ISSN : 0974 - 7451 Volume 7 Issue 7

Trade Science Inc.

Environmental Science
An Indian Journal

Current Research Paper

ESAIJ, 7(7), 2012 [239-250]

Removal of methylene blue, a basic dye from aqueous solutions by adsorption using mango (*Mangifera indica*) leaf powder

Satish Patil[1], Sameer Renukdas[2], Naseema Patel[3]*

[1]Department of Chemistry, A.P.Science College, Nagothane - 402106, MS, (INDIA)

[2]Department of Chemistry, Vaidyanath college, Parli Vaijnath - 431515, MS, (INDIA)

[3]Department of Chemistry, Yashwant Mahavidyalaya, Nanded - 431602, MS, (INDIA)

E-mail: sdpatil72@gmail.com

Received: 2nd August, 2012 ; Accepted: 20th August, 2012

ABSTRACT

Systematic batch mode studies of adsorption of methylene blue (MB) on mango leaf powder (MLP) were carried out as a function of process of parameters includes initial dye concentration, adsorbent dose, pH, agitation time, agitation speed, particle size of adsorbent and temperature. MLP was found to have good adsorption capacity. Freundlich, Langmuir and Temkin isotherm models were used to test the equilibrium data. The best fitting isotherm models was found to be Langmuir and Freundlich. The linear regression coefficient R^2 was used to elucidate the best fitting isotherm model. Lagergen pseudo –first order model, Lagergen pseudo -second order model, Natrajan and Khalaf model, Bhattacharya and Venkobachar models were tested for the kinetic study. Lagergen pseudo - second order model best fits the kinetics of adsorption ($R^2 \approx 1$). Intra particle diffusion plot showed boundary layer effect and larger intercepts indicates greater contribution of surface sorption in rate determining step. Adsorption was found to increase on increasing pH, increasing temperature and decreasing particle size. Thermodynamic analysis showed negative values of ΔG indicating adsorption was favourable and spontaneous, positive values of ΔH indicating endothermic physisorption and positive values of ΔS indicating increased disorder and randomness at the solid-solution interface of MB with the adsorbents.

KEYWORDS

Adsorption isotherm;
Methylene blue (MB);
Mango leaf powder (MLP);
Kinetic and thermodynamic parameters.

INTRODUCTION

Among the various class of dyes, basic dyes is the brightest class of soluble dyes used in textile industry, as their tinctorial value is very high[1]. Direct discharge of industrial effluents into municipal wastewater plants or environment may cause the formation of toxic carcinogenic breakdown products. The highest rates of toxicity tested in ETDA (Ecological and Toxicological Dyestuff Association) were found due to basic and diazo direct dyes[2]. Recently the Minimum National Standards (MINAS) have been developed for different in-

dustries by Central Pollution Control Board, New Delhi (India). Accordingly, industries have been required to reduce the pollution including decolourization of their effluents before discharge into surface water. Adsorption is one of the most effective methods and activated carbon is the preferred adsorbent used to treat wastewater[1]. But due to the high cost of activated carbon, the use of various inexpensive alternatives has been studied by many researchers. Agricultural wastes or by-products include rice husk[3], rice bran[4], coir pith[5], soybean hull and sugar beet fibre[6], banana pith[7], were applied for the removal of dyes from wastewater.

This paper focuses on the use of mango leaf powder (MLP) as an adsorbent for the removal of methylene blue (MB) from aqueous solutions. Mango, a native South- East Asia, is being grown in India since prehistoric times. 90% of total world production comes from India alone. Mangoes cultivated in Konkan region of Maharashtra state of India have a great demand in foreign countries. Now it has become a favourite fruit of world and is being grown in many other countries. Leaves of mango plants are simple, alternate, dark green, elliptical or lanceolate and careacious.

EXPERIMENTAL (MATERIAL AND METHODS)

Adsorbent

Adsorbent used in the present study is Mango leaf powder (MLP). Mature mango leaves were collected from one of the garden of Konkan region of Maharashtra state in India and washed thoroughly with distilled water to remove dust and other impurities. Washed leaves were dried for 5-6 days in sunlight. Dried leaves were ground in a domestic mixer- grinder. After grinding, the powders were again washed and dried. Different sized MLP's were stored in plastic container for further use.

Dye solution

MB ($C_{16}H_{18}ClN_3S$), the sorbate used in the present study, is a monovalent cationic dye. In dye classification it is classified as C.I.Basic blue 9 and C.I.52015. It has a molecular weight of 373.9 and was supplied by S.D.Fine Chemicals, Mumbai, India. A stock solution of 1000 mg/l was prepared in double- distilled water and the experimental solutions of the desired concentration were obtained by successive dilutions.

Methods

Standard solution of the dye was taken and absorbance was determined at different wavelengths using Equiptronics single beam u.v. visible spectrophotometer to obtain a plot of absorbance verses wavelength. The wavelength corresponding to the maximum absorbance (λmax= 665 nm) as determined from the plot, was noted and this wavelength was used for measuring the absorbance in the present study. pH of solutions were adjusted using 1M HCl and 1M NaOH by Equiptronics pH- meter.

The efficiency of adsorbents is evaluated by conducting laboratory batch mode studies. 25 mg of adsorbents were shaken in 25 ml aqueous solution of dye of varying concentration for different time periods at natural P^H and temperatures. At the end of pre-determined time intervals, adsorbent was removed by centrifugation at 10000 rpm and supernant was analysed for the residual concentration of MB, spectrophotometrically at 665 nm wavelength.

Also, variations in pH, adsorbent dose, particle size, agitation speed, temperature were studied.

Effect of initial dye concentration and contact time

25 mg of adsorbent of ≥ 120 mesh size with 25 ml of dye solution was kept constant for batch experiments. Initial MB concentration of 100, 150, 200, 250, 300, 350 and 400 mg/l were performed at nearly 303K on a oscillator at 230 rpm for 5,10, 15, 20, 30, 40, 50 and 60 minutes at pH = 7. Then optimum contact time was identified for further batch experimental study.

Effect of adsorbent dosage and initial dye concentration

Initial MB concentrations of 400, 500, 600 and 700 mg/l were used in conjunction with adsorbent dose of 1, 2, 3, 4, 5, and 6 g/l. Contact time, pH, agitation speed, temperature and particle size of 30 minutes, 7, 230 rpm, 303K and ≥ 120 mesh respectively were kept constant.

Effect of pH

Initial P^H of MB solutions were adjusted to 3, 4, 5, 6, 7, 8, 9, 10 and 11 for 200 mg/l concentration.

Contact time, adsorbent dose, agitation speed, temperature and particle size of 30 minutes, 1 g/l, 230 rpm, 303K and ≥ 120 mesh respectively were kept constant.

Effect of particle size and initial dye concentration

Three different sized particles of ≥ 120, 120 ≤ 85 and 85 ≤ 60 mesh were used in conjunction with 100, 150, 200, 250, 300 and 350 mg/l MB concentration. Contact time, adsorbent dose, agitation speed, temperature and pH of 30 minutes, 1 g/l, 230 rpm, 303K and 7 respectively were kept constant.

