Sorption dynamics of methylene blue removal using indian activated coir pith

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ABSTRACT

Experiments are conducted for discoloration of methylene blue from synthetic waste water using activated coir pith, a bioadsorbent. The experiments are performed at five different temperatures using fixed concentration of methylene blue. Maximum percentage removal at these temperatures is also evaluated. Models reported in the literature used for explaining the sorption dynamics are used to test the experimental data. It has been observed that of all the three models considered, pseudo-second order explained the experimental data satisfactorily. Pore diffusion coefficients calculated at these temperatures suggested pore diffusion to be the controlling mechanism.

Keywords: Methylene Blue, discoloration, dynamics, diffusion coefficient.

1. INTRODUCTION:

Textile industries use a lot of synthetic dyes. Dyes have synthetic origin and complex aromatic structure which make them more difficult to biodegrade (Sayan E,2006). It is reported that 10 to 15% of the dye is lost in the effluent (Garg, V.K et al.2003, Young, L et al.1997). The effluents generated from these industries cause of lot of environmental problems. Dyes even at low concentrations, as low as 0.005ppm draw the attention of both public and authorities (D.A. Oxspring et al. 1996). Dyes interfere with the growth of bacteria and interfere with photosynthesis in aquatic plants (D.A. Oxspring et al. 1996). Moreover, the stability of dyes towards light and oxidizing agents also create a problem for their removal by different waste treatment procedures (J. Pierce et al.1994) Hence, their treatment methods are to be chosen with great care and thoughtfulness. Conventional methods like flotation and flocculation for removal of these dyes were found to be incompetent (V.K. Gupta Alok Mittal et al.2004) Adsorption was found to be superior method for removal of the dye contaminants from effluents. Literature presents data on separation of different concetrations of the dyes using waste products as adsorbents which include peat (B. Chen et al. 2001, V.K. Gupta et al.2001) coal(V.K. Gupta et al,2002) bagasse fly ash (J.M. Chern and C.Y. Wu ,2001) activated carbon (S.J. Aitcheson et al 2000) iron slag (G.P. Handreck et al ,1998), shale oil ash (J. Chen et al,2002), zeolites(B.H. Tan et al,2000) magnesium chloride(S.J. Culp et al 1996), maize cob (M.S. El-Geundi, 1991) bottom ash of power plant (D.A. Oxspring et al. 1996). coir pith (Kavitha D and Namasivayam C, 2007) etc. Kavitha and Namasivayam (Kavitha D and Namasivayam C, 2007) performed experiments using activated coir pith for

removal of methylene blue in the concentration range of 10 to 40 mg/l. The effect of temperature on adsorption dynamics could not be established by the authors. Hence, the present study is envisaged to obtain data on sorption dynamics of coir pith on methylene blue at 100 mg/l concentration. The concentration considered can give rise to different equilibrium times and hence different percentage removals. Moreover, the effect of temperature on adsorption dynamics is also contemplated in the present study. The experimental values are verified for different models reported in the literature. Further, the diffusion coefficient at various temperatures is also calculated and the effect of temperature on % removal of methylene blue is also established.

2. MATERIALS AND METHODS

2.1. CHEMICALS

Adsorbate: The present study deals with the adsorption of methylene blue (MB) on Coirpith (CP). The adsorbate, methylene blue (MB) dye was supplied by Sairam chemicals Pvt. Ltd., Tiruchirappalli, India. The specifications of Methylene blue are given below in the following table (Table-1). These specifications are same as that reported in the literature.

Table-1: Specification of Methylene blue

Molar mass	319.85 g/mol
Melting point	100-110 °C (with decomposition)
Boiling point	Decomposes
density	1.0 g/mL at 20 °C
Water Solubility	40 g/L (20 ºC)

Accurately weighed quantity of the dye was dissolved in double-distilled water to prepare stock solution (1000 mg/l). Experimental solutions of the desired concentrations were obtained by successive dilutions with distilled water. Concentrations of dyes were before and after adsorption were determined by finding out the absorbance at the characteristic wavelength using a double beam UV-Visible spectrophotometer by monitoring the absorbance changes at a wavelength of maximum absorbance (668 nm). Calibration curves were plotted between absorbance and concentration of the dye solution.

