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ORIGINAL ARTICLE

Removal of methylene blue by adsorption onto activated carbon developed from *Ficus carica* bast



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Abstract In this study, activated carbon was developed from *Ficus carica* bast (FCBAC). The experiments were carried out to explore methylene blue (MB) uptake by FCBAC. The influence of various experimental factors such as contact time, initial dye concentration, adsorbent dosage, temperature and pH of dye solution was investigated. The adsorption equilibrium was represented with Langmuir, Freundlich and Temkin isotherm models. Langmuir and Temkin equations were found to have the correlation coefficient value in good agreement. Adsorption of MB onto FCBAC followed pseudo second order kinetics. The calculated values of ΔH° , ΔS° and ΔG° were found to be 21.55 kJ/mol, 76.24 J/mol K and -1.55 kJ/mol, respectively. Adsorption process was spontaneous and endothermic in nature.

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1. Introduction

Effluents from dyeing and other related industrial processes are known to contain highly colored species. Over 10,000 dyes with a total yearly production over 7×10^5 MT are commercially available. It is estimated that approximately 15% of the dye stuffs are lost in industrial effluents during manufacturing and processing operations (Auta and Hameed, 2011; Tunc et al., 2009; Gupta et al., 2012). Highly colored wastes are not only esthetically unpleasant but also hinder light pen-

etration and may disturb the ecosystem. Moreover, dyes itself are toxic to some organism. Methylene blue (MB) is a cationic dye having various applications in chemistry, biology, medical science and dyeing industries. Its long term exposure can cause vomiting, nausea, anemia and hypertension (Foo, 2012; Hameed, 2009).

Various physical, chemical and biological methods, including adsorption, biosorption, coagulation/flocculation, advanced oxidation, ozonation, membrane filtration and liquid–liquid extraction have been widely used for the treatment of dye-bearing wastewater. The advantages and disadvantages of every removal technique have been extensively reviewed (Hameed, 2009; Salleh et al., 2011). The removal of dyes in an economic way remains an important issue for researchers and environmentalists. Adsorption is a very effective separation technique in terms of initial cost, simplicity of design, ease of operation and insensitive to toxic substances. Activated carbon (powdered or granular) is the most efficient adsorbent used for dye removal. But it is expensive to produce

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and regenerate (Gupta and Suhas, 2009; Salleh et al., 2011). During last decade, a number of non conventional, low cost adsorbent such as rice hull ash, sugarcane bagasse, sawdust, pine needle, eucalyptus bark, prawn shell activated carbon, and mango seed kernel powder have been used for the removal of dyes and heavy metal ions from aqueous solution (Sud et al., 2008; Salleh et al., 2011).

Ficus carica is a monoecious and deciduous tree. Its bark, leaves, tender shoots, fruits, seeds, and latex are used to cure many diseases (Gilani et al., 2008). The porous wood and bast are of little use and considered a waste product. To the best of our knowledge, no study has been reported on the preparation of activated carbon from *Ficus carica* bast fiber. Therefore, the main objective of this study was to evaluate the possibility of using *Ficus carica* bast to develop a new low cost activated carbon and study its application to remove methylene blue dye from aqueous solution. Kinetics, thermodynamic studies and adsorption isotherm models were investigated to evaluate experimental data.

2. Materials and methods

2.1. Adsorbent

Ficus carica bast was collected from the locally available plant in Solan, Himachal Pradesh, India. The bast was washed several times with distilled water to remove adhered impurities from its surface. The biomass was dried at 105 °C for 24 h. The dried biomass was milled and sieved to 10 µm particle size. The dried biomass (1.0 kg) was added in small portion to 800 mL of 98% H₂SO₄ during 6 h and the resulting reaction mixture was kept overnight followed by refluxing for 12 h in fumehood. After cooling to room temperature, the reaction mixture was poured onto cold water (3 L) and filtered. The resulting material was heated in an oven at 150 °C for overnight followed by washing with 3 L distilled water and then soaked in 1% NaHCO₃ solution overnight to remove any acid. The obtained carbon was washed with distilled water until pH of activated carbon reached six and dried in oven at 150 °C for 24 h. The resulting activated carbon (FCBAC) was preserved and used as an adsorbent. FCBAC was characterized by using FTIR, SEM and EDS techniques.

