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Research Article

ADSORPTION OF METHYLENE BLUE ONTO *CISSUS QUADRANGULARIS*

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ABSTRACT
The removal of the textile dye methylene blue (MB) was studied by adsorption on *Cissus quadrangularis*. The batch technique was adopted under the optimized condition of the amount of adsorbent, contact time, concentration, temperature, and pH. The removal data were fitted into the Freundlich and Langmuir adsorption isotherm equations. The values of their corresponding constants were determined. Thermodynamic parameters like free energy, enthalpy, and entropy of the systems were calculated using Freundlich constant. The values of the rate constants and percentage removal of the dye MB were calculated at different temperatures in the range 303–323 K. The present study shows that about 67% removal of MB was observed on *Cissus quadrangularis*.

Keywords: *Methylene Blue, Adsorption, Cissus Quadrangularis*

INTRODUCTION
Dyes are widely used in many industries, mainly in textile industries. Effluents let off from those industries often cause serious environmental problems due to their deep color. These effluents need pretreatment for color prior to disposal into any water body. Due to large amounts of metal complexes present in the dyes, most commercial dyes are treated with difficulty by the conventional biodegradation or chemical oxidizing method. Liquid-phase adsorption of dyes from streams by various adsorbents becomes one of the major treatments for such wastewater, because this process is simple, inexpensive and easy to design. Activated carbon, due to its effectiveness, is the most widely used adsorbent. Many researchers (McKay *et al.*, 1985, 1988, 1990, 1991; Juang *et al.*, 1996) have reported on the adsorption of dyes onto activated carbon. With the exception of activated carbon, the use of other low-cost adsorbents has also been the focus of recent research. These include silica gel (Alexander *et al.*, 1978), clays, sawdust (McKay *et al.*, 1986), bagasse pith, peat (McKay *et al.*, 1988) and fly ash (Gupta *et al.*, 1990).
The purpose of this work is to obtain the equilibrium relationship and a model that describes the contact time of the adsorption of the dye, Methylene Blue (MB) on *Cissus quadrangularis* as adsorbent. The common name of the plant *Cissus quadrangularis* is Bonesetter and also it is called Pirandai (in Tamil). The adsorbent carbon was prepared from the plant (Bonesetter) *Cissus quadrangularis* (BSC-Bonesetter carbon). The plant Bonesetter itself has its own medicinal importance. The whole plant is used to cure injuries, muscular pain, sprains, diarrhoea, piles, stomach ailments, ulcer and asthma. The molecular structure of the adsorbate methylene blue (MB) is shown in Figure 1.

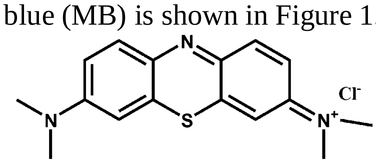

Figure 1: The chemical structure of methylene blue (MB)

MATERIALS AND METHODS

Reagents: Reagents include methylene blue (MB) (Merck), hydrochloric acid (Merck) and sodium hydroxide (Merck). All chemicals used in the present investigation were of spectroscopic grade.

Preparation of adsorbent carbon (BSC)

The stem parts of the Bonesetter plant were collected, washed with water, and dried under shadow. The dried materials were powdered and treated with concentrated sulphuric acid. The carbonized material was washed repeatedly with distilled water to remove free acid and dried at 110^{o} C. The dried carbon was finally crushed and sieved through 75, 150, 300 and 425 μm sieves. The chemical analysis of carbon was done by standard methods (Vogel, 1961; Snell *et al.*, 1994).

Experimental

Batch adsorption experiments were conducted by shaking 0.1g of Bonesetter carbon (BSC) with 50 mL aqueous solution of dye (MB) at different concentrations, temperatures and pH values. The pH values ranged from 2 to 10. 1.0 N HCl and 1.0 N NaOH were used for pH adjustment. The adsorbent was removed by centrifugation and the concentration of dye in the supernatant liquid was determined spectrophotometrically.

RESULTS AND DISCUSSION

Effect of contact time

The time dependent behavior of the dye adsorption was examined by varying the contact time between MB and BSC in the range of 10 to 60 min. The concentration of MB was kept as 10 ppm while the amount of adsorbent added was 0.1 g of BSC. The amount of dye adsorbed (in mg/g and per cent) is given in Table 1. The dye removal capacity plotted as a function of contact time is shown in Figure 2. This indicates that the equilibrium between the dye and the adsorbent was attained within 50 min. Therefore, 50 min shaking time was found to be appropriated for the maximum adsorption and was used in all subsequent experiments. The curves are smooth and continuous, leading to saturation. This suggests the possible monolayer coverage of the dyes on the carbon surface (Senthikumar et al., 2005). The observed percentage removal of MB was 59 with BSC in 50 min.