2.2 Preparation of adsorbent

Coir pith was dried in atmosphere. The dried material was grounded in the ball mill, and the obtained grounded material is sieved to obtain the desired size particle size such as 0.3 - 0.15 mm. Thereafter the desired size material is washed with distilled water and then dried in muffle furnace for 2 hrs at 600^0C. The dried material obtained from the muffle furnace was treated with 0.1 N HCl at room temperature for 24 h to oxidize the adhering organic matter. HCl treatment can improve the surface area of material which ultimately increases the adsorption capacity. Finally the resulting material was thoroughly washed with distilled water and then subjected to the temperature of 100^0C for the moisture removal.

2.3. Experimental method

Batch adsorption studies: To study the effect of removal of MB, batch experiments were conducted by keeping the samples in a constant temperature

bath. For each experimental run, 250 ml solution of known concentration and a known amount of the adsorbent were taken in a 1liter stopper conical flask. The samples were shaken in a thermostatic orbital shaker at 150 rpm for the desired time periods. All the experiments are performed at a pH of 6 by considering a particle size of 0.075mm. Samples were withdrawn at appropriate time intervals. Some Coir pith particles remain suspended and do not settle down easily. The samples were separated from the adsorbent by centrifugation and filtered using Whatman No. 42 filter paper. The residual concentrations of Methylene blue were determined using spectrophotometer at a wave length mentioned above.

3.0 RESULTS AND DISCUSSION

3.1. Variation of % removal of methylene blue with temperature: The following plot (fig.1) illustrates the variation of % removal at various temperatures.

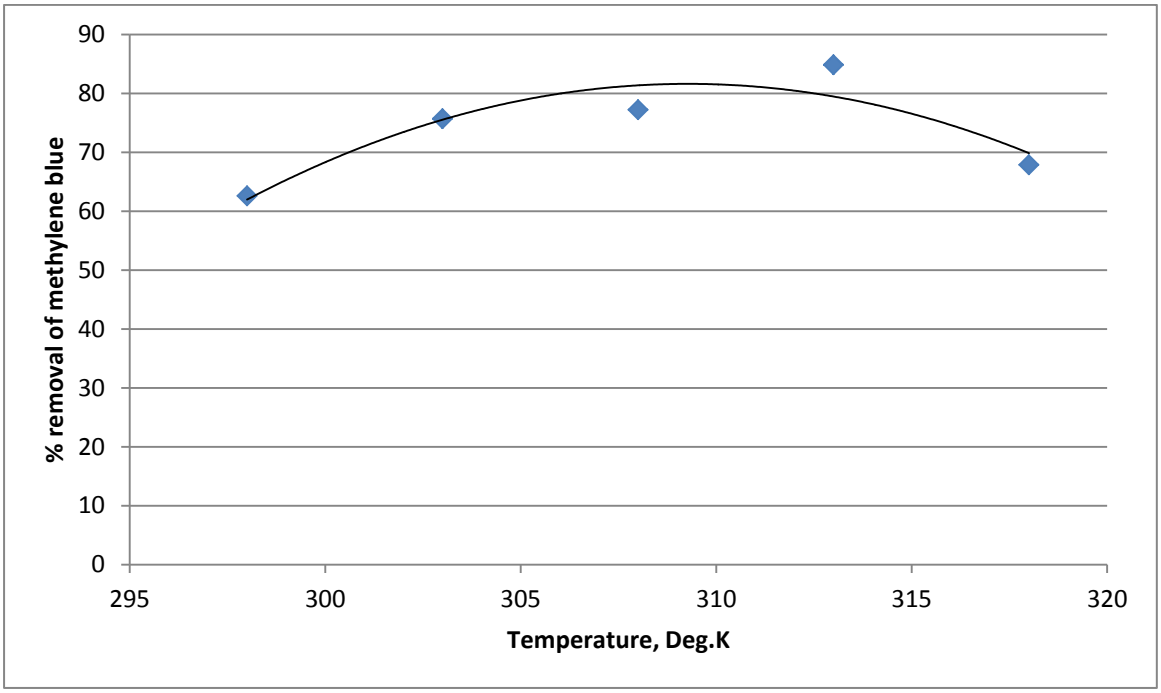

Fig.1 : Variation of % removal with temperature (Methylene blue concentration= 100mg/lt, rpm=150, pH=6)

It can be seen from the plot that as the temperature is increased; percentage removal also increases up to 308 K and then decreases when the temperature is raised from 308K to 315K which is quite surprising. The attrition of adsorbent could be possible reason for this reduction in percentage removal with increase in the temperature beyond 308K.

