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Orthophosphoric Acid Activated Babul Seed Carbon as an Adsorbent for the Removal of Methylene Blue

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Abstract: An Experimental and theoretical study has been conducted on the adsorption of methylene blue dye using activated carbon prepared from babul seed by chemical activation with orthophosphoric acid. BET surface area of the activated carbon was determined as 1060 m^2/g. Adsorption kinetics, equilibrium and thermodynamics were investigated as a function of initial dye concentration, temperature and pH. First order Lagergren, pseudo-second order and Elovich kinetic models were used to test the adsorption kinetics. Results were analyzed by the Langmuir, Freundlich and Temkin isotherm models. Based on regression coefficient, the equilibrium data found fitted well to the Langmuir equilibrium model than other models. The characteristics of the prepared activated carbon were found comparable to the commercial activated carbon. It is found that the babul seed activated carbon is very effective for the removal of colouring matter.

Keywords: Adsorption, Activated carbon, Methylene blue dye, Kinetics, Isotherm.

Introduction

India is a highly populated country, safe drinking and domestic water demand is very high. Dying industries are the largest sector of chemical industries in India[1]. Among this textile industry is the largest consumer of dyestuff, consuming more than 80% of the total production[1] and they are carcinogenic also[2]. The disposal of coloured wastes into water affects the environment as they are highly toxic to human and aquatic life[3,4]. Dyes usually have synthetic origins and complex aromatic molecular structures. They are highly coloured polymers and fewer biodegradables. Trace amount of dye affects living being with several allergies, reproductive and neurological disorders. One among them is methylene blue (3,9 *bis* dimethyl aminophenazothionium chloride) is a basic dye which is used as a colorant in textile industry. Adverse effect on human /animal health and variety of uses of methylene blue attracted considerable global attention to develop easy and powerful methods for its determination. The present investigation is an attempt to remove methylene blue by adsorption process. Adsorption is an important technique in separation and purification

process. The objective of this study was to prepare activated carbon from babul seed by chemical activation with ortho phosphoric acid. Large availability of this material around our city attracted us to utilize it as potential adsorbent for the removal of toxic dyes.

Activated carbon adsorption capacity depends on different factors like texture (surface area, pore size distributions), surface chemistry (surface functional groups) and ash content[5-8]. It also depends on adsorptive characteristics like molecular weight, polarity, pk_a, molecular size and functional groups. The solution condition is other factor to be taken into account: pH, adsorptive concentration and presence of other possible adsorptives[7-10]. Adsorption kinetics, equilibrium and thermodynamics were investigated as a function of initial dye concentration, temperature and pH.

Experimental

Adsorbent preparation

Babul seed is collected from local area of Erode district. It was dried, charred with excess quantity of ortho phosphoric acid keeping at 120°C for 10h. Then the resultant carbon is washed with excess quantity of distilled water and dried at 110°C for 1 hour and stored in a tight lid container for further studies. It is then screened through a mesh sieve with a particle size range of 180-300 µm.

Adsorbate preparation

Stock solution (1000 mg/L) of methylene blue is prepared by dissolving 1g of dye in 1000 mL of double distilled water. The stock solutions were diluted with double distilled water to obtain required standard solution. Batch adsorption studies were performed at 30 °C, 100 mg of adsorbent is mixed with known initial concentration say (20, 40, 60 & 80 mg/L respectively) of methylene blue solution and agitated. The adsorbent and the adsorbate were separated by filtration and filterate was analysed for residual methylene blue concentration spectrophotometrically (using Elico make Bio-UV Spectrophotometer, model BL-192) at λ_{max} = 661 nm.

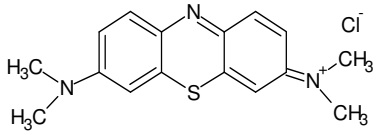

Figure 1. Structure of methylene blue

The surface area was calculated from the nitrogen adsorption isotherm and BET surface area of the activated carbon was determined as 1060 m^2/g. Effect of pH on the removal of dye were studied using 50 mL of dye solution of 20 mg/L initial concentration, adjusted to a desired initial pH values using HCl or NaOH and agitated with 100 mg of adsorbent for 120 minutes. In this study, influence of initial concentration on amount of methylene blue removed is examined.

Adsorption dynamics

In order to investigate the mechanism of sorption, several kinetic models were tested including Lagergren, Pseudo second order and Elovich model.