Table 1: Percentage removal of methylene blue (MB) using BSC at various contact times

SI No.	Contact time (min)	Initial concentration of MB (ppm)	Final concentration of MB (ppm)	Amount of MB adsorbed	q_e	log C_e	log q_e	K min^{-1}	% removal of MB
1	10	10	8.85	1.15	11.5	0.94	1.06	0.02	11.5
2	20	10	8.33	1.67	16.7	0.92	1.22	0.02	16.7
3	30	10	6.43	3.57	35.7	0.80	1.55	0.03	35.7
4	40	10	5.28	4.72	47.2	0.72	1.67	0.03	47.2
5	50	10	4.68	5.32	53.2	0.67	1.72	0.03	53.2
6	60	10	4.10	5.90	59.0	0.61	1.77	0.03	59.0

Effect of adsorbent dosage

The effect of various adsorbent dosages of BSC on MB was studied keeping other parameters, like contact time (50 min), initial dye concentration (10 ppm) and pH 4 as constants at 303 K. The amount of dye adsorbed (in mg/g and percent) is given in Table 2. The dye removal capacity plotted as a function of adsorbent dosage is shown in Figure 3. A significant increase in percentage removal of MB with increase in adsorbent dosage was observed as expected. This has been attributed to the fact that an increase in the adsorbent dosage increases the surface area of carbon which provides more adsorption sites which in turn enhances the percentage of dye removal (Hema *et al.*, 2007). The rate of adsorption depends on the driving forces per unit area in this case since the increase in the adsorbent dosage increases the surface area available for adsorption; hence percentage removal of MB increases. The percentage removal for initial concentration of 10 ppm of MB for contact time of 50 min with a dosage of 0.1 g of BSC was 89.

Table 2: Percentage removal of methylene blue (MB) using BSC at various adsorbent dosages

SI No.	Adsorbent dosage (g)	Initial concentration of MB (ppm)	Final concentration of MB (ppm)	Amount of MB adsorbed	q_e	log C_e	log q_e	K min^{-1}	% removal of MB
1	0.025	10	2.11	7.89	315.6	0.32	2.49	0.05	78.9
2	0.050	10	1.82	8.18	163.6	0.26	2.21	0.06	81.8
3	0.075	10	1.25	8.75	116.6	0.09	2.06	0.07	87.5
4	0.1	10	1.09	8.91	89.1	0.03	1.94	0.08	89.1
5	0.125	10	1.06	8.94	71.5	0.02	1.85	0.08	89.4
6	0.150	10	1.03	8.97	59.8	0.01	1.77	0.08	89.7

Effect of pH

Of all experimental parameters affecting MB sorption, the influences of initial pH has significant role as it alters the surface charge of the adsorbent. The initial pH of the dye solutions were adjusted to pH 2, 4, 6, 8, and 10. The amount of dye adsorbed (in mg/g and percent) is given in Table 3. Dye adsorption was determined by fixing the other parameters as constants and the results are given in Figure 4. The pH of the working solution was controlled by adding HCl or NaOH solution. It is apparent from the figure that the percentage removal of MB was increasing with increase in acidity and there was no significant increase in the dye removal while increasing the alkalinity (Ravichandran *et al.*, 2010). Hence, throughout the study, the pH of the medium was maintained at pH 4.

Table 3: Percentage removal of methylene blue (MB) using BSC at various pH values

SI No.	pH	Initial concentration of MB (ppm)	Final concentration of MB (ppm)	Amount of MB adsorbed	q_e	log C_e	log q_e	K min^{-1}	% removal of MB
1	2	10	1.25	8.75	87.5	0.94	1.94	2.39	87.5
2	4	10	1.83	8.17	81.7	0.91	1.91	0.97	81.7
3	6	10	3.50	6.50	65.0	0.81	1.81	0.40	65.0
4	8	10	3.64	6.36	63.6	0.80	1.80	0.29	63.6
5	10	10	3.73	6.27	62.7	0.79	1.79	0.22	62.7

Effect of dye concentration

The effect of concentration of MB on the BSC was studied at constant contact time, temperature and pH. The percentage removal of dye gets increased with increase in concentration of the dye. The initial MB concentrations were set at 10, 20, 30, 40, and 50 ppm with adsorbent dosage of 0.1 g for a contact time of 60 min. The percentage removal of MB gets increased gradually as 67, 74, 79, 81, and 97 respectively with the increase in dye concentrations. The rate constants for the removal of MB with BSC for varying dye concentrations were calculated.