The % removal of dye is less than that reported for 10-40mg/liter concentration by Kavitha and Namasivayam (Kavitha D and Namasivayam C,2007). For concentration of 10mg/l, the authors reported an equilibrium time of 30 min which was increased to 60 min at 20mg/l concentration of dye. This clearly suggests that as the concentration of the dye increases, the equilibrium time also increases. In the present case, it was found to be 7 hours.

3.2 SORPTION DYNAMICS

The mechanism of adsorption can be explained based on several steps. In order to investigate the mechanism of sorption, the mechanism on pseudo first order model, pseudo second order model and intra particle diffusion model were used.

3.2.1 PSEUDO FIRST ORDER MODEL

A simple kinetic analysis of adsorption was the Lagergren (Lagergren, S., 1898)or pseudo first-order equation:

$$\frac{dq_t}{dt} = K_f(q_e - q_t) \qquad (1)$$

This upon integration yields the following equation.

$$\log(q_e - q_t) = \log q_e - \frac{K_f}{2.303} t \qquad (2)$$

Where q_t was the amount of adsorbate adsorbed at time t (mg/g), q_e was the adsorption capacity at equilibrium (mg/g), k_f was the pseudo-first-order rate constant (min^{-1}), and t was the contact time (min).
The rate constant, k_f was obtained from slope of the linear plots of $\log(q_e/q_e-q_t)$ vs t.

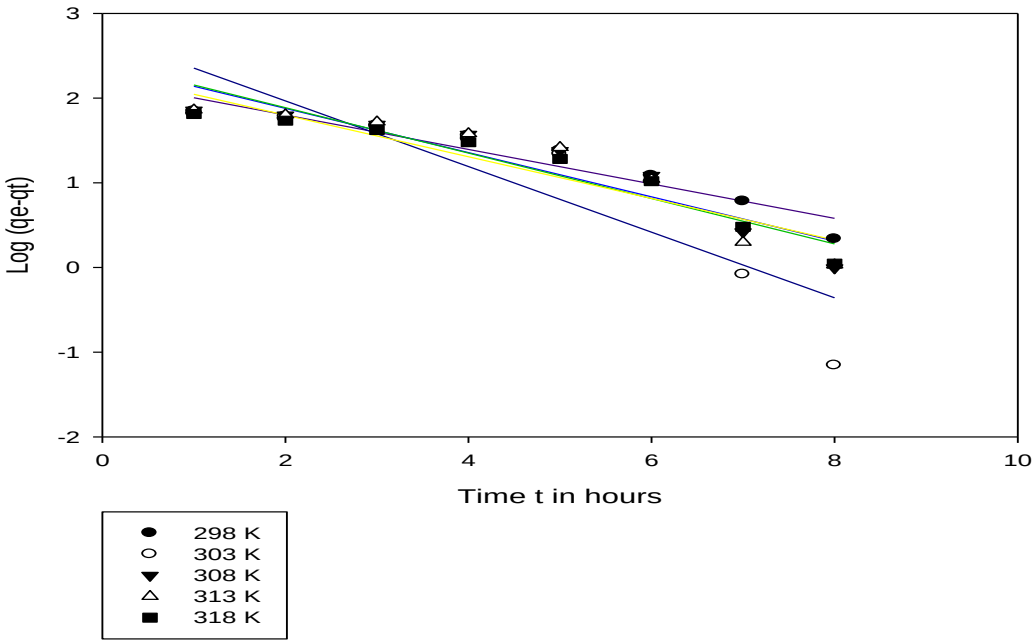

Fig.3.2. shows the Pseudo-first-order kinetics for 100mg/l initial concentration

In order to obtain the rate constants, the straight line plots of log(q1- qt) against t for different dyes and different experimental conditions have been analyzed. The rate constant, k_1 value of the dye under different conditions was calculated. The rate constant value is shown in table-3.