Effect of temperature and initial dye concentration

303K, 313K and 323K temperatures were used in conjunction with 100, 150, 200, 250, 300 and 350 mg/l MB concentration. Contact time, adsorbent dose, agitation speed, particle size and pH of 30 minutes, 1 g/l, 230 rpm, ≥ 120 mesh and 7 respectively were kept constant.

Effect of agitation speed

100, 170 and 230 rpm agitation speeds were used in conjunction with initial MB concentration of 250 mg/l for 5,10, 15, 20, 30, 40, 50 and 60 minutes. Adsorbent dose, pH, temperature and particle size of 1 g/l, 7, 303K and ≥ 120 mesh respectively were kept constant.

Kinetic models

The Lagergen pseudo- first order rate expression[8] is given as

$$\log (q_e - q_t) = \log q_e - (k_1 / 2.303)\, t \quad (1)$$

Where q_e and q_t are amounts of dye adsorbed (mg/g) on adsorbent at equilibrium and at time t, respectively and k_1 is rate constant of pseudo first order adsorption (min^{-1}). The slope and intercept values of plot log (q_e - q_t) against t, used to determine pseudo first order rate constant (k_1) and theoretical amount of dye adsorbed per unit mass of adsorbent $q_{e(the)}$, respectively.

The Langergen pseudo- second order kinetic model[8] is given as

$$t/q_t = 1/(k_2 q_e^2) + t/q_e \quad (2)$$

Where k_2 is rate constant of second order adsorption (g/mg/min). Slope and intercept of plot of t/q_t against t, gives values of $q_{e(the)}$ and k_2 respectively.

The linearized form of Natarajan and Khalaf first order kinetic equation is presented as

$$\log (C_o/C_t) = (K_{ad} /2.303)\, t \quad (3)$$

Where C_o and C_t are concentration of MB (mg/l) at time zero and time t respectively, K_{ad} is first order adsorption rate constant (min^{-1}) calculated from slope of the plot log (C_o/C_t) against t.

The linearized form of Bhattacharya and Venkobachar first order kinetic equation is presented as

$$\log [1 - U(T)] = - (k /2.303)\, t \quad (4)$$

Where $U(T) = [(C_o - C_t) / (C_o - C_e)]$; C_e is equilibrium MB concentration (mg/l); k is first order adsorption rate constant (min^{-1}) calculated from slope of the plot log [1–U(T)] against t. According to Weber and Morris, the intra particle diffusion rate constant (K_i) is given by the following equation

$$q_t = K_i\, t^{1/2} + A \quad (5)$$

K_i (mg /g/ $min^{1/2}$) intraparticle diffusion constant value can be determined from the slope of the plot q_t against $t^{1/2}$. *A* (mg/g) is a constant that gives an indication of the thickness of the boundary layer, i.e. the higher the value of *A*, the greater the boundary layer effect.

The linearized form of Elovich kinetic equation is presented as

$$q_t = 1/\beta[\ln(\alpha\beta)] + \ln t /\beta \quad (6)$$

Where α is the initial adsorption rate (mg /g /min), β is desorption constant ($g \cdot mg^{-1}$) during any experiment. Constants α and β are the calculated, from the intercept and slope of plot q_t against ln t.

Adsorption isotherms

Freundlich, Langmuir and Temkin adsorption isotherms were used to study the adsorption behaviour of MB on MLP.

The linear form of Freundlich isotherm equation was employed for the adsorption of MB onto the adsorbent MLP was represented by

$$\log q_e = \log K_f + 1/n \log C_e \quad (7)$$

Where q_e is amount of MB adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration of MB in solution (mg/l), a plot of log q_e against log C_e gives a straight line, K_f and n are constant incorporating factors

affecting the adsorption capacity and intensity of adsorption calculated from the intercept and slope of the plot respectively.

The linear form of Langmuir isotherm was represented by the following equation

$$C_e / q_e = 1/ (q_m b) + C_e /q_m \quad (8)$$

Where q_m is monolayer (maximum) adsorption capacity (mg/g) and b is Langmuir constant related to energy of adsorption (1/mg) obtained from the slope and intercept values of the plot Ce/qe against Ce respectively.

The essential features of the Langmuir isotherm can be expressed in terms of dimensionless constant separation factor, R_L, which is defined by the following relation given by Hall[11]

$$R_L = 1/ (1+bC_o) \quad (9)$$

Where C_o is initial MB concentration (mg/l).

If,

R_L > 1 Unfavourable adsorption

R_L = 1 Linear adsorption

R_L = 0 Irreversible adsorption

0 < R_L < 1 Favourable adsorption

The Temkin isotherm is given as

$$q_e = B \ln A + b \ln C_e \quad (10)$$

Where A (1/g) is the equilibrium binding constant, corresponding to the maximum binding energy and constant B is related to heat of adsorption calculated from the intercept and slope of the plot q_e against ln C_e respectively.

RESULTS AND DISCUSSION

Effect of initial dye concentration and contact time

Effect of initial dye concentration with contact time on adsorption of MB is presented in Figures 1 and 2. Uptake of MB was rapid in first 5 minutes and after 30 minutes amount of dye adsorbed was almost constant. Therefore, further batch experiments were carried out at 30 minutes optimum contact time. Percentage sorption decreased from 98.7 to 61% but amount of MB adsorbed per unit mass of adsorbent increased from 98.4 to 244 mg/g with increase in MB concentration from 100 to 400 mg/l.

To investigate the mechanism of adsorption, pseudo - first order and pseudo- second order, Natarajan and Khalaf first order and Bhattacharya and Venkobachar first order kinetic models were used.

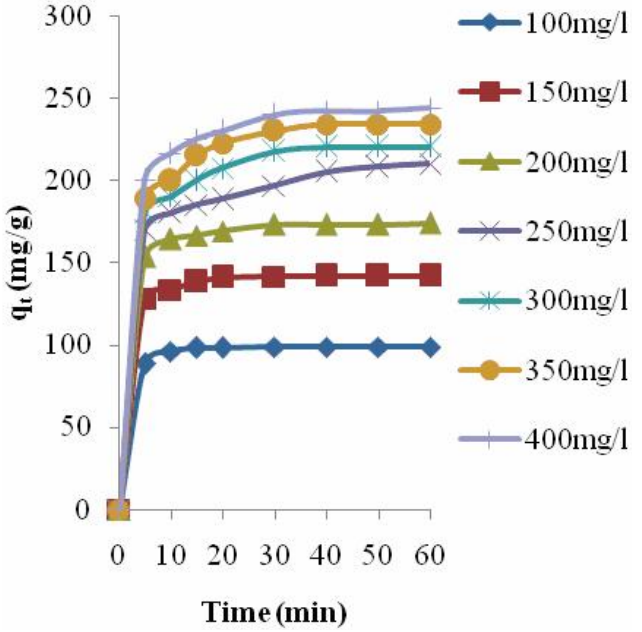

Figure 1 : Effect of initial dye concentration and contact time on adsorption of MB on MLP.