Lagergren model

For a batch contact time process, where rate of sorption of dye on to given adsorbent is proportional to amount of dye sorbed from solution, first order Langergren kinetic equation may be expressed as

$$\log q_e - q_t = \log q_e - (k_L / 2.303)t \quad (1)$$

where,

q_e = amount of dye adsorbed at equilibrium (mg/g),

q_t = amount of dye adsorbed at time t (mg/g) and

k_L = rate constant for first order adsorption(min^{-1}).

Hence a linear trace is obtained between the two values log ($q_e - q_t$) and t, provided the adsorption follows first order kinetics. In order to examine the efficiency of an adsorbent, this study is useful in removal of adsorbate species from aqueous solution by an adsorbent.

Pseudo second order model

To describe dye adsorption, modified pseudo second order equation is expressed as follows[11]

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (2)$$

where,

q_e = amount of dye adsorbed at equilibrium (mg/g),

q_t = amount of dye adsorbed at time t (mg/g) and

k_2 = rate constant for pseudo second order adsorption, (g/mg/min).

For the boundary conditions t=0 to t=1 & $q_t = 0$, $q_t = q_t$

Intergrated form of equation is as follows,

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \quad (3)$$

Linear form of equation can be expressed as follows,

$$\frac{t}{q_t} = \frac{t}{k\ q_e^{\ 2}} + \left(\frac{1}{q_e}\right)t \quad (4)$$

Thus a plot of t / q_t *Vs* t of above equation should give a linear relation with a slope of $1/ q_e$ and an intercept of $1 / k_2 q_e^2$

Elovich model

Elovich or Roginsky-Zeldovich equation is generally expressed as follows[12]

$$\frac{dq_t}{dt} = \alpha e^{-\beta q} \quad (5)$$

intergrating the rate equation with the boundary condition t=0 to t=t and q=0 to q=q, gives

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t + t_0) \quad (6)$$

where, α and β are the parameters of the equation and $t_o = 1/\alpha\beta$,

α represents the rate of chemisorption at zero coverage (mg/g/min) and β is related to the extent of surface coverage and activation energy for chemisorption (g/mg) where $t_o << t$, then equation (6) is replaced by

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \quad (7)$$

A plot q_t *Vs* ln t gives a straight line and the constants α and β are calculated from slope and intercept.

Isotherm models

Adsorption isothermal data could be interpreted by the Langmuir, Freundlich and Temkin isotherm models.

Langmuir isotherm

The study of Langmuir isotherm is essential in assessing the adsorption efficiency of adsorbent. This model was based on assumption of formation of monolayer of adsorbate species onto the surface of adsorbent. This study is useful in optimizing the operating condition for effective adsorption. Langmuir equation is,

$$\frac{C_e}{q_e} = \frac{C_e}{Q_0} + \frac{1}{Q_0 b} \tag{8}$$

where,

q_e = amount of dye adsorbed at equilibrium (mg/g),

Ce = equilibrium constant of dye (mg/L),

Q_0 = Langmuir Constant related to adsorption capacity (mg/g) and

b = Langmuir Constant related to energy of adsorption capacity (L/mg).

The values Q_0 and b at different temperatures were determined from slopes and intercepts of the plot of C_e / q_e *Vs* C_e. Equilibrium parameter R_L is represented as follows

$$R_L = \frac{1}{(1 + bC_O)} \tag{9}$$

C_o is initial dye concentration (mg/L)

R_L values between 0&1 indicate favourable adsorption for all initial concentration and temperature studied. R_L indicates isotherm shape and whether it is favourable or not as per the criteria given subsequently

R_L values	Adsorption
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

Freundlich isotherm

At equilibrium conditions, adsorbed amount q_e can be predicted by using Freundlich equation

$$\log q_e = \frac{1}{n} \log C_e + \log k_f \tag{10}$$

where,

q_e = dye concentration in solid at equilibrium (mg/g),

Ce = dye concentration in solution at equilibrium, (mg/L),

k_f = measure of adsorption capacity and

n = adsorption intensity.

A plot of log q_e *Vs* log C_e gives a slope of 1/n and intercept of log k_f.

Temkin isotherm

The derivation of Temkin isotherm assumes that the fall in heat of sorption is linear rather than logarithmic as implied in Freundlich equation. Heat of sorption of all the molecules in the layer would decrease linearly with coverage due to sorbate / sorbent interaction.