Adsorption isotherms

The quantity of dye that could be taken up by an adsorbent is measured as a function of both the concentration of the dye and the temperature. The amount of dye adsorbed is determined as a function of different concentrations at constant temperature, which could be explained by adsorption isotherms. In this study, two most commonly used isotherms, namely Freundlich and Langmuir have been adopted. The observed data on the adsorption of the dye at different temperatures have been analyzed on the basis of the Langmuir isotherm model.

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

Where Q_0 = Langmuir constants related to the capacity and b = Langmuir constants related to the energy of adsorption.

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The linear plot of C_e/q_e *Vs* C_e (Figure 5) confirms that in the present investigation, Langmuir isotherm model is suitable in explaining the adsorption process and also indicates the monolayer coverage of the dyestuffs onto the outer surface of the BSC (McKay *et al.*, 1985). The Q_0 and b values, as given in Table 4, are obtained from the slope and intercepts of the linearized plots of the Langmuir isotherm. The values of correlation coefficient, r, obtained from linear plot (Figure 5) are listed in Table 4. The values are very close to unity which indicates the applicability of Langmuir isotherm model.

Table 4: Langmuir isotherms for the sorption of MB on BSC

Adsorbent	Temp. K	Q^o, mg/g	b, L/g	r	sd	R_L	X^2
BSC	303	9.257	0.018	0.966	0.010	0.422	0.001
	313	8.968	0.019	0.980	0.014	0.444	0.004
	323	8.124	0.021	0.986	0.027	0.401	0.006

The equilibrium adsorption data at different dye concentrations are fitted with Freundlich isotherm model (McKay *et al.*, 1985)

$$q_e = K_f C_e^{\,n}$$

$$\log q_e = \log K_f + n\log C_e$$

Where *n* and K_f (mg/g) are Freundlich constants related to the intensity of adsorption and adsorption capacity, respectively. The plot of log q_e against log C_e is shown in Figure 6. The values of Kf and n are calculated from the intercept and slope of these linearized plots and are listed in Table 5 along with the r values. The r values are very close to unity, which indicate that Freundlich isotherm is applicable.

Table 5: Freundlich isotherms for the sorption of MB on BSC

Adsorbent	Temp. K	1/n	n	KF,mg/g 1/n(L/mg)	r	sd	X^2
BSC	303	0.218	0.896	0.322	0.952	0.018	0.006
	313	0.259	0.842	0.244	0.919	0.046	0.006
	323	0.281	0.784	0.201	0.914	0.035	0.008

The values of K_f and Q, the respective Freundlich and Langmuir constants, decrease with increase in temperature, showing the temperature dependence of the rate of sorption. The decrease in adsorption with increase in temperature suggests weak adsorption between the surface and sorbents, which supports physisorption. From the r values, it is found that the Langmuir model is the best-fit model for the adsorption of MB onto BSC than the Freundlich model.

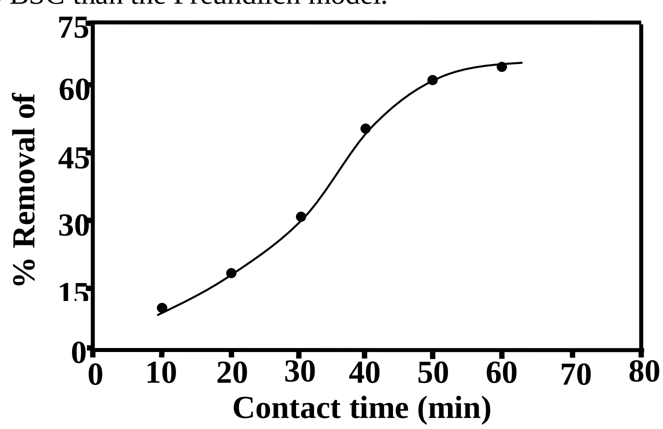

Figure 2: Effect of contact time on the adsorption with the initial concentration of 10 mg/L on 0.1 g of BSC.