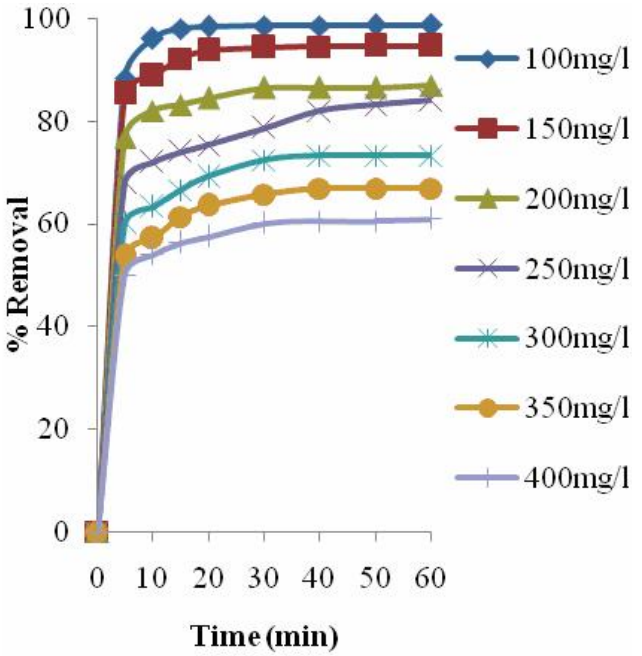

Figure 2 : Effect of initial dye concentration and contact time on % removal of MB on MLP.

The slope and intercept values of plot log (q_e-q_t) against t, Figure 3 were used to determine pseudo first order rate constant (k_1) and theoretical amount of dye adsorbed per unit mass of adsorbent $q_{e(the)}$, respectively. $q_{e(the)}$ were compared with the $q_{e(exp)}$ values in TABLE

1. $q_{e(exp)}$ values differ from the corresponding $q_{e(the)}$ values showed that pseudo first order equation of Langergen does not fit well with whole range of contact time and is generally applicable for initial stage of adsorption.

The slopes and intercepts of plot of t/q_t against t, Figure 4, were used to determine pseudo second order rate constant (k_2) and theoretical amount of dye adsorbed per unit mass of adsorbent $q_{e(the)}$, respectively. From highly linear plot it is cleared that there may be a possibility of chemisorption playing a significant role in the rate determining step. The pseudo second order parameters, $q_{e(the)}$, h and k_2 obtained from the plot are represented in TABLE 1. Where h is initial adsorption rate (mg g^{-1}.min), $h = k_2 qe^2$.

The correlation coefficient R^2 for second order adsorption model has very high values for both the adsorbents ($R^2 \approx 1$) and $q_{e(the)}$ values are consistent with $q_{e(the)}$ showed that pseudo second order adsorption equation of Langergen fit well with whole range of contact time and dye adsorption process appears to be controlled by chemisorptions.

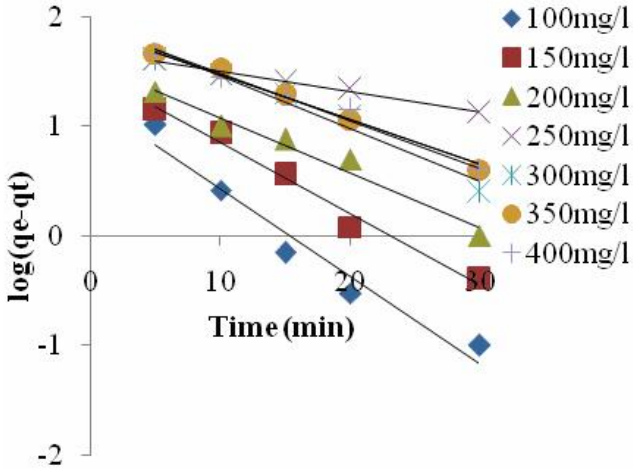

Figure 3 : Pseudo first order plot of effect of initial dye concentration and contact time on adsorption of MB on MLP.

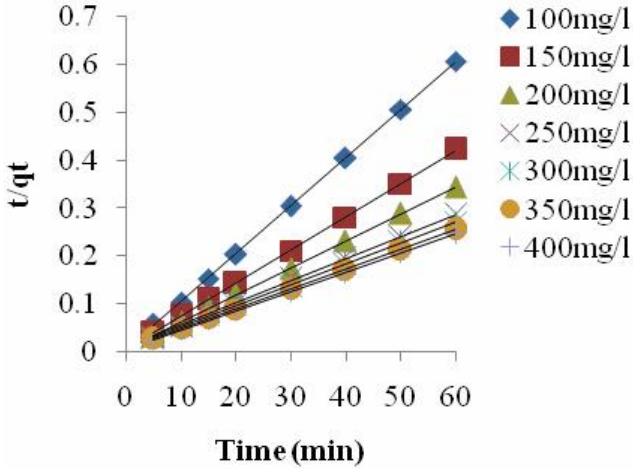

Figure 4 : Pseudo second order plot of effect of initial dye concentration and contact time on adsorption of MB on MLP.

TABLE 1 : Effect of initial dye concentration and contact time on adsorption of MB on MLP

Initial MB Conc. (mg/l)	Pseudo -first order model				Pseudo -second order model				
	$q_{e(exp)}$ (mg/g)	K_1 (min^{-1})	$q_{e(the)}$ (mg/g)	R^2	$q_{e(exp)}$ (mg/g)	K_2 (g/mg/min)	$q_{e(the)}$ (mg/g)	h (mg/g .min)	R^2
100	98.7	0.1819	16.788	0.952	98.7	0.0333	100	333.33	1
150	142	0.1474	31.769	0.983	142	0.0123	142.86	251.02	1
200	174	0.1152	37.757	0.969	174	0.00625	200	250	1
250	210	0.0415	48.195	0.991	210	0.0016	250	100	0.999
300	220	0.1105	88.105	0.955	220	0.00229	250	143.12	0.999
350	234	0.0921	83.56	0.994	234	0.00229	250	143.12	0.999
400	244	0.0921	74.645	0.981	244	0.00267	250	166.88	0.999

K_{ad} is first order adsorption rate constant (min^{-1}) which was calculated from slope of the Natarajan and Khalaf first order kinetic linear plot $\log(C_o/C_t)$ against t, Figure 5, TABLE 2. The overall rate constant K_{ad} for adsorption of dye decreased with increase in concentration. K is first order adsorption rate constant. Bhattacharya and Venkobachar first order kinetic equation (min-1) which was calculated from slope of the linear plot log [1 – U(T)] against t, Figure 6, TABLE 2.

Correlation coefficient values (R^2) values were not high for all concentrations showed that Natarajan and Khalaf (R^2 = 0.762 to 0.982) does not fit well with whole range of concentration but quiet good linearity (R^2 = 0.952 to 0.994) was observed for Bhattacharya and Venkobachar first order equation for adsorption of MB on MLP. Steps involved in sorption of the dye by adsor-

bent includes transport of solute from aqueous to surface of solid and diffusion of solute into the interior of pores, which is generally a slow process. The intra particle diffusion rate constant K_i (mg/ g/ $min^{1/2}$) values was determined from the slope of the plots q_t against $t^{1/2}$, Figure 7 showed a linear relationship after certain time but they do

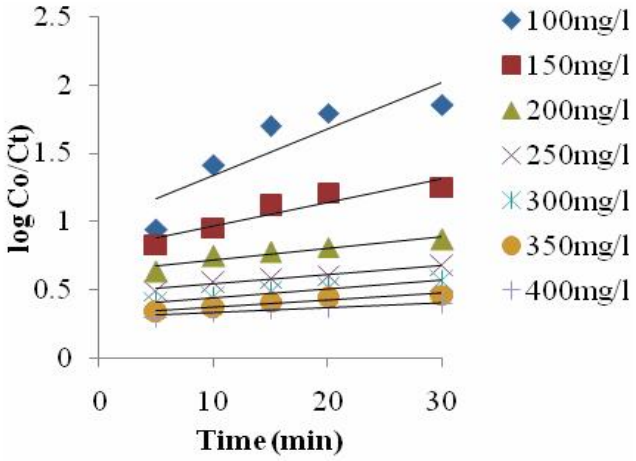

Figure 5 : Natarajan and Khalaf first order plot of effect of initial dye concentration and contact time on adsorption of MB on MLP.