The linear form of the Temkin isotherm can be expressed as,

$$q_e = B \ln A + B \ln Ce \tag{11}$$

where,

Ce = concentration of the dye at equilibrium (mg /L),

q_e = amount of dye adsorbed at equilibrium (mg/g) and

RT/h =B and A & h are constants

A plot of q_e *Vs* ln Ce is used to determine the constants A and B.

Adsorption thermodynamics

Rate of a reaction can be found from kinetic studies. But the changes in the reaction can be expected during sorption process require brief idea of thermodynamic parameters. Thermodynamic parameters characterized the equilibrium of a system are Gibbs free energy change ΔG, enthalpy change ΔH and entropy change ΔS. They are determined using the following equation [13,14]

$$\Delta G = -RT \ln K_L \tag{12}$$

Where,

$$K_L = q_0 . b \tag{13}$$

where,

q_0 and b are Langmuir constants obtained at various temperatures.

Substituting the values of (13) in (12),

$$\log K_L = \left[\frac{\Delta S}{2.303R}\right] - \left[\frac{\Delta H}{2.303RT}\right] \tag{14}$$

Thus the value of ΔS & ΔH can be calculated from the intercept and slope of the plot of log K_L *Vs* 1/T.

Results and Discussion

Effect of initial dye concentration

The initial concentration of methylene blue solution was varied from 20, 40, 60 and 80 mg/L and batch experiments were carried out with 100 mg of the adsorbent at 30°C and at pH 7.0. An increased percentage removal of methylene blue from 75.10 to 96.41% observed with 100 mg of the adsorbent in agitation time of 100 minutes and results are shown in Figure 2. In order to establish equilibration time for maximum uptake and to know the kinetics of adsorption process, the adsorption of methylene blue on adsorbent was studied as a function of contact time. It was found that time of equilibrium as well as time required to achieve a definite fraction of equilibrium adsorption is independent of initial concentration.

Effect of pH

Adsorption is also affected by change in pH of the solution[15,16] as shown in Figure 3.The dependence of adsorption process on pH of dye solution was studied by varying pH of dye solution from 2 to 11. The hydrogen ion concentration (pH) primarily affects the degree of ionization of the dyes and the surface properties of the adsorbents. The % of dye adsorbed increased from 89.41 to 94.12 with increase in pH from 2 to 11 at temperature of 30°C. This is attributed to the increasing electronegative charge on the adsorbent as the pH of the solution is increased. As the adsorbent is negatively charged, the increasing electrostatic attraction between positive adsorbate dye species and the negative adsorbent particles would lead to increased adsorption of dyes. The optimum pH value for the adsorption of methylene

blue was observed 13.40 by Ravikumar *et* al[17.] Though there is no much variation of adsorption above pH of 5.0. For further studies pH fixed as 7.0 for convenience.

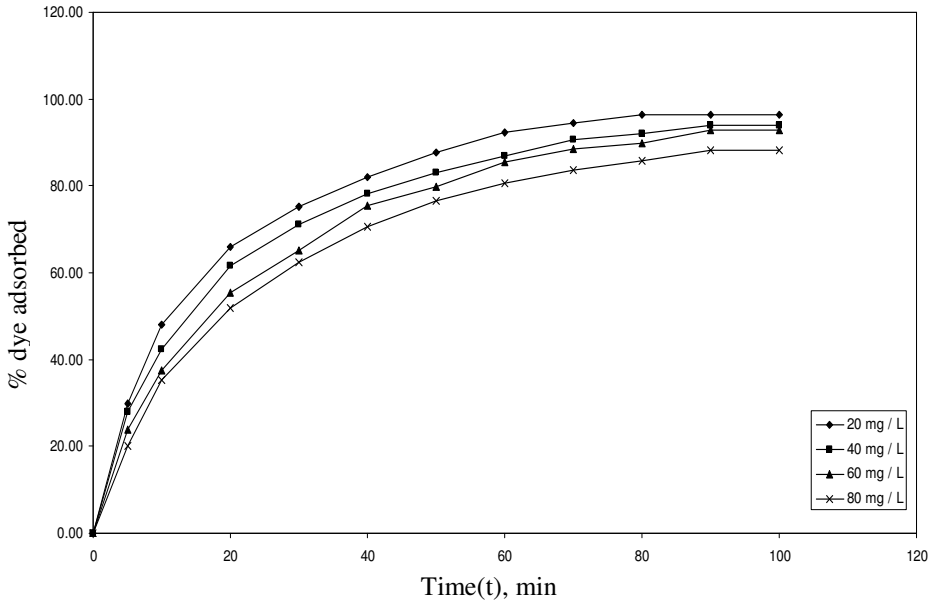

Figure 2. Effect of agitation time on adsorption –initial concentration variation

Effect of pH

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Sorption kinetics

In order to examine the controlling mechanisms of adsorption process first-order kinetics model , pseudo second order kinetics and Elovich models are used to test the experimental data.