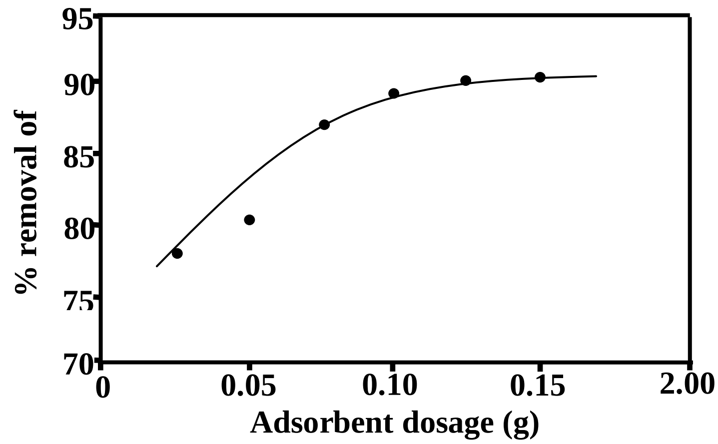

Figure 3: Effect of adsorbent dosage on the removal of dye.

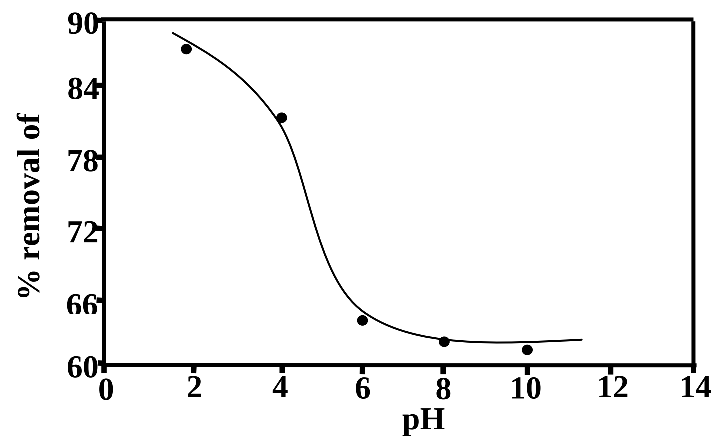

Figure 4: Effect of pH on the removal of dye

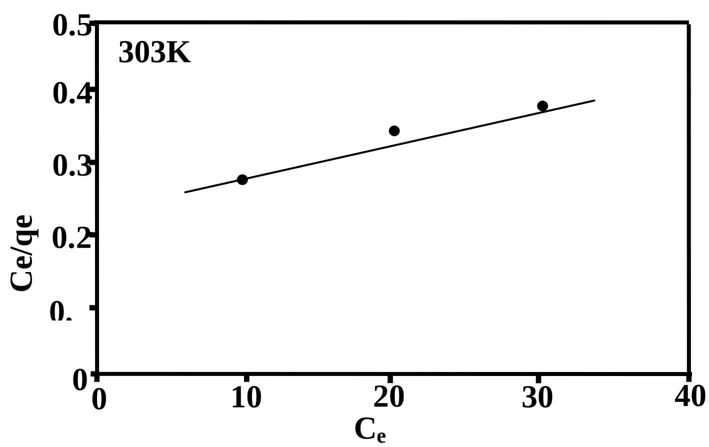

Figure 5: Langmuir isotherm of sorption of MB on BSC at 303K

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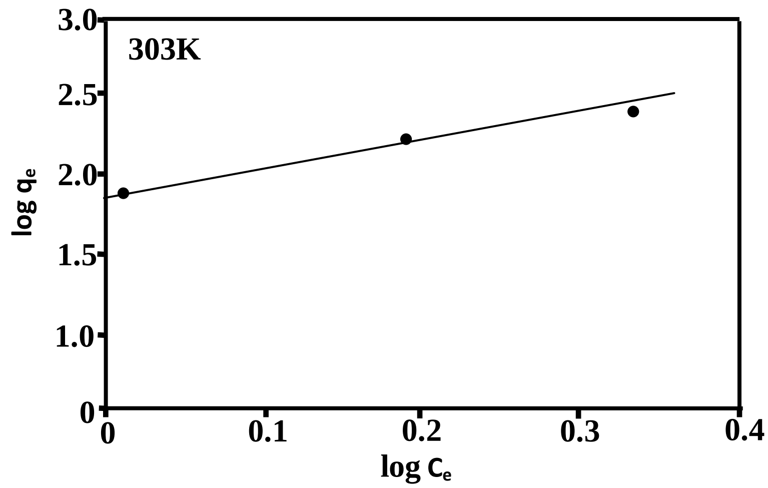

Figure 6: Freundlich isotherm of sorption of MB on BSC at 303K

Conclusion

The adsorption of methylene blue (MB) on *Cissus quadrangularis* is explained well by the Langmuir and Freundlich isotherm models. The fitness of Langmuir's model indicates the formation of monolayer coverage of the adsorbate on the outer surface of the adsorbent. The removal of dye between 65 and 96 percent is quite significant and it indicates that *Cissus quadrangularis* is a potent adsorbent for the removal of MB from textile waste water.

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