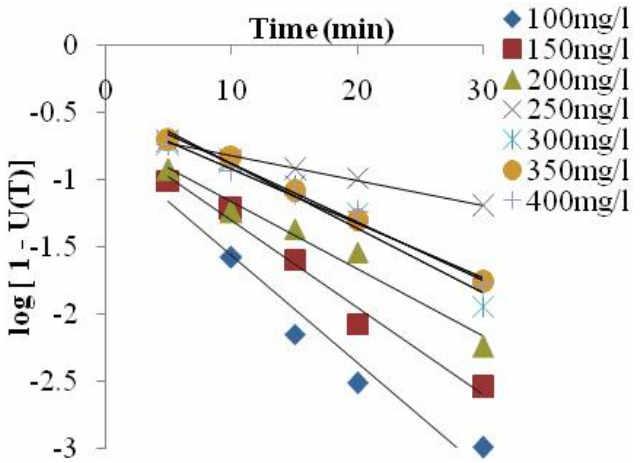

Figure 6 : Bhattacharya and Venkobachar first order plot of effect of initial dye concentration and contact time on adsorption of MB on MLP.

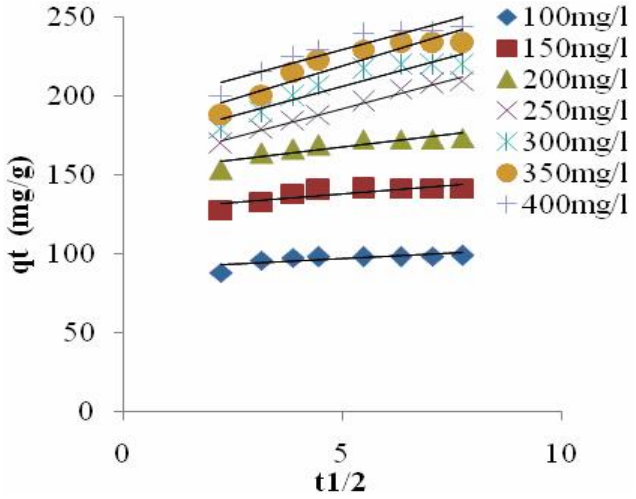

Figure 7 : Intra particle diffusion plot of effect of initial dye concentration and contact time on adsorption of MB onto MLP.

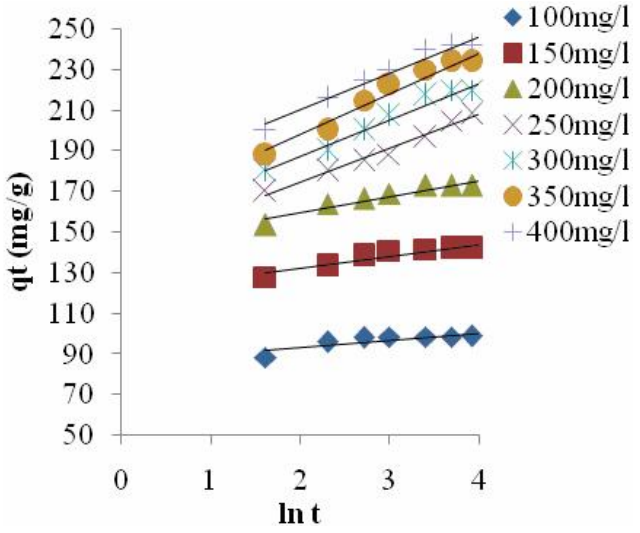

Figure 8 : Elovich plot of effect of initial dye concentration and contact time on adsorption of MB on MLP.

TABLE 2 : Effect of initial dye concentration and contact time on adsorption of MB on MLP

Initial MB Conc. (mg/l)	Intra particle diffusion model			Elovich Model			Natarajan and Khalaf model		Bhattacharya and Venkobachar model	
	K_i (mg/g/$min^{1/2}$)	A (mg/g)	R^2	α (mg/g/min)	B (g.mg^{-1})	R^2	K (min-1)	R^2	K (min-1)	R^2
100	1.37	90.12	0.552	3.526	0.295	0.677	0.078	0.762	0.182	0.952
150	2.276	127	0.732	5.769	0.178	0.865	0.039	0.881	0.147	0.983
200	3.199	152.2	0.793	8.246	0.128	0.911	0.018	0.9	0.115	0.969
250	7.374	155.6	0.984	18.862	0.0597	0.984	0.014	0.976	0.042	0.991
300	7.525	168.9	0.886	19.966	0.0563	0.958	0.014	0.986	0.111	0.955
350	8.36	177.5	0.86	22.6	0.0502	0.948	0.012	0.934	0.099	0.994
400	7.522	191.9	0.874	19.862	0.0558	0.963	0.007	0.939	0.094	0.981

not pass through origin due boundary layer effect. The larger the intercept, the greater the contribution of surface sorption in rate determining step. The intercepts and K_i values of plots q_t against $t^{1/2}$ increased with increase the initial concentration of dye, TABLE 2. Initial portion is attributed to the liquid film mass transfer and linear portion to the intra particle diffusion. Elovich kinetic model constants α and β were calculated, TABLE 2 from the intercept and slope of plot q_t against ln t, Figure 8. This Elovich kinetic model gave quiet satisfactory results for MLP. Here α is initial rate of adsorption in mg/g/min which generally increased with increase in initial concentration of dye and β is desorption constant in g/mg which decreased with increase in concentration of dye.

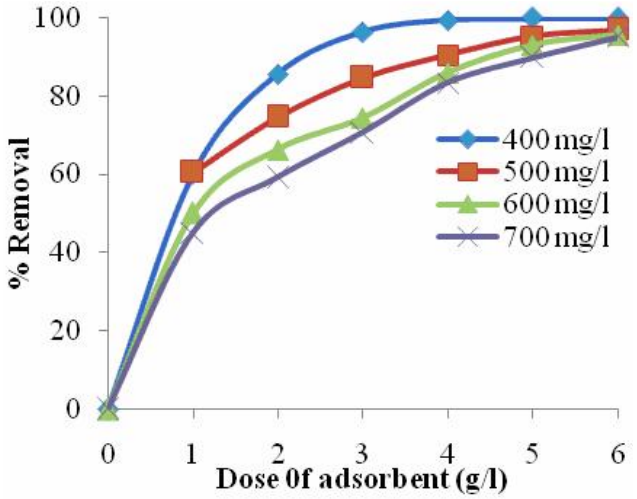

Figure 9 : Effect of adsorbent dosage and initial dye concentration on % removal of MB on MLP.