2.2. Adsorbate

Methylene blue (C₁₆H₁₈N₃SCl.3H₂O) was obtained from E. Merck, India and was used without further purification. The solution was prepared by dissolving the required amount of dye in distilled water.

2.3. Experimental protocol

The batch adsorption experiments were conducted in a set of 250 ml of Erlenmeyer flask containing adsorbent and 100 ml of MB solution with various initial concentrations. The flasks were agitated in an isothermal water-bath shaker at 120 rpm and 30 ± 1 °C until the equilibrium is reached. After decantation and filtration, the equilibrium concentrations of dye in the solution were measured at 665 nm using UV-visible spectrophotometer. The pH of solution was adjusted with 1N HCl

and 1N NaOH solutions. The amount of dye adsorbed and percentage removal of MB were calculated using Eqs. (1) and (2), respectively:

$$q_e = (C_0 - C_e) \frac{V}{M} \quad (1)$$

$$\% \text{Removal} = \frac{C_i - C_e}{C_i} \quad (2)$$

where:

q_e amount of dye in mg per gram of adsorbent.

C_i and C_e are respectively initial concentration and equilibrium time of MB (mg/l).

V volume of solution.

M mass of adsorbent.

2.4. Adsorption isotherm

2.4.1. Langmuir isotherm

The Langmuir sorption isotherm is applied to equilibrium sorption assuming monolayer sorption onto a surface with a finite number of identical sites.

The Langmuir equation is written as (Langmuir, 1916):

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L q_m C_e} \quad (3)$$

The shape of this isotherm can also be expressed in terms of separation factor (R_L), which is given as follows (Foo, 2012):

$$R_L = \frac{1}{1 + K_L C_0} \quad (4)$$

where K_L is Langmuir constant (L/mg) related to the affinity of binding sites and the free energy of sorption. q_e is dye concentration at equilibrium onto biosorbent (mg/g). C_e is dye concentration at equilibrium in solution (mg/l).

q_m is dye concentration when monolayer forms on biosorbent (mg/g).

2.4.2. Freundlich isotherm

The Freundlich equation for heterogeneous surface energy systems is given by Eq. (5) (Foo, 2012; Nemr et al., 2009).

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

where K_F and n are Freundlich constants, determined from the plot of $\ln q_e$ versus $\ln C_e$. The parameters K_F and $1/n$ are related to sorption capacity and the sorption intensity of the system. The magnitude of the term $(1/n)$ gives an indication of the favorability of the sorbent/adsorbate systems (Malik, 2003).

2.4.3. Tempkin isotherm

The linearized Tempkin equation is given by the following equation. (Foo, 2012; Wang and Qin, 2005).

$$q_e = \beta \ln \alpha + \beta \ln C_e \quad (6)$$

where $\beta = \frac{RT}{b}$

T is the absolute temperature in Kelvin, R is the universal gas constant (8.314 J/mol K), and b is the Tempkin constant related to heat of sorption (J/mg). The Tempkin constants α and b are calculated from the slope and intercept of q_e versus $\ln C_e$.

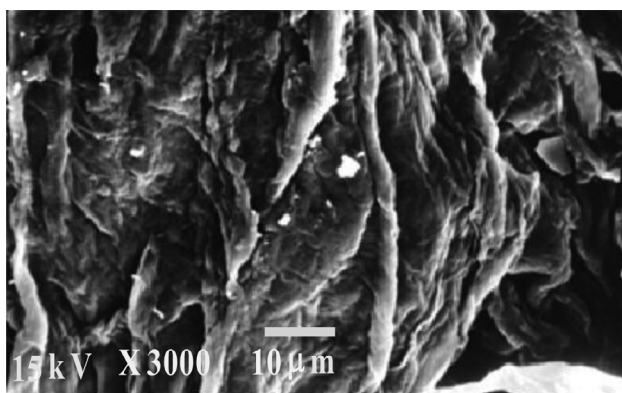


Figure 1 SEM micrograph of FCBCAC at 3000 magnification.