3.2.2 PSEUDO SECOND ORDER MODEL

The second-order kinetic model (McKay and Ho, 1999) is expressed as

$$\frac{dq_t}{dt} = K_f (q_e - q_t)^2 \quad (3)$$

Where, k_s was the pseudo-second-order rate constant (gm/g hr^{-1}). Integrating equation (3) and applying the initial conditions t = 0 and $q_t = 0$ to t = t and $q_e = q_t$, the following equation (5) was obtained: The initial sorption rate, h (mg/g hr^{-1}), at t → 0 was defined as:

$$h = Ksq_e^{\ 2} \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{K_s q_e^{\ 2}} + \frac{1}{q_e} t \quad (5)$$

A plot of t/qt vs t is shown plotted in fig 3.2

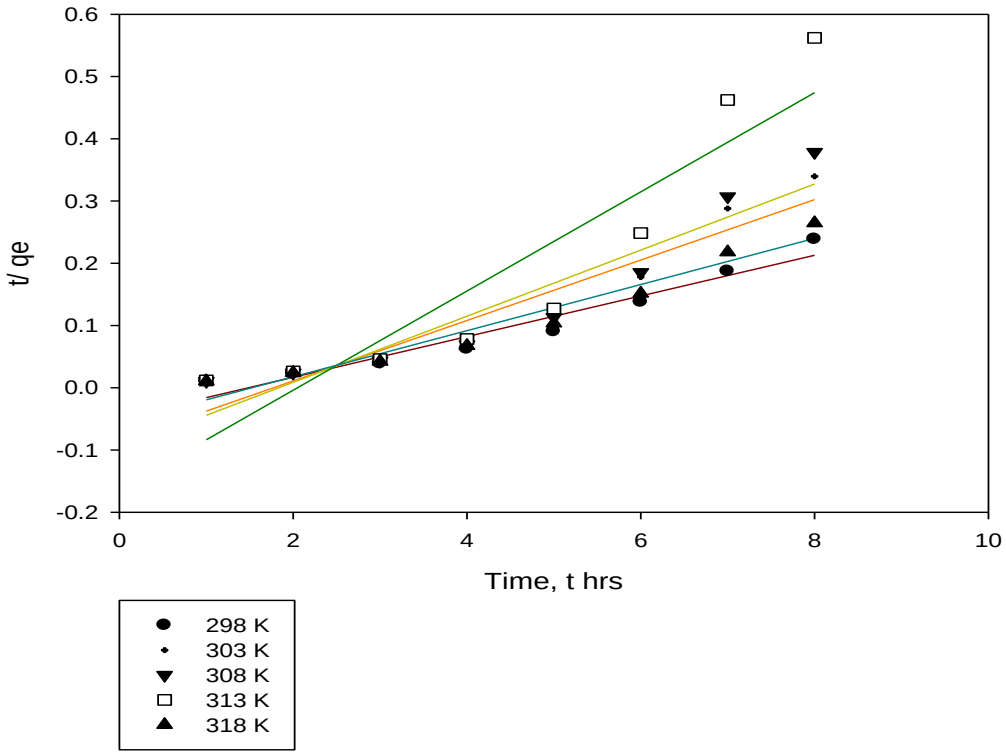

Fig.3.2: Pseudo-second-order kinetics for 100 mg/l initial concentration

3.2.3 INTRAPARTICLE DIFFUSION MODEL

Theoretical treatments of intraparticle diffusion yield rather complex mathematical relationships which differ in form as functions of the geometry of the sorbent particle (Crank J.1979) A functional relationship common to most treatments of intraparticle diffusion is that uptake varies almost proportionately with the half power of time, $t^{0.5}$, rather t than nearly linear and is given by

$$q_t = k_i t^{0.5} \quad (6)$$

k_i is the intraparticle diffusion rate constant, mg $g^{-1}min^{-0.5}$. The plot of q_t vs $t^{0.5}$ (t in hrs) is shown in the following figure (fig.3.3).