Effect of pH

pH is an important factor in controlling the adsorption of dye onto adsorbent. The adsorption of MB from 200mg/l concentration on MLP was studied by varying the pH from 3 to 11. The amount of dye adsorbed per unit mass of adsorbent at equilibrium (q_e) increased from 56.7 to 184 mg/g by variation in pH from 3 to 11, Figure 11.

Effect of particle size and initial dye concentration

Adsorption of MB on three sized particles ≥ 120, 120 ≤ 85 and 85 ≤ 60 mesh of MLP was studied for 100 to 350 mg/l concentrations of MB. The results of variation of these particle sizes on dye adsorption are shown in Figure 12.

Effect of adsorbent dosage and initial dye concentration

The adsorption of MB on MLP was studied by varying the adsorbent dosage. The percentage of adsorption increased with increase in dosage of adsorbent. Percentage removal of MB increased (Figure 9) but amount of MB adsorbed in mg/g of adsorbent decreased (Figure 10) with increase in dose of adsorbent. After 3 - 4 g/l adsorbent dose % removal of dye remains almost constant. For above 95% removal of MB, adsorbent dosage of 3, 4, 6, 6 g/l for MLP were needed for initial MB concentrations 400, 500, 600 and 700 mg/l respectively.

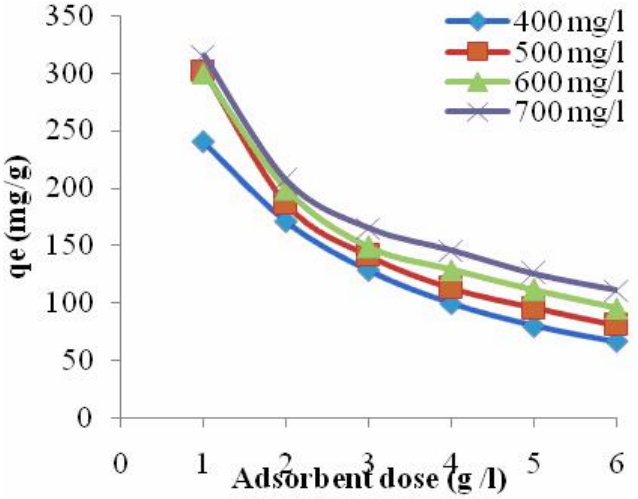

Figure 10 : Effect of adsorbent dosage and initial dye concentration on amount adsorbed of MB in mg/g of MLP.

It can be observed that as the particle size increased the adsorption of dye decreased and hence the percentage removal of dye also decreased. This is due to larger surface area that is associated with smaller particles. For larger particles, the diffusion resistance to mass transfer is higher and most of the internal surface of the particle may not be utilized for adsorption and consequently amount of dye adsorbed is small.

K_f and n are Freundlich constants incorporating factors affecting the adsorption capacity and intensity of adsorption respectively. The plots of log q_e against log C_e showed good linearity (R^2 = 0.987 to 0.998) indicating the adsorption of MB obeys the Freundlich adsorption isotherm, Figure 13. The values of K_f and n are given in the TABLE 3. Values of n between 1 to 10 indicate an effective adsorption[10] while higher values of K_f repre-

sent an easy uptake of adsorbate from the solution[4].

q_m is monolayer (maximum) adsorption capacity (mg/g) and b is Langmuir constant related to energy of adsorption (1/mg). A linear plots of C_e / q_e against C_e suggest the applicability of the Langmuir isotherms Figure 14 (R^2= 0.983 to 0.994). The values of q_m and b were determined slope and intercepts of the plots, TABLE 3. Dimensionless constant separation factor, R_L values lies in between 0 to 1 for MLP indicates favourable adsorption, TABLE 5.

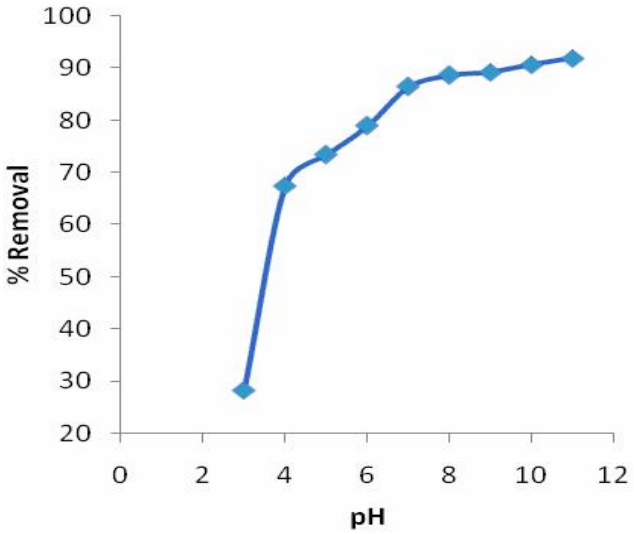

Figure 11 : Effect of pH on adsorption of MB from initial concentration 200 mg/l MB solution on MLP.

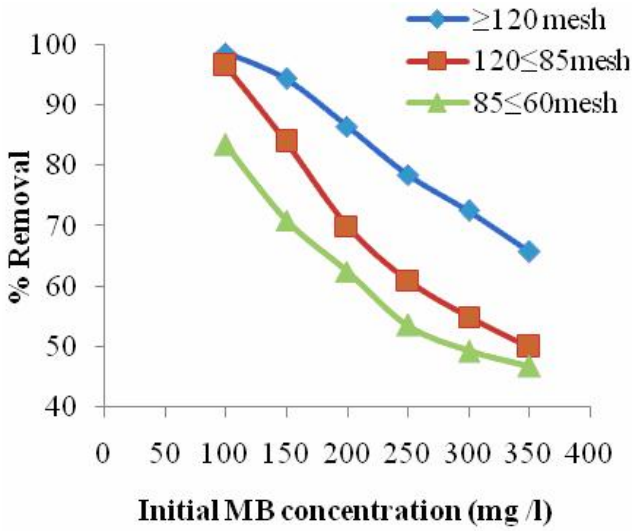

Figure 12 : Effect of particle size and initial dye concentration on % removal of MB on MLP.

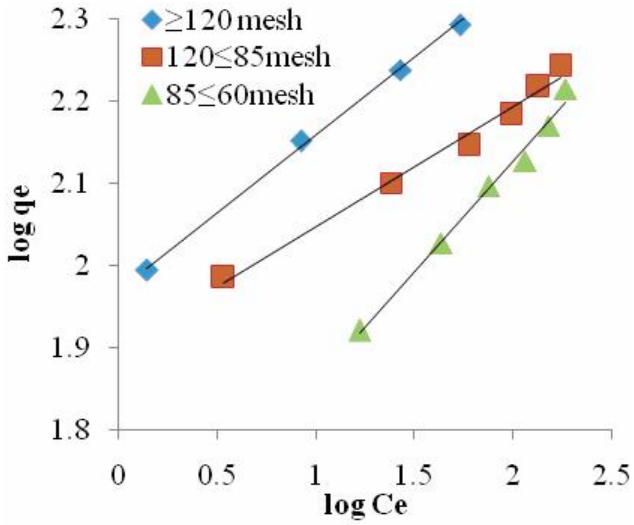

Figure 13 : Freundlich isotherm plot of effect of particle size and initial dye concentration on adsorption of MB on MLP.