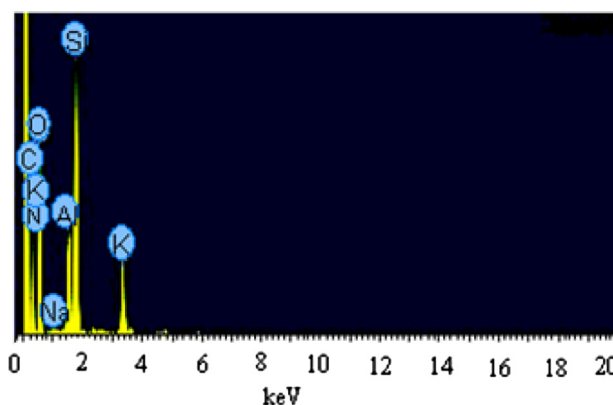


Figure 2 EDS spectrum of FCBCAC.

3. Results and discussion

3.1. Characterization of FCBCAC

Fig. 1 shows SEM micrograph of FCBCAC. Through this micrograph irregular and porous surface activated carbon could be observed. On the basis of this fact, it can be concluded that FCBCAC presents an adequate morphology for MB adsorption. EDS results demonstrate that elements such as oxygen (65.9%), carbon (24.9%) silicon (5.1%), aluminum (2.09%), nitrogen (1.17%) and potassium (1.31%) are contained in FCBCAC sample (Fig. 2).

FTIR analysis was used to identify some characteristic functional groups of activated carbon (FCBCAC) before and after the dye adsorption (Fig. 3). The broad absorption peak at 3433 cm^{-1} corresponds to the O–H stretching vibration of alcohols, phenols and carboxylic acids as in pectin, cellulose, and lignin, thus showing the presence of “free” hydroxyl groups on the adsorbent surface (Li et al., 2007; Liang et al., 2010). The other peaks at 2918.53 , 1629.99 , 1431.02 , 1162.2 and 876.05 cm^{-1} are due to $-\text{CH}_2$, C–C, C=O, C–O and C–N stretching, respectively. However, after the dye adsorption onto FCBCAC (Fig. 3), additional peaks at 1373 , 1251.54 , 1031.52 and 781.52 cm^{-1} are identical to N=O, C–N,

$>\text{C}=\text{O}$, C–S functionalities. Also the peaks at 3433.79 , 2918.53 , 1629.99 and 1113.28 cm^{-1} are shifted to 3420.91 , 2904.22 , 1624.04 and 1112.91 cm^{-1} , respectively. This shift in the absorption peak suggested the interactions of dye molecules with the functional groups of biosorbent (Liang et al., 2010).

3.2. Removal of MB

3.2.1. Effect of adsorbent dose and initial dye concentration

The adsorbent doses varied from 0.1 to 0.9 g/50 ml. It is evident from Fig. 4 that the MB removal increased sharply with an increase in the adsorbent concentration from 0.1/100 to 0.5 g/100 ml. This may be due to the availability of more adsorbent sites as well as greater availability of specific surfaces of the adsorbents (Fig. 4). However, no significant changes in removal efficiency were observed beyond 0.5 g/100 ml adsorbent dose. Due to conglomeration of adsorbent particles, there is no increase in effective surface area of FCBCAC.

(Barka et al., 2011) So, 0.5 g/100 ml is considered the optimal dose for FCBCAC loading.

