amount increased with an increase in initial dye concentration. This is because a higher initial concentration enhanced the driving force between the aqueous and solid phases and increased the number of collisions between dye ions and adsorbents¹³.

Effect of adsorbent dose

The influence of adsorbent dosage on dye removal by AC in individual dyes is presented in Fig. 4b. The percentage of removal of the dye increased from 38.5% to 75.5% as the AC dose was increased from 0.05 to 0.25 g/l. The increased removal at high dosages is expected, because of the increased adsorbent surface area and availability of more adsorption sites¹⁴.

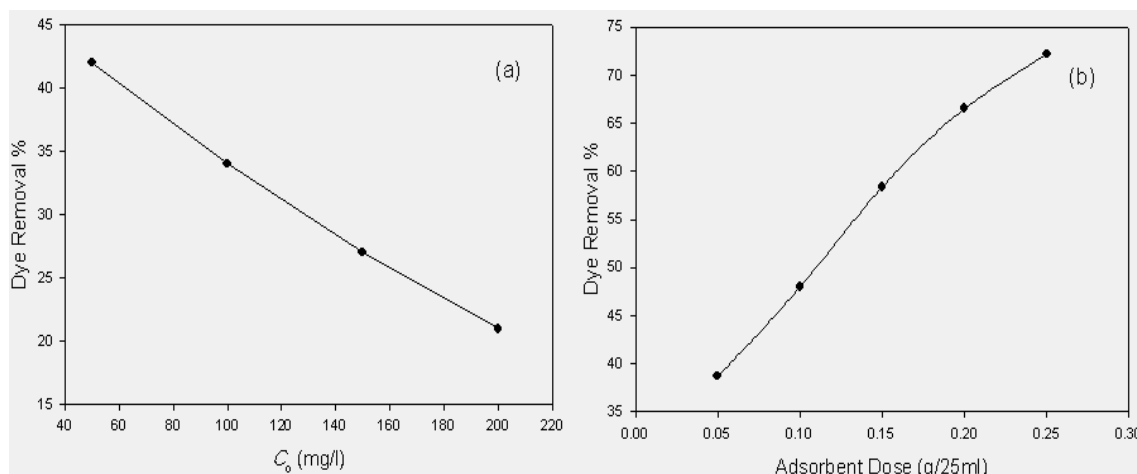


Figure 4. Effect of (a) initial dye concentration at 2 g/l of AC (b) adsorbent dose on the removal of disperse 2BLN dye by AC ($C_0 = 50$ mg/l of adsorbent and pH 1.5.

Effect of ionic strength

Generally, various salts and metal ions exist in dye containing wastewater. These salts lead to high ionic strength, which may affect the dye adsorption onto adsorbents. Fig. 5a. shows the effect of ionic strength on dye uptake. The amount of disperse dye adsorbed showed a remarkable increase in the dye uptake with increasing ionic strength. This increase is an expected and previously reported behavior¹⁵. The reason is that increase in the ionic strength increases the positive charge of the surface, thus increases the electrostatic interaction between the active groups in

the dye and AC. Similar results were obtained with different adsorbents with different dyes^{16,17}.

Effect of Stirring rate

The effect of agitation speed on the dye adsorption (Fig. 5b) at the adsorbent dosage of 2.0 g/l, initial dye concentration of 50 mg/L, pH 7.2. This effect can be attributed to the increase in turbulence and the decrease in boundary layer thickness around the adsorbent particles as a result of increase in the degree of mixing. This result also indicates that external mass transfer was the rate limiting step¹⁸.

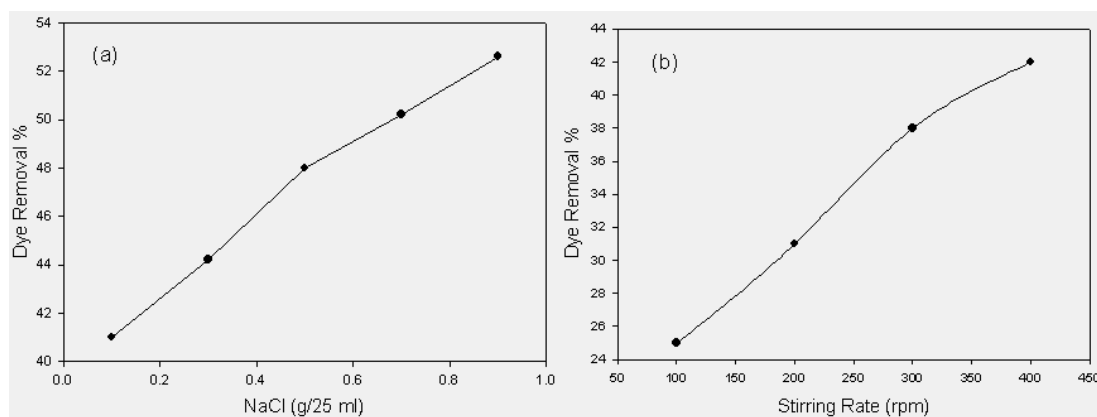


Figure 5. Effect of (a) ionic strength and (b) stirring rate on the removal of disperse 2BLN dye by AC at pH 1.5, initial dye concentration 50 mg/l at equilibrium and 2 g/l of AC.