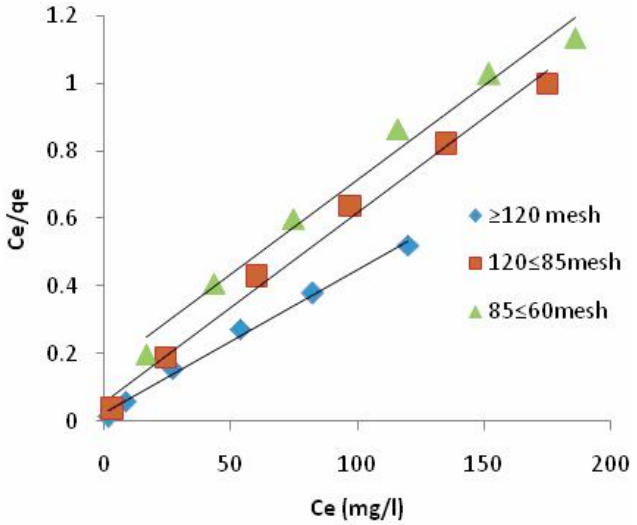

Figure 14 : Langmuir isotherm plot of effect of particle size and initial dye concentration on adsorption of MB on MLP.

Linear plot of q_e against ln C_e, enables the determination of the Temkin constants B and A from the slope and intercept. The results of the plots are given Figure 15 in TABLE 3. Constant A which is a equilibrium binding constant, decreased with increase in particle size of adsorbents.

Effect of temperature and initial dye concentration

Temperature has important effects on adsorption process. Adsorption of MB at three different temperatures (303K, 313K and 323K) onto MLP was studied for 100 to 350 mg/l initial MB concentrations. The results variation in temperatures on dye adsorption is shown in Figure 16.

It is observed that as the experimental temperature increases from 303K to 323K, the dye adsorption also increases. As the temperature increases, rate of diffusion

of adsorbate molecules across external boundary layer and internal pores of adsorbent particle increases[7]. Changing the temperature will change the equilibrium capacity of the adsorbent for particular adsorbate[7,8].

TABLE 3 : Effect of particle size and initial dye concentration on adsorption of MB on MLP

Mesh	Freundlich isotherm parameters			Langmuir isotherm parameters			Temkin isotherm parameters		
	K_f	n	R^2	q_m	b	R^2	A	B	R^2
≥ 120	92.897	5.291	0.998	250	0.1481	0.994	17.036	29.39	0.985
120 ≤ 85	79.616	6.849	0.987	200	0.0877	0.991	38.346	18.99	0.96
85 ≤ 60	38.905	3.745	0.989	200	0.0318	0.983	0.754	31.43	0.964

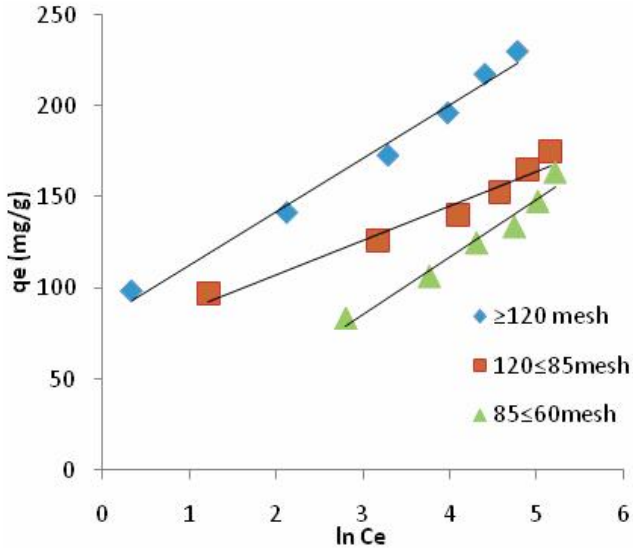

Figure 15 : Temkin isotherm plot of effect of particle size and initial dye concentration on adsorption of MB on MLP.

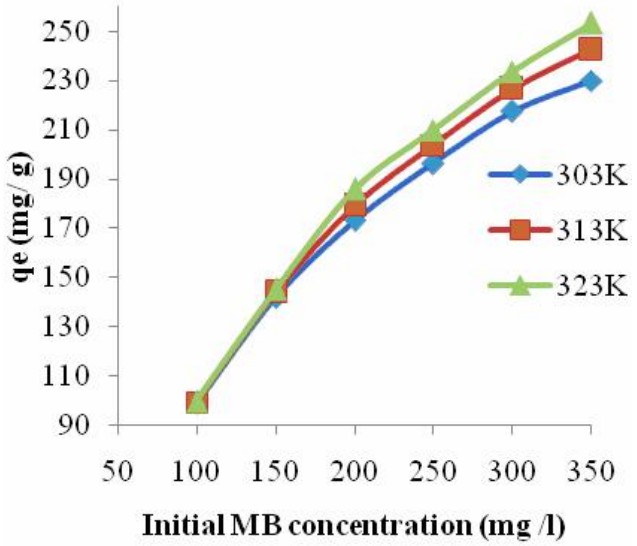

Figure 16 : Effect of temperature and initial dye concentration on adsorption of MB on MLP.

Freundlich and Langmuir adsorption isotherms were employed for 303K, 313K and 323K temperatures. Plot of log q_e against log C_e, Figure 17 and plots of C_e / q_e against C_e, Figure 18 showed good linearity with regression coefficients ($R^2 > 0.99$). Freundlich constants K_f and n as well as Langmuir constants q_m and b are given in TABLE 5. Dimensionless constant separation factor (R_L) values lies in between 0 to 1 for both the

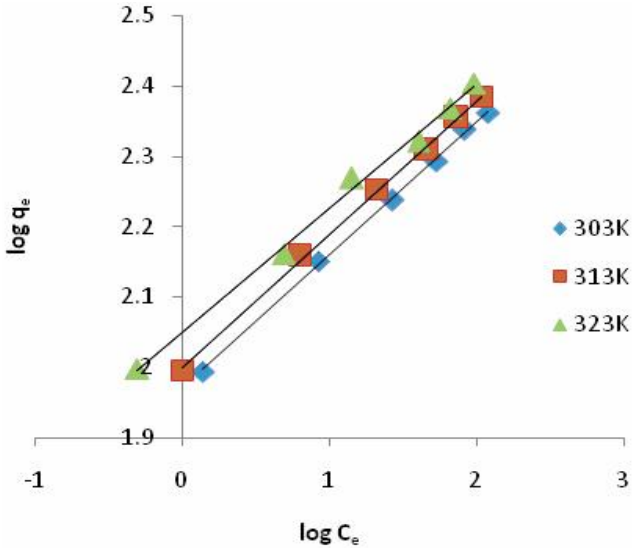

Figure 17 : Freundlich isotherm plot of effect of temperature and initial dye concentration on adsorption of MB on MLP.