First order kinetics

Langergren first order plot for the adsorption of methylene blue at various initial concentration is given in the Figure 4. The applicability of Lagergren model suggests the formation of a monomolecular layer of dye species onto surface of adsorbent. The study of influence of initial dye concentration on Lagergren rate constant from Table 1 shows a decrease in rate constant with increase in initial dye concentration.

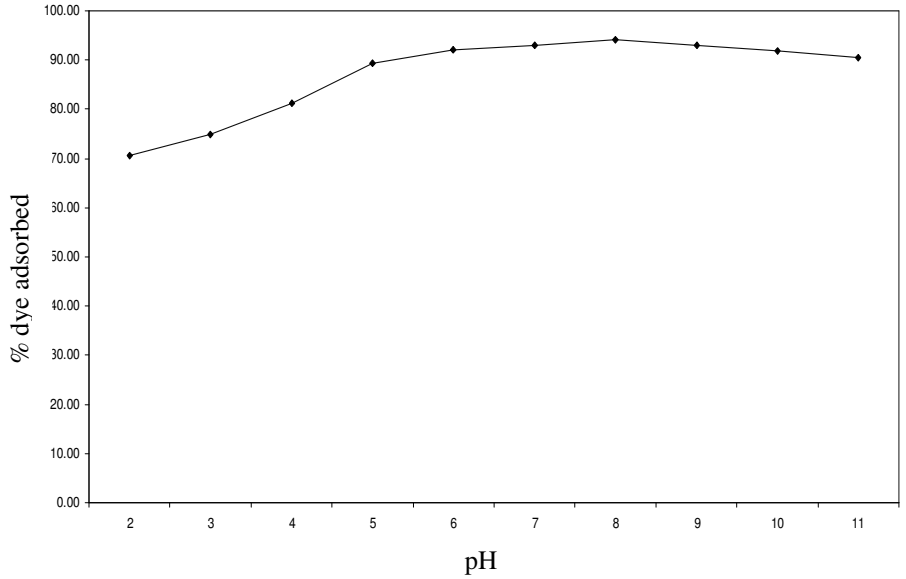

Figure 3. Effect of pH on methylene blue adsorption

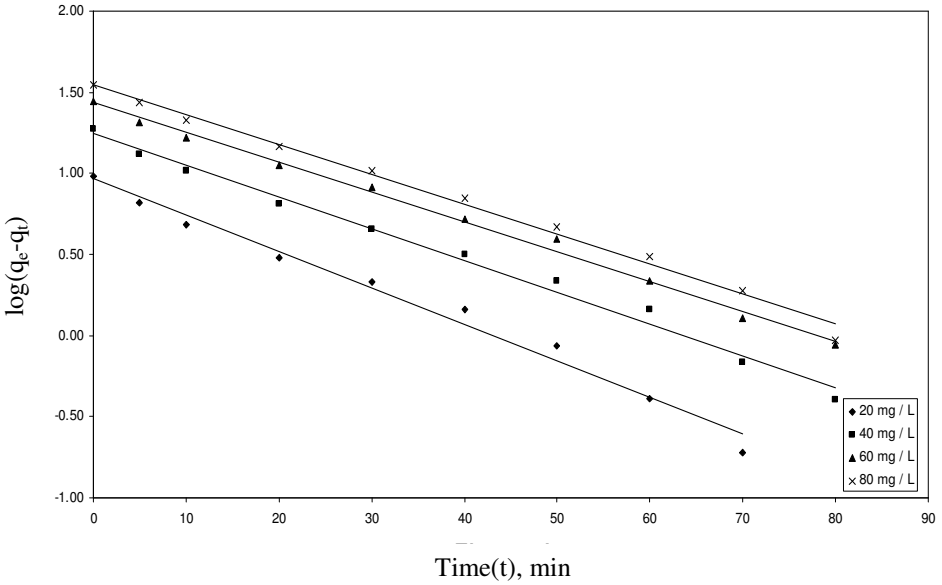

Figure 4. First order plot -initial methylene blue concentration variation

Pseudo second order model

Figure 5 shows that pseudo second order equation at various initial dye concentration (20, 40, 60 & 80 mg/L). These plots show that data had good correlation coefficients when pseudo second order equation was employed and was possible to ascertain from them whether rate determining process is a chemical reaction. Thus increasing dye concentration from 20 to 80 mg/L, equilibrium sorption capacity q_e increases. methylene blue sorbed at any contact time increases.