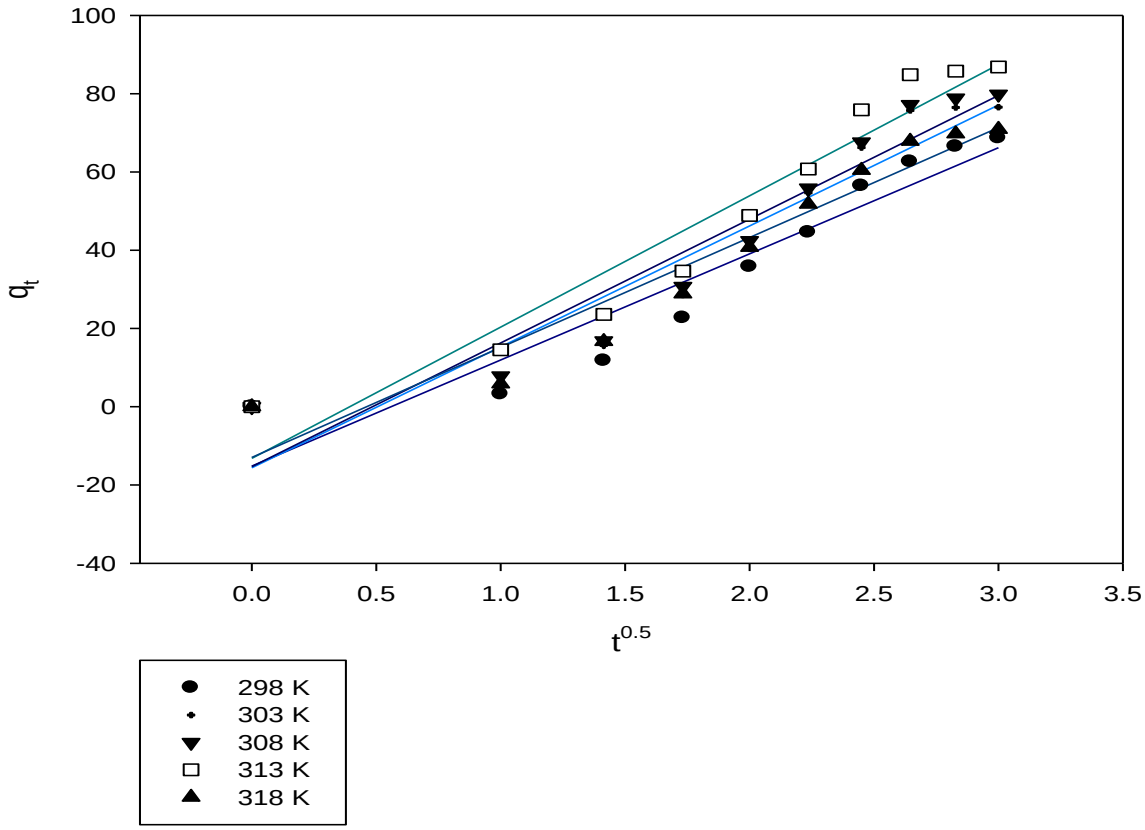

Fig.3.3: Plot of intraparticle diffusion for 100mg/l concentration

It can be seen from figures 3.1,3.2 and 3.3 that pseudo second order model was more close to experimental values compared to other models as shown by the R^2 values which is in accordance with (Kavitha D and Namasivayam C,2007).

3.3 Pore diffusion coefficient:

Assuming spherical geometry for the adsorbent, the time
for half adsorption can be correlated to the pore diffusion coefficient [24] and is given by

$$t_{1/2} = 0.03\frac{r_0^{\ 2}}{D_p} \qquad (7)$$

where $t_{1/2}$ is the time for half adsorption (s), r_0 is the radius of the adsorbent particle (cm) and D_p is the diffusion coefficient (cm^2/s). Values of D_p is calculated for 100mg/liter concentration of dye for different temperatures is shown in the following table (Table-2).

The table suggests that beyond 313K, there is a reduction in diffusion coefficient which is attributed to the attrition of the coir pith. The values of diffusion coefficient are in good agreement with values reported in the literature and the data on table also confirms to the fact that removal of dye follows pore diffusion model (Kavitha D and Namasivayam C,2007).

Table-2: Diffusion coefficient at different temperature.

S.No	Temperature (deg.K)	Diffusion coefficient (cm^2/s)X10^{11}
1	298	8.55
2	303	9.76
3	308	9.97
4	313	11.4
5	318	9.82

4. CONCLUSIONS

Some of the conclusions of the above study are:

1. Maximum percentage removal of methylene blue using activated coir pith is 84% when exposed for a time period of 7 hours.
2. The removal efficiency increases up to 313 K and then surprisingly decreases possibly due to attrition of activated coir pith.
3. The sorption dynamics could be explained better by pseudo second-order kinetic model.
4. The diffusion coefficient also increases with increase in temperature up to 313K and then decreases when temperature is raised to 318K. The diffusion coefficient values reported are in good agreement with literature value of 10^{-11} to 10^{-12} cm^2/s

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