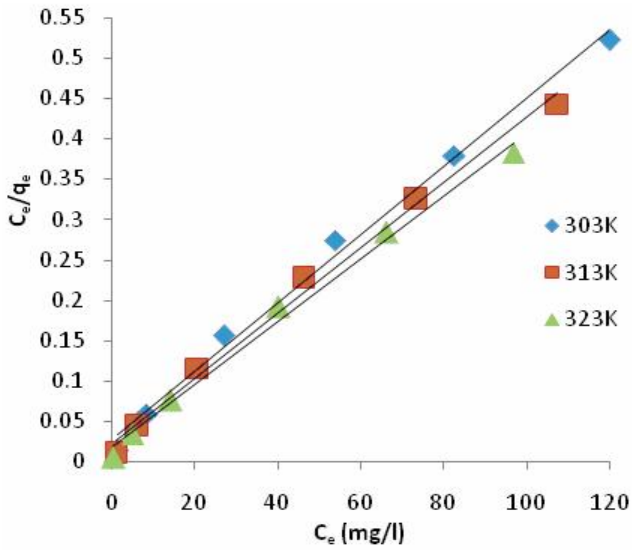

Figure 18 : Langmuir isotherm plot of effect of temperature and initial dye concentration on adsorption of MB on MLP.

adsorbents. Monolayer (maximum) adsorption capacity (q_m) obtained from Langmuir plots were 250, 250 and 333.333 mg/g for 303K, 313K and 323K respectively. Both Langmuir as well as Freundlich adsorption isotherms fits well for 313 to 323K temperature range.

Temkin plot q_e against ln C_e, Figure 19 also showed linearity (R^2 = 0.985 to 0.99). Temkin constants A and B are given in TABLE 4.

TABLE 4 : Effect of temperature and initial dye concentration on adsorption of MB on MLP

Temp. in Kelvin	Freundlich isotherm parameters			Langmuir isotherm parameters			Temkin isotherm parameters		
	K_f	n	R^2	q_m	b	R^2	A	B	R^2
303	92.897	5.291	0.998	250	0.1481	0.994	17.036	29.39	0.985
313	99.77	5.291	0.999	250	0.1818	0.993	21.483	30.33	0.986
323	111.944	5.682	0.995	333.333	0.1765	0.993	21.14	32.25	0.99

TABLE 5 : Dimensionless separation factor (R_L) calculated from Langmuir constant (b) for MLP

Initial MB Conc. (mg/l)	Mesh			Temperature		
	≥ 120	120 ≤ 85	85 ≤ 60	303K	313K	323K
100	0.0633	0.1024	0.2392	0.0633	0.0521	0.0536
150	0.0431	0.0706	0.1733	0.0431	0.0354	0.0364
200	0.0327	0.0539	0.1359	0.0327	0.0268	0.0275
250	0.0263	0.0436	0.1117	0.0263	0.0215	0.0222
300	0.022	0.0366	0.0949	0.022	0.018	0.0185
350	0.0189	0.0316	0.0824	0.0189	0.0155	0.0159

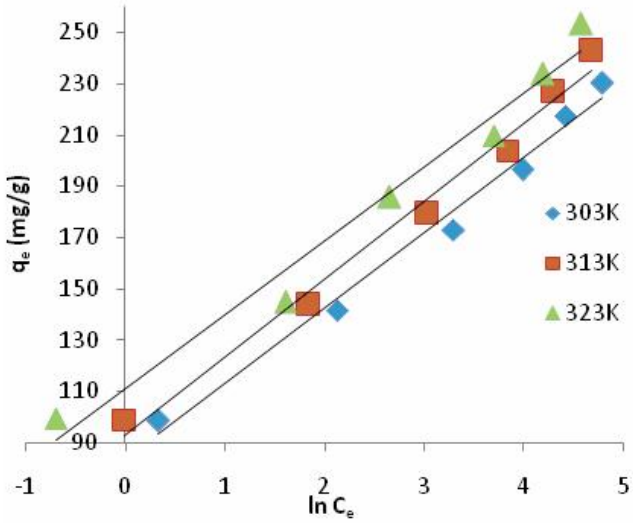

Figure 19 : Temkin isotherm plots of effect of temperature and initial dye concentration on adsorption of MB on MLP.

Thermodynamic analysis

Thermodynamic parameters such as change in free energy (ΔG) (J/mole), enthalpy (ΔH) (J/mole) and entropy (ΔS) (J/K/mole) were determined using following equations

$$K_o = C_{solid}/C_{liquid} \quad (11)$$

$$\Delta G = -RT\ln K_o \quad (12)$$

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

$$\ln K_o = -\Delta G/RT$$

$$\ln K_o = \Delta S/R - \Delta H/RT \quad (13)$$

Where K_o is equilibrium constant, C_{solid} is solid phase concentration at equilibrium (mg/l), C_{liquid} is liquid phase concentration at equilibrium (mg/l), T is absolute temperature in Kelvin and R is gas constant.

ΔG values obtained from equation (12), ΔH and ΔS values obtained from the slope and intercept of plot ln K_o against 1/T, Figure 20 presented in TABLE 6. The negative value of ΔG indicates the adsorption is favourable and spontaneous. ΔG values increases with increase in temperature and decreases with increase in initial concentration of MB. The low positive values of ΔH indicate physisorption and endothermic nature of adsorption[12-14]. The positive values of ΔS indicate the increased disorder and randomness at the solid solution interface of MB with the adsorbent. The adsorbed water molecules, which were displaced by adsorbate

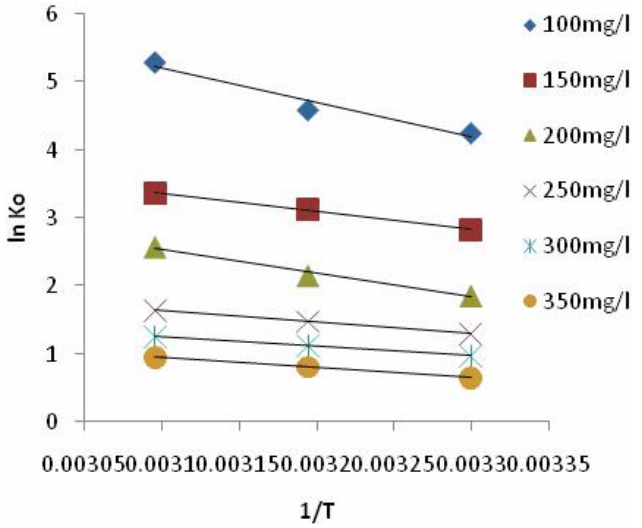

Figure 20 : Von't Hoff plot of effect of temperature and initial dye concentration on adsorption of MB on MLP.

TABLE 6 : Equilibrium constants and thermodynamic parameters for the adsorption of MB on MLP

Initial MB Conc. (mg/l)	Ko			ΔG (J/mole)			ΔH (J/mole)	ΔS (J/K/mole)
	303K	313K	323K	303K	313K	323K		
100	70.429	99	198.2	-10717.9	-11957.8	-14203.9	41927.5	173.1806
150	16.857	22.81	29	-7116.01	-8137.8	-9042.61	22090.3	96.4424
200	6.407	8.615	13.085	-4679.19	-5604.14	-6905.37	28982.6	110.9088
250	3.651	4.411	5.219	-3262.4	-3862.2	-4437.09	14532.87	58.75504
300	2.636	3.082	3.518	-2442.06	-2928.76	-3378.03	11739.37	46.83276
350	1.917	2.256	2.616	-1638.92	-2116.98	-2582.12	12645.59	47.17364

molecules, gain more translational energy than is lost by the adsorbate molecules, thus allowing prevalence of randomness in the system. The increase of adsorption capacity of the adsorbent at higher temperatures was due to enlargement of pore size and activation of adsorbent surface[12-16].