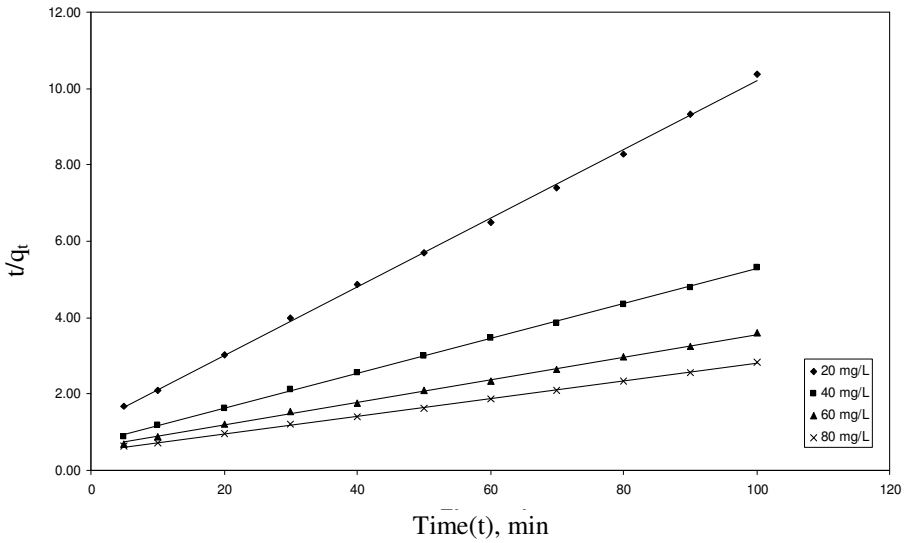

Figure 5. Pseudo second order plot-initial methylene blue concentration variation

Elovich model

The results of sorption of methylene blue onto babul seed carbon have been represented in the form of Elovich equation in Figure 6 at various dye concentration (20, 40, 60 & 80 mg/L). From the plot of linear relationship between the amount of methylene blue adsorbed, q_t and ln*t* was established. Table 1 shows the kinetic constants obtained from Elovich equation. It will be seen from the data that the values of α and β varied as a function of methylene blue concentration. Thus an increasing the initial concentration of methylene blue from 20mg/L to 80mg/L, value of α increases and β value decreases. Although Elovich equation does not provide any mechanistic evidence, it has proved suitable for highly heterogenous systems of which adsorption of methylene blue onto babul seed carbon is undoubtedly such a case.

Table 1. Kinetic model values for adsorption of methylene blue onto activated babul seed carbon

Concentration	1st Order			Pseudo second order				Elovich		
mg/L	k_L	q_e	r^2	q_e	k_2	h	r^2	β	α	r^2
20	0.05182	9.2725	0.9853	11.11	0.0067	0.8273	0.9991	0.4347	3.55290	0.9881
40	0.04514	17.6278	0.9905	21.88	0.00296	1.4152	0.9996	0.2171	5.72216	0.9938
60	0.04214	27.1300	0.9951	33.67	0.0015	1.7007	0.999	0.1368	8.37953	0.9946
80	0.04261	35.3427	0.9925	43.48	0.00107	2.0198	0.9995	0.1194	9.43952	0.9834

Isotherm modeling

Langmuir Adsorption Isotherm

Adsorption isotherm obtained by fixing adsorbent dosage of 100 mg and 100 minutes of agitation time is shown in the Figure 7. The result of Langmuir adsorption isotherm for the selected adsorbent/adsorbate system is given in the Table 2. The adsorption capacity Q_o values found to be comparable with commercial activated carbon. The values of R_L obtained in this study indicate the applicability of Langmuir adsorption isotherm. The calculated value R^2 confirm the applicability of Langmuir adsorption isotherm.