The effect of dye concentration on the sorption of MB onto FCF was carried out in the concentration range of 10–70 mg/100 ml (Fig. 5). Equilibrium adsorption capacity increased with an increase in MB concentration from 50 mg to 50 ml.

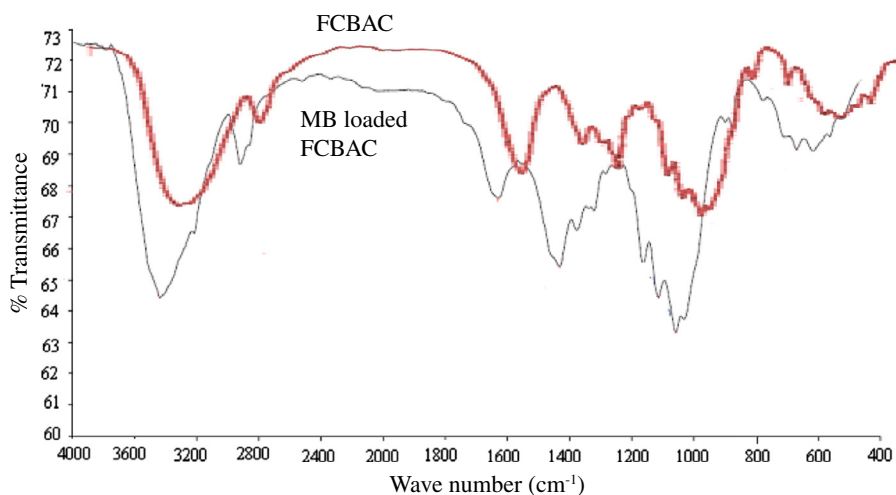


Figure 3 FTIR spectrum of FCBCAC.

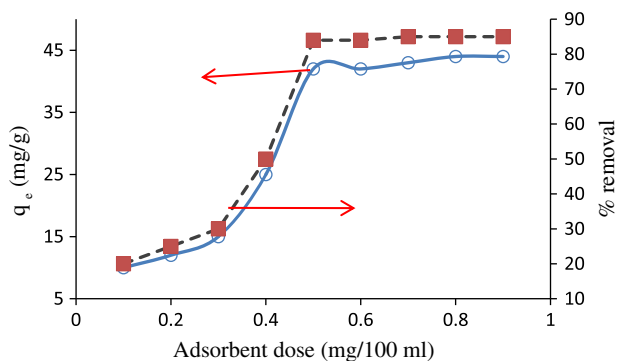


Figure 4 Effect of adsorbent dose on MB removal.

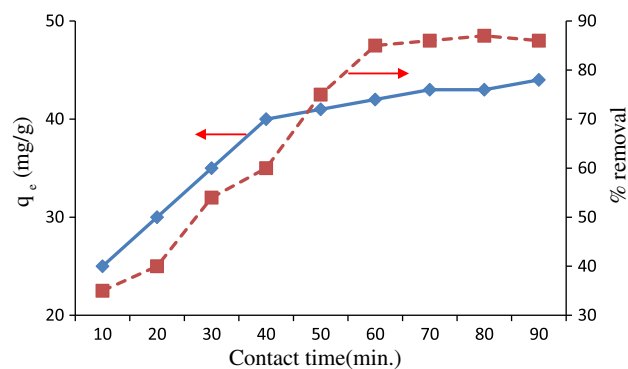


Figure 6 Effect of contact time on MB removal.

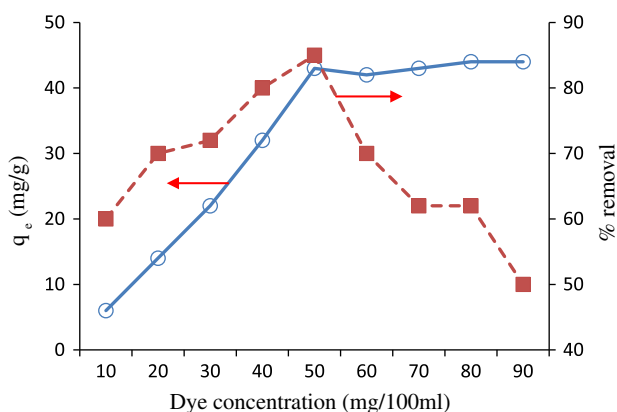


Figure 5 Effect of dye concentration on MB removal.