Effect of temperature

Adsorption experiments were carried out for 100 mg/l eosin at four different temperatures (20, 30, 40 and 50 °C) using 2.0 g of activated carbon per liter of the solution in order to observe the effect of temperature on the adsorption capacity. It was observed that with an increase in temperature, adsorption capacity decreased as shown in table 1.

Table 1. Effect of temperature on removal percent of disperse 2BLN dye on AC

Temperature (°C)	Dye Removal %
20	26.5
30	38.0
40	47.5
50	52.0

Adsorption isotherms

The adsorption data were analyzed using adsorption isotherm models, Langmuir and Freundlich. The Langmuir model¹⁹ is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface. The expression of the Langmuir model is given by the following equation:

$$q_e = \frac{Q_0 b C_e}{1 + b C_e} \quad (1)$$

where q_e (mg/g) and C_e (mg/l) are the amount of adsorbed dye per unit mass of sorbent and dye concentration in solution at equilibrium, respectively. Q_0 is the maximum amount of the adsorbed dye per unit mass of sorbent to form a complete monolayer on the surface bound at high C_e (mg/g), and b (L/mg) is a constant related to the affinity of the binding sites on the adsorbent surface.

The linear form of the Langmuir equation is written as follows:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (2)$$

A plot of (C_e/q_e) versus C_e should be a straight line with a slope of $1/Q_0$ and intercept $1/Q_0 b$. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L that is given by the following equation [20]:

$$R_L = \frac{1}{1 + b C_0} \quad (3)$$

where C_0 represents the initial concentration (mg/l) and b the Langmuir constant related to adsorption energy (l/mg). R_L value implies the shape of the isotherms to be either unfavorable (R_L), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$)²¹. As can be seen in Table 2, for the sorption system, R_L values at different temperatures are between 0 and 1, showing favorable adsorption ($C_0 = 50$ mg/l). All R_L values at different temperatures and concentrations were between 0 and 1.

The Freundlich model²² assumes heterogeneous adsorption due to the diversity of active sites on the surface. The Freundlich equation is expressed as:

$$q_e = K_F C_e^{1/n} \quad (4)$$

where K_F (mg/g) is an indicator of the biosorption capacity and $1/n$ (l/mg) is the biosorption intensity. A value for $1/n$ below one indicates a normal Freundlich isotherm while $1/n$ above one is an indicative of cooperative adsorption²³.

Eq. (4) can be written in the logarithmic form as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (5)$$

A plot of $\log q_e$ vs. $\log C_e$ is shown in Fig. 7, where the values of K_F and $1/n$ are determined from the intercept and slope of the linear regressions (Table 2). As seen, a very high regression correlation coefficient was shown by the Langmuir model. This indicates that the Langmuir model was very suitable for describing the sorption of disperse 2BLN dye on AC.

Table 2 . Langmuir and Freundlich constants of adsorption of 2BLN on AC

Langmuir Constants				Freundlich Constants		
Q_0 (mg/g)	b (L/mg)	R^2	R_L	K_F	$1/n$	R^2
27.10	0.0238	0.9935	(0.173-0.456)	2.669	0.4221	0.9446

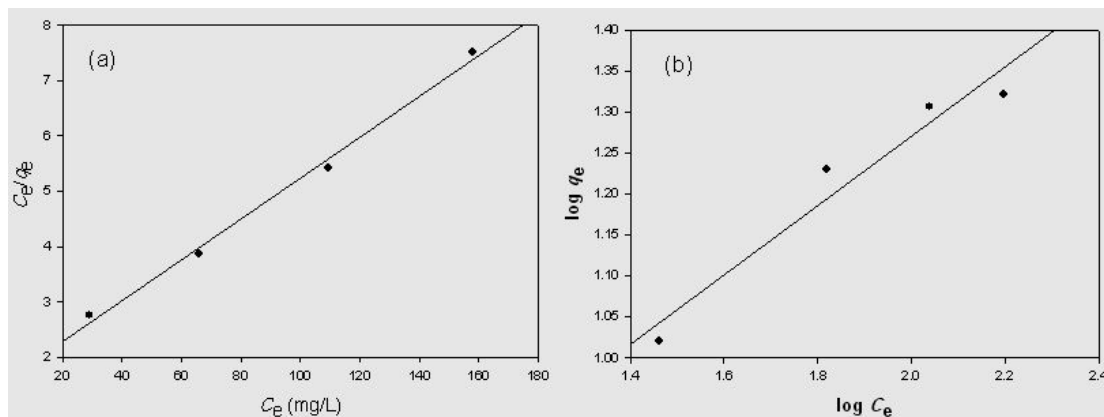


Figure 6. (a) Langmuir and (b) Freundlich isotherm plots of adsorption of disperse 2BLN dye on AC.