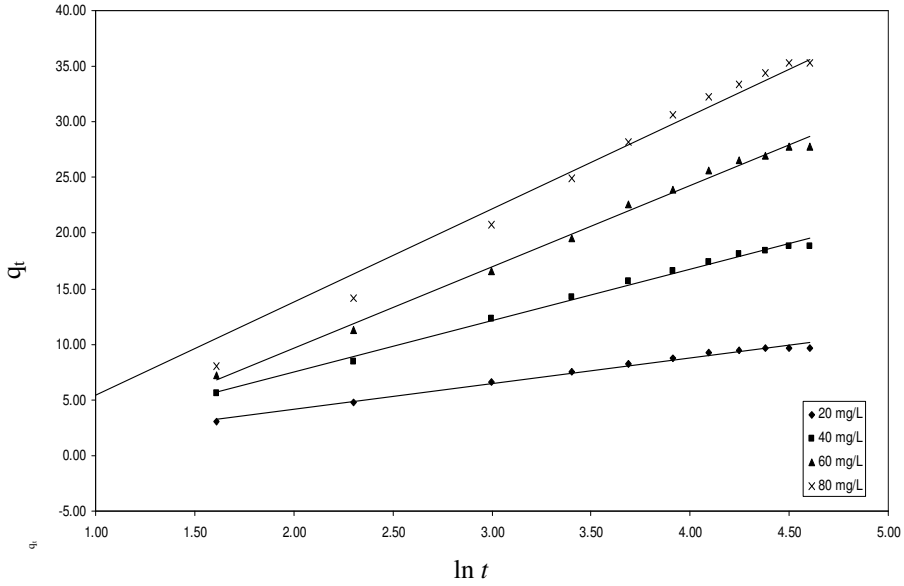

Figure 6. Elovich plot-initial concentration variation

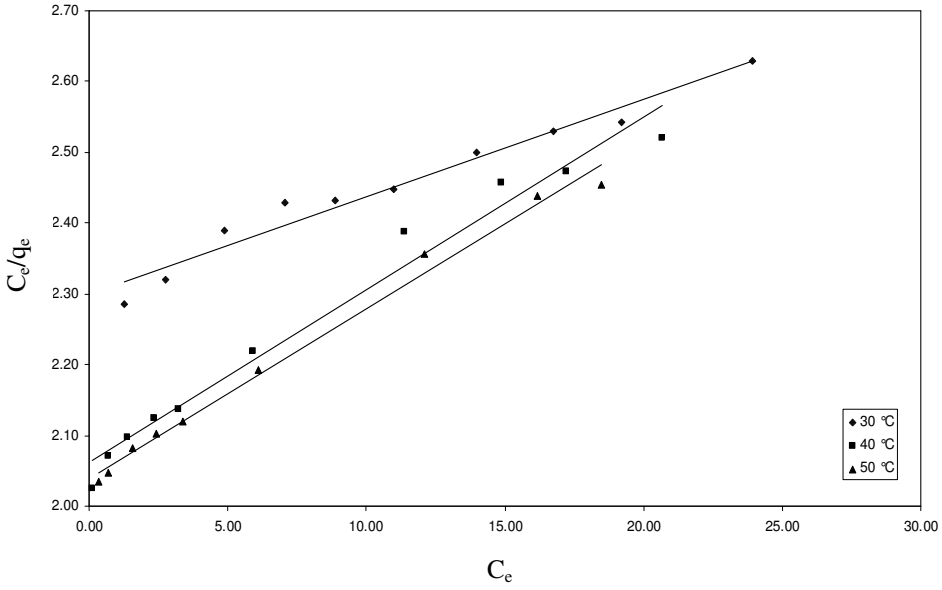

Figure 7. Langmuir plot-temperature variation

Freundlich adsorption isotherm

Freundlich plot for the adsorption of methylene blue on to babul seed activated carbon is given in the Figure 8 and the results of Freundlich plot are given in the Table 2. It shows that the values of adsorption intensity 1/n > 1 reveal that applicability of Freundlich adsorption is not good compared to Langmuir Adsorption Isotherm. Study of temperature effects on Freundlich parameters reveals increasing trend in adsorption capacity with increase in temperature.