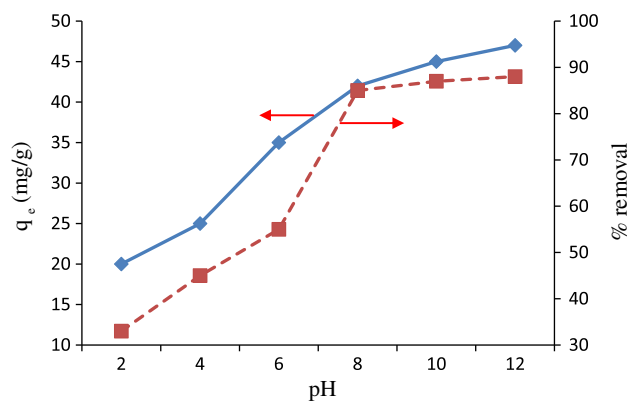


Figure 7 Effect of pH on MB removal.

Further increase in dye concentration showed no significant changes in removal efficiency (Fig. 5). This is due to the fact that with increased dye concentration, the driving force for mass transfer also increases. At low concentrations there will be unoccupied active sites on the adsorbent surface. Above optimal MB concentration, the active sites required for the adsorption of dye will lack (Barka et al., 2011; Iqbal et al., 2011). This retards the overall MB adsorption by activated carbon.

3.2.2. Effect of contact time

The effect of contact time on the removal of Cr(VI) is shown in Fig. 6. 85% dye removal takes place in 60 min for FCBC. The equilibrium was reached after 90 min. The change in the rate of adsorption might be due to fact that initially all the adsorbent sites are vacant and solute concentration gradient is very high. Later, the lower adsorption rate is due to a decrease in number of vacant sites of adsorbent and dye concentrations. The decreased adsorption rate, particularly, toward the end of experiments, indicates the possible monolayer formation of MB on the adsorbent surface (Abd et al., 2009; Nemer et al., 2010). This may be attributed to the lack of available active sites required for further uptake after attaining the equilibrium (Liang et al., 2010).

3.2.3. Effect of pH

The pH of a dye solution is an important influencing factor for the adsorption of MB onto FCBC. Fig. 7 shows the effect of

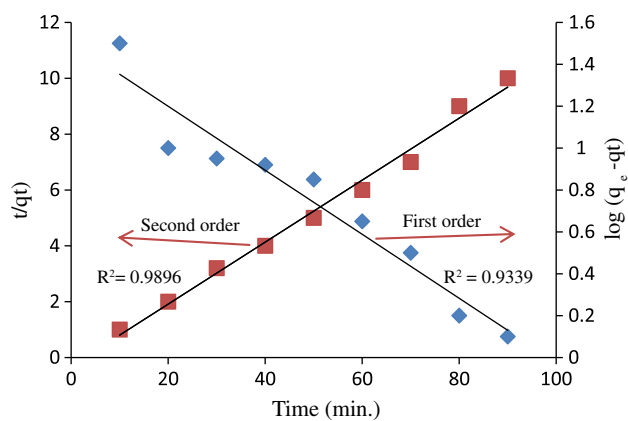


Figure 8 Pseudo first order and second order kinetic plot for MB adsorption.