Effect of agitation speed

The sorption is influenced by mass transfer parameters. Figure 21 illustrates the sorption kinetics of MB by MLP for different agitation speeds ranging from 100 to 230 rpm.

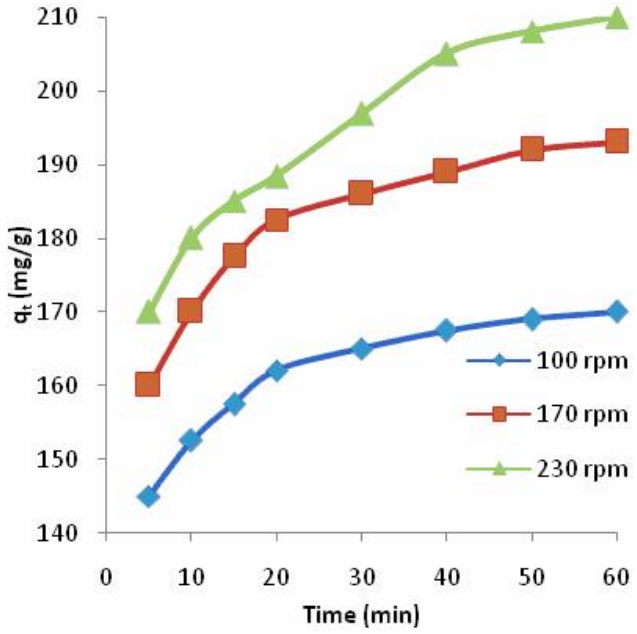

Figure 21 : Effect of agitation speed on adsorption of MB on MLP.

The amount adsorbed at equilibrium was found to increase from 170, 193 and 210 mg/g of MLP with increased in agitation speed from 100, 170 and 230 rpm of an oscillator from 250 mg/l initial MB solution. With increased the agitation speed, the rate of diffusion of dye molecules from bulk liquid to the liquid boundary layer surrounding the particle become higher because of an enhancement of turbulence and a decrease of thickness of the liquid boundary layer.

CONCLUSION

The goal of this work was to explorer the potential use of mango leaf powder (MLP) as low cost adsorbent for the removal of MB from aqueous solutions. Sorption amount increased with increase of initial MB concentration but percentage removal decreased with increased in initial MB concentration.

Freundlich, Langmuir and Temkin isotherm models were used to test the equilibrium data. The best fitting isotherm models was found to be Langmuir and Freundlich. The linear regression coefficient R^2 was used to elucidate the best fitting isotherm model. Monolayer (maximum) adsorption capacity (q_m) for MLP was found to be 250 mg/g.

Lagergen pseudo –first order model, Lagergen pseudo -second order model, Natrajan and Khalaf model, Bhattacharya and Venkobachar models were tested for the kinetic study. Lagergen pseudo -second order model best fits the kinetics of adsorption ($R^2 \approx 1$). Intra particle diffusion plot showed boundary layer effect and larger intercepts indicates greater contribution of surface sorption in rate determining step.

Adsorption was found to increase on increasing pH, increasing temperature, increasing agitation speed and decreasing particle size.

Thermodynamic analysis showed negative values of ΔG indicating adsorption was favourable and spontaneous, positive values of ΔH indicating endothermic physisorption and positive values of ΔS indicating increased disorder and randomness at the solid- solution

interface of MB with the adsorbents. Biosorption technology, utilizing natural materials to passively remove dyes from aqueous solutions, offers an efficient and cost effective alternative compared to traditional chemical and physical remediation and decontamination techniques. MLP, a zero cost and easily available material was found to be effective adsorbent for removal of basic dyes.

REFERENCES

[1] K.G.Bhattacharyya, A.Sharma; Kinetics and thermodynamics of methylene blue adsorption on Neem (*Azadirachta indica*) leaf powder, Dyes and Pigments, **65**, 51-59 **(2005)**.

[2] G.M.Walker, L.R.Weatherley; Fixed bed adsorption of acid dyes onto activated carbon, Enviornmental Pollution, **99**, 133-136 **(1998)**.

[3] Y.S.Ho, G.Mckay; Water Res., **33**, 578-584 **(1999)**.

[4] A.H.Mahvi, A.Maleki, A.Eslami; Potential of rice husk and rice husk ash for phenol removal in aqueous system. Am.J.Appl.Sci., **1(4)**, 321-326 **(2004)**.

[5] J.Potgeiter, S.Potgeiter-Vermaak, P.Kalibatonga; Heavy metals removal from solution by Palygorskite clay. Minerals Engineering, **(2005)**.

[6] C.Namasivayam, N.Kanchana; Removal of congo red from aqueous solution by waste banana pith, J.Partanica., **1**, 33 **(1993)**.

[7] S.H.Lin; Adsorption of disperse dye on various adsorbents, J.Chem.Tech.Biotechnol., **58**, 159-162 **(1993)**.

[8] A.K.Singh, D.P.Singh, K.K.Pandey, V.N.Singh; Wollastonite as adsorbentfor removal of Fe(II) from water, J.Chem.Technol., **42**, 39 **(1988)**.

[9] W.J.Weber Jr., J.C.Morris; Kinetics of adsorption on carbon from solutions, J.Sanitary Eng.Div.ASCE, **89**, 31-60 **(1963)**.

[10] J.Potgeiter, S.Potgeiter-Vermaak, P.Kalibatonga; Heavy metals removal from solution by Palygorskite clay. Minerals Engineering, **(2005)**.

[11] K.R.Hall, L.C.Eagleton, A.Acrivos, T.Vermeulen; Ind.Eng.Chem.Fund., **5**, **(1966)**.

[12] S.Arivoli, B.Venkatraman, T.Rajachandrasekar, M.Hema; Res.J.Chem.Enviorn., **17**, 70 **(2007)**.

[13] S.Arivoli, K.Kalpana, R.Sudha, T.E.Rajachandrasekar; J.Chem.., **4**, 238 **(2007)**.

[14] G.Renmin, S.Yingzhi, C.Jian, L.Huijun, Y.Hao; Dyes and Pigments, **67**, 179 **(2005)**.

[15] V.Vadivelan, K.Vasnthkumar; J.Colloid Inter.Sci., **286**, 91 **(2005)**.

[16] W.J.Weber; Principle and Application of Water Chemistry, S.D.Faust, J.V.Hunter, (Eds); Wiiley, New York, **(1967)**.

[17] C.Namasivayam, R.T.Yamuna; Envior.Pollution, **89**, 1 **(1995)**.

[18] I.Langmuir; J.Amer.Chem.Soc., **40**, 1361 **(1918)**.

[19] H.Freundlich; Phys.Chemie., **57**, 384 **(1906)**.

[20] P.Nigam, G.Armour, R.M.Banat, D.Singh, R.Marchant; Bioresour.Technol., **72**, 219-226 **(2002)**.

[21] G.Mckay; J.Chem.Technol.Biotechnol., **32**, 759 **(1982)**.

[22] J.Shore; Advances indirect dyes. Indian J.Fib.Text. Res., **21**, 1-29 **(1996)**.