The maximum capacity Q_0 determined from the Langmuir isotherm defines the total capacity of the AC for the dye as 27.1 mg/g sorbent. The fact that the Langmuir isotherm fits the experimental data compared to Freundlich isotherm may be due to the homogeneous distribution of active sites on the surface of sorbent.

Effect of Temperature

The adsorption capacity of the carbon increased with increase in the temperature of the system from 20° to 50°C. Thermodynamic parameters such as change in free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) were determined using the following equations²⁴.

$$K_s = C_{\text{solid}}/C_{\text{liquid}} \quad (6)$$

$$\Delta G^\circ = -RT \ln K_s \quad (7)$$

$$\log K_s = \Delta S^\circ / (2.303RT) - \Delta H^\circ / (2.303RT) \quad (8)$$

Where, K_s is the equilibrium constant, C_{solid} is the solid phase concentration at equilibrium (mg/l), C_{liquid} is the

liquid phase concentration at equilibrium (mg/L), T is the temperature in Kelvin, and R is the gas constant. The ΔH° and ΔS° values obtained from the slope and intercept of the Van't Hoff plots have been presented in Table 3. The increase in surface coverage with increasing temperature may be attributed to increased penetration of reactive dyes inside micropores at higher temperatures or to the creation of new active sites²⁵.

As shown in Table 3, The positive values of ΔH° show the endothermic nature of adsorption and it governs the possibility of physical adsorption. ΔH° value suggests that adsorption process is physisorbed onto AC²⁶. The enthalpy of adsorption of organic molecules from aqueous solution on activated carbon is usually within the range 8-65 kJ/mol²⁷. Enhancement of the adsorption capacity of the activated carbon at higher temperatures has been attributed to the enlargement of pore size and activation of the adsorbent surface²⁶.

Table 3. Thermodynamic parameters for adsorption of disperse 2BLN dye on AC

T (°C)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)
293	0.8536		
303	-0.4131	29.09	96.37
313	-1.3868		
323	-2.3605		

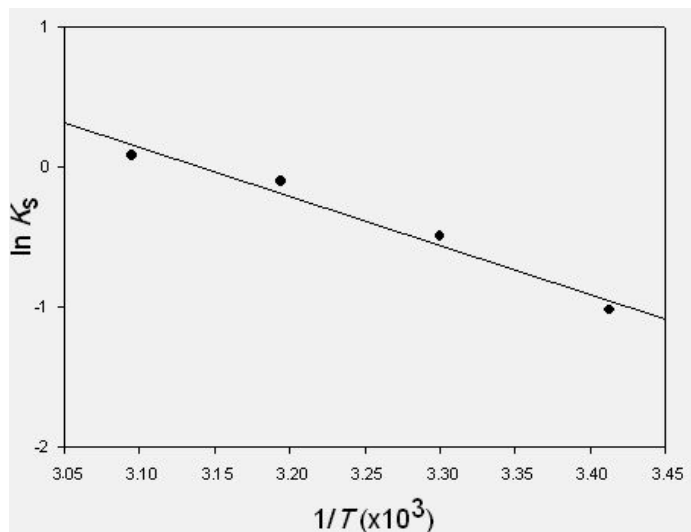


Figure 7. Effect of temperature for the removal of disperse 2BLN dye on AC.

Gibbs free energy of adsorption (ΔG°) was calculated from the following relation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

The negative values of ΔG° (Table 3) indicated (Table 3), the feasibility of the process and the spontaneous nature of adsorption at temperatures higher than 20°C. These results indicated the non-spontaneous nature of the adsorption process at lower temperatures being. This phenomenon had also been observed in the adsorption of other organic molecules on palm pith carbon²⁸.

Conclusion

The results of different experiments showed that activated carbon derived from maize stalks has an ability to adsorb disperse 2BLN dye from aqueous

solutions. Different variables, such as contact time, adsorbent dose, solution pH and temperature influenced the adsorptive quantity. The sorption process was found to be pH dependent. The adsorption process has nearly reached equilibrium in 60 min and the optimum pH is near 1.5. The experimental data of adsorbing disperse 2BLN dye are fit well to Langmuir isotherm model more than Freundlich model and the maximum adsorptive quantity of activated carbon was 27.1 mg/g according to Langmuir model. The adsorptive process is endothermic and spontaneous. These values obtained from thermodynamic parameters demonstrated that adsorption process is physical in nature and the adsorption process is endothermic and spontaneous.

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