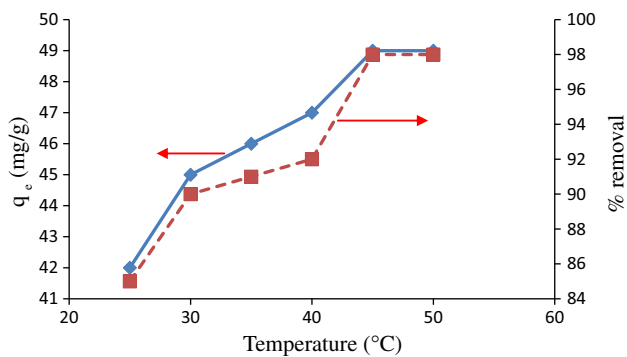
pH on adsorption onto FCBC. The maximum MB removal was observed at pH 8. The basic dye gives positively charged ions when dissolved in water. Thus, in acidic medium the positively charged surface of sorbent tends to oppose the adsorption of the cationic adsorbate. When pH of dye solution is increased the surface acquires a negative charge, thereby resulting in an increased adsorption of MB due to an increase in the electrostatic attraction between positively charged dye and negatively charged adsorbent (Abd et al., 2009; Malik, 2003).

Table 1 Kinetic and thermodynamic parameters for the sorption of MB onto FCBAC.

<i>Pseudo first order model</i>			
k_1 (min^{-1})	q_e (mg/g)	R^2	
0.0205	65.31	0.933	
<i>Pseudo second order model</i>			
k_2 (g/(mg min))	q_e (mg/g)	R^2	
0.00019	55.56	0.989	
<i>Intraparticle diffusion model</i>			
k_d (mg/g min)	C (mg/g)	R^2	
3.04	3.35	0.992	
<i>Thermodynamic parameters</i>			
ΔH° (kJ/mol)	ΔS° (J/mol K)	ΔG° (kJ/mol)	
21.55	76.24	-1.55	

Table 2 Results of various isotherm plots for the adsorption of MB onto FCBAC.

Models	Isotherm constants			
Langmuir	q_m (mg/g)	K_L (L/mg)	R_L	R^2
	47.62	0.04	0.05–0.35	0.997
Freundlich	n	(mg/g)		R^2
	2.51	5.69		0.95
Tempkin	(L/g)	(mg/L)	(J/mg)	R^2
	0.53	9.17	274.66	0.98

**Figure 9** Effect of temperature on MB adsorption.

3.3. Adsorption kinetics

The pseudo first order rate expression is given as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (7)$$

where, q_e and q_t are the amount of dye adsorbed on sorbent at equilibrium and time t (mg/g) and k_1 is the first order rate constant (min^{-1}). A plot of $\log(q_e - q_t)$ versus t gives a linear relationship, from which the value of k_1 and q_e can be determined from the slope and intercept.

The linearized form of pseudo second order rate expression is given as (Ho et al., 2000):

$$\frac{dq_1}{dt} = k_2(q_e - q_e)^2 \quad (8)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (9)$$

where q_e is the amount of adsorbate adsorbed per unit mass of sorbent at equilibrium (mg/g), q_t is the amount of adsorbate adsorbed at contact time t (mg/g) and k_2 is the pseudo second order rate constant (g/mg min). A plot of t/q_t versus t gives a linear relationship, from which q_e and k_2 can be determined from the slope and intercept (Bhattacharyya and Sharma, 2005).

The data for the adsorption of MB on FCBAC were applied to pseudo first and second order kinetic models and the results are presented in Table 1. The correlation coefficient of second order kinetic model (0.989) is greater than for first order kinetic model (0.933) (Table 1, Fig. 8). This confirmed that the rate limiting step is chemisorption, involving valence forces through sharing or exchange of electrons (Bhattacharyya and Sharma, 2005).

The intraparticle diffusion equation is expressed as follows:

$$q_t = K_d t^{1/2} + C \quad (10)$$

where, k_d is the intraparticle diffusion rate constant (mg/g $\text{min}^{1/2}$). The data for intraparticle diffusion are given in Table 1. The linear portion of the plot does not pass through origin. This deviation from the origin may be due to the variation of mass transfer in the initial and final stages of the adsorption process. This confirms that the adsorption of MB on FCBAC was a multi-step process involving adsorption on the external surface and diffusion into the interior (Kumar and Kumaran, 2005).