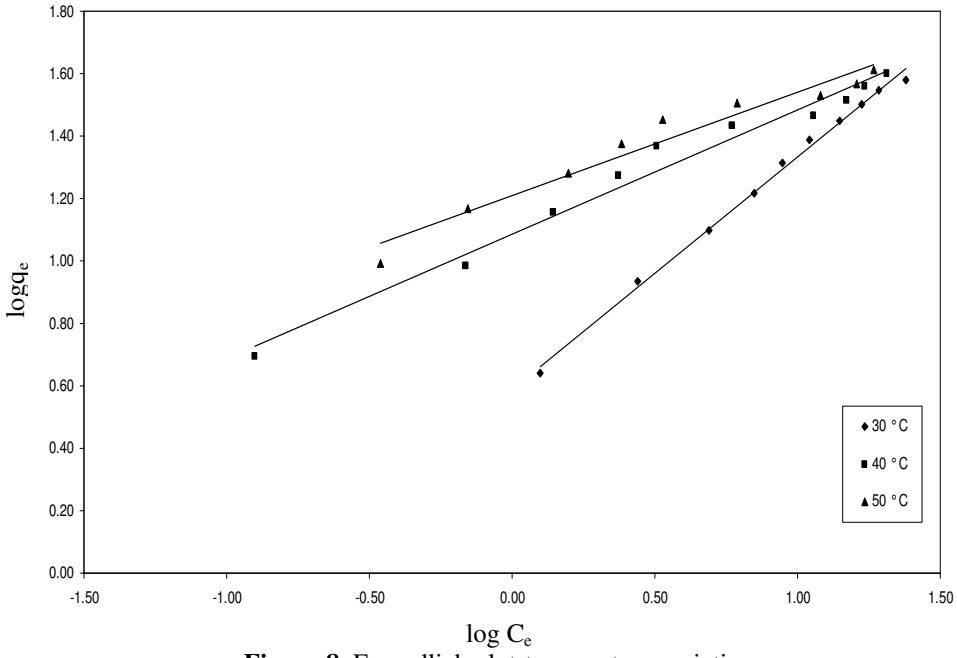

Figure 8. Freundlich plot-temperature variation

Table 2. Parameters of Langmuir adsorption isotherm and Freundlich adsorption isotherms for methylene blue adsorption calculated for 100 minutes of agitation time onto activated babul seed carbon

Temperature °C	Langmuir adsorption isotherm				Freundlich adsorption isotherm			
	b, L/mg	Q_o, mg/g	R_L	R^2	1/n	n	k_f	R^2
30	0.006003	72.46	1.060	0.9954	0.7462	1.34	3.895	0.9963
40	0.011887	40.81	1.119	0.9870	0.3984	2.51	12.164	0.9787
50	0.011767	41.66	1.118	0.9912	0.3289	3.04	16.221	0.9552

Temkin adsorption isotherm

Temkin sorption potential increases with increase in temperature and reached maximum value at 50°C. However model is unable to describe data, compared to other two parameter models as low correlation coefficients was observed.

Table 3. Parameters of Temkin adsorption isotherm of methylene blue onto activated babul seed carbon

Temperature °C	lnA	B	R^2
30	-0.2489	11.93	0.935
40	2.1779	6.849	0.9467
50	2.3504	7.413	0.9827

Thermodynamic parameters

The heat of adsorption was calculated by plotting a graph of log K *versus* reciprocal of temperature as shown in Figure 10. ΔH and ΔS were got from slope and intercept of Vant Hoff plot. The negative value of free energy change ΔG indicate the feasibility and spontaneous nature of adsorption of methylene blue. ΔH value suggests endothermic nature of methlyene blue onto babul seed carbon. Positive value of ΔS is due to increase randomness during adsorption of methylene blue. The behavior similar to this was also observed by Amina *et al*[18] for the adsorption of methylene blue The reorientation or restructuring of water around the nonpolar solute or surface is very unfavourable in term of entropy, since it disturbs the existing water structure and imposes a new and more ordered structure on the surrounding water molecules. As a result of adsorption of methylene blue onto activated carbon surface, the number of water molecule surrounding the methylene blue decreases and thus the degree of freedom of the water molecule increases. Therefore, the positive value of entropy suggested the increased randomness at the solid-solution interface during the adsorption of methylene blue.