3.4. Adsorption isotherm

The adsorption capacity and other parameters were evaluated using Langmuir, Freundlich and Tempkin isotherm models. It has been observed that the sorption capacity (q_m) was found to

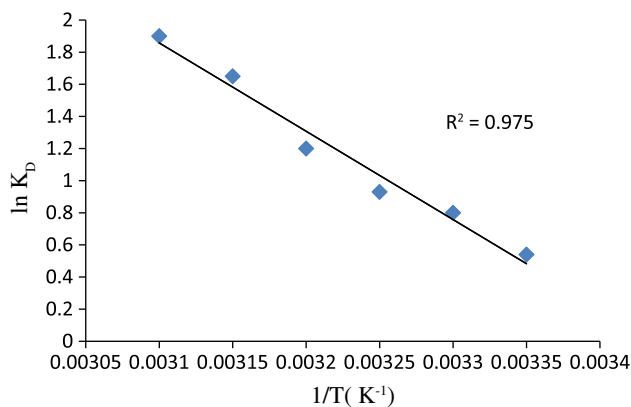


Figure 10 Enthalpy and entropy determination for MB removal.

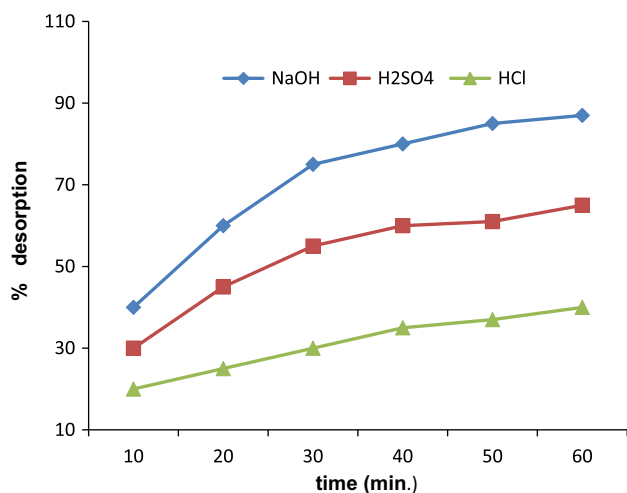


Figure 11 Desorption studies of methylene blue dye.

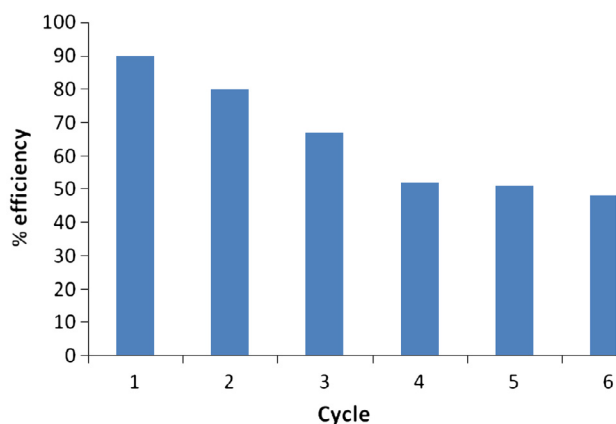


Figure 12 Recycling efficiency of FCBC for MB removal.

be 47.62 mg/g (Table 2). The high value of correlation coefficient (0.997) indicates the applicability of Langmuir isotherm which assumes a monolayer coverage and uniform activity distribution on the sorbent surface. In the present study, R_L val-

ues ($0 < R_L < 1$) favor the adsorption of MB onto FCBC (Table 2).

Eq. (5) was used to evaluate Temkin isotherm. The value of correlation coefficient R^2 obtained from Temkin isotherm was found to be 0.98 constant b (274.66 J/mg) is related to heat of sorption indicating physio-chemical nature of the sorption process.

The equilibrium data were also fitted to the Freundlich equation. The parameters K_F and n indicated the sorption capacity and the sorption intensity of the system. The magnitude of the term $(1/n)$ gives an indication of the favorability of the sorbent/adsorbate systems (Malik, 2003). The correlation coefficient value (0.95) is lower than Langmuir and Temkin values. Therefore, adsorption onto FCBC does not follow Freundlich isotherm closely.

3.5. Adsorption thermodynamics

Thermodynamic parameters evaluated for MB adsorption onto FCBC are the free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°). These parameters were calculated using the following equation (Hameed et al., 2007).

$$\Delta G^\circ = -2.303RT \log K_D \quad (11)$$

$$K_D = \frac{q_e}{C_e}$$

Also,

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (12)$$

$$\ln K_D = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (13)$$

where q_e is MB concentration at equilibrium onto FABAC (mg/L), R is universal gas constant (8.314 J/mol K), and C_e is MB concentration at equilibrium in solution (mg/L). The values of ΔH° and ΔS° were determined from the slope and intercept of the plot of $\ln K_D$ versus $1/T$. Gibbs free energy change of sorption (ΔG°) was calculated using Eq. (11).

The adsorption of dye increases rapidly with an increase in temperature from 303 to 343 K (Fig. 9). The increase in adsorption capacity of FABAC was attributed to the enlargement of pore size and activation of the sorbent surface with temperature. Further rise in temperature increases the mobility of the large dye ions and reduces the swelling effect thus enabling the large dye molecule to penetrate further (Liu and Liu, 2008; Ozar et al., 2009). The results also indicated that the adsorption of MB is an endothermic process.

Thermodynamic parameters (ΔH° , ΔS° and ΔG°) for MB adsorption were evaluated using Eqs. (10)–(12). The values of ΔH° and ΔS° were determined from the slope and intercept of the plot of $\ln K_D$ versus $1/T$ (Fig. 10). Table 2 shows the thermodynamic parameters for MB adsorption onto FCBC. The positive value of ΔH° (21.55 kJ/mol) indicates that the adsorption of MB onto FCBC is an endothermic reaction. The calculated value of ΔG° (−1.55 kJ/mol) indicates spontaneous nature of the adsorption process. Further the positive

value of entropy change, ΔS° (76.24 J/mol K) reflects the affinity of FABAC for MB dye.

3.6. Desorption and recycling efficiency

Desorption studies were performed with 1% HCl, H₂SO₄ and NaOH. FCBAC (100 mg/50 mL) saturated with 5 mg/L of MB was placed in different desorption media and was constantly stirred on a rotatory shaker at 100 rpm for one hour. The adsorbent was separated and washed with distilled water. NaOH was found to be an efficient desorption medium with the efficiency for the removal of chromium ion (Fig. 11). 84% of MB was desorbed in 60 min using HCl as a desorption medium. Recycling efficiency of FCBAC was investigated for the removal of MB. After six cycles, the adsorption efficiency of FCBAC was reduced to 45% from 90% (Fig. 12). After every cycle, NaOH was used as a desorption medium to remove adsorbed MB ions from the FCBAC surface.

4. Conclusion

In this study, FCBAC shows promising adsorption capacity for methylene blue removal. The operating parameters for the maximum sorption were dye solution concentration (0.05 g/100 ml), sorbent dosage (0.5 g/100 ml), contact time (80 min) and temperature (303 K). Removal of methylene blue dye is pH dependent and the maximum removal was attained at pH 7.8. Equilibrium data were fitted well in the Langmuir, Freundlich and Tempkin isotherm models which confirmed that the sorption is heterogeneous and occurred through physico-chemical interactions. The rate of sorption was found to obey pseudo-second order kinetics and intraparticle diffusion model with a good correlation coefficient. The negative ΔG° values indicated that the sorption of dye onto biosorbent was feasible and spontaneous. The positive ΔH° value depicted endothermic nature of the sorption.

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