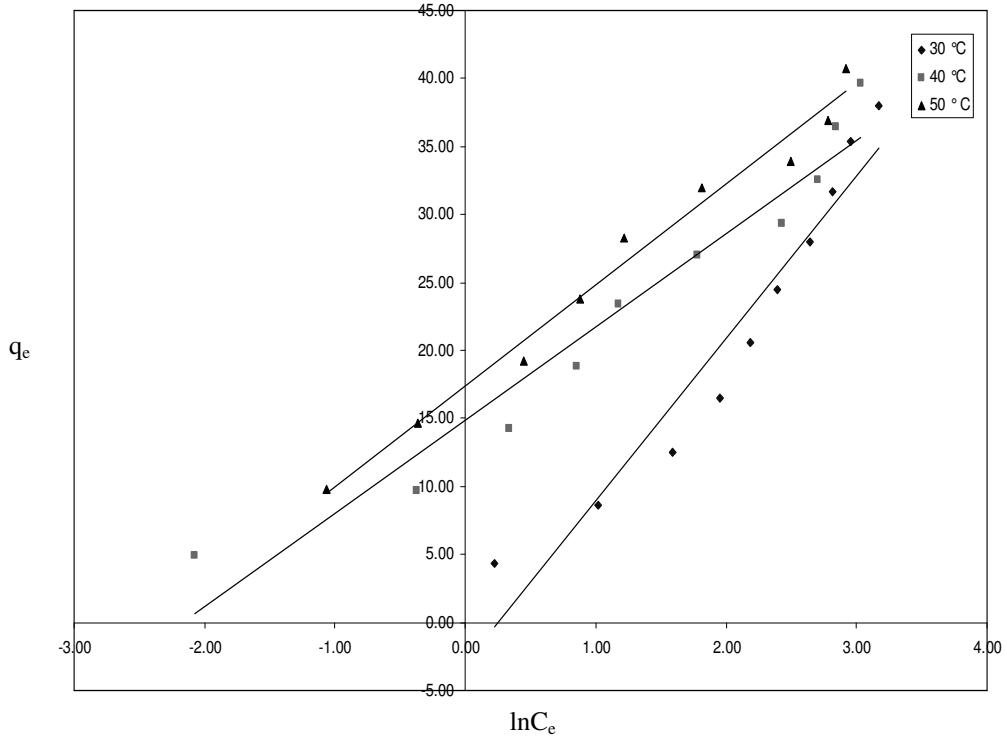

Figure 9. Temkin plot-temperature variation

Table 4. Thermodynamic parameters

Temperature°C	ΔH	ΔS	ΔG
30	-71.0733	9.4184	-353.6277
40			-447.81
50			-541.99

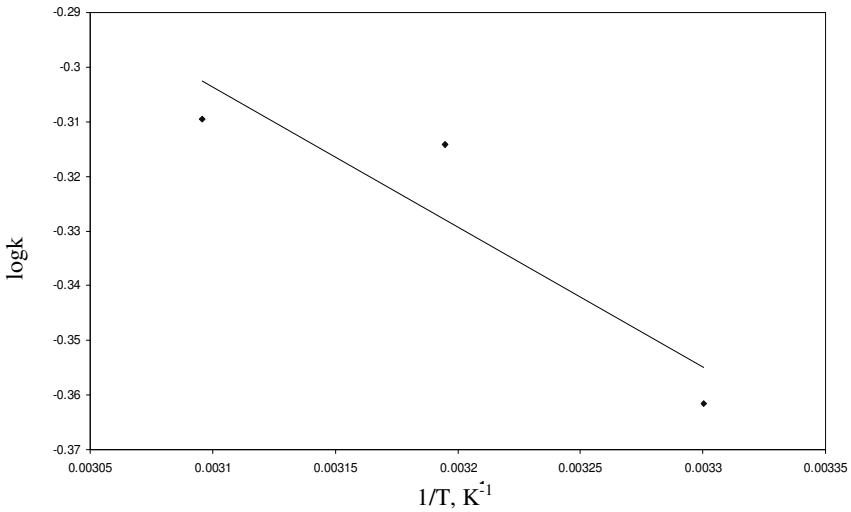

Figure 10. Vant Hoff's plot

Conclusions

Adsorption of methylene blue is dependent on initial concentration and agitation time. The % of dye adsorbed increased with increase in pH at temperature of 30°C. Based on the regression coefficient value, the adsorption of methylene blue on to babul seed activated carbon followed second order kinetics. The values of $R_L < 1$ obtained indicate the applicability of Langmuir adsorption isotherm. Study of temperature affects on Freundlich parameters reveals increasing trend in adsorption capacity with increase in temperature. Applicability of Freundlich adsorption is not good compared to Langmuir adsorption isotherm. It is an endothermic reaction based on enthalpy change value. The data obtained through this work supports that babul seed carbon is an effective low cost adsorbent for removal of methylene blue from aqueous solution.

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