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Comparative Study of Adsorption of Methylene Blue onto Mangrove Plant (*Sonneratiaapetala*) Leaf and Fruit Powder: Equilibrium, Kinetic and Thermodynamic Analysis

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Abstract: *Batch adsorption of methylene blue (MB) onto mangrove plant leaf powder (MPLP) and mangrove plant fruit powder (MPFP) was investigated. The parameter studied includes initial dye concentration, adsorbent dose, pH, agitation time, agitation speed, temperature and particle size. Freundlich, Langmuir and Temkin isotherm models were used to test the equilibrium data. The best fitting isotherm model was found to be Langmuir (R^2 = 0.988 to 0.997 for MPLP and 0.974 to 0.989 for MPFP). Lagergen pseudo -second order model best fits the kinetics of adsorption ($R^2 \geq 0.99$). 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 for MPLP as well as MPFP. Thermodynamic analysis showed negative values of ΔG indicating adsorption was favourable and spontaneous, positive values of ΔH indicating endothermicphysisorption and positive values of ΔS indicating increased disorder and randomness at the solid- solution interface of MB with the adsorbents. The forward rate constant was much higher than reverse rate constant suggesting dominance of rate of adsorption. But from overall observations, MPLP was found to be slightly better adsorbent than MPFP.*

Keywords: *Adsorption, methylene blue, Mangrove plant leaf and fruit powder, isotherms*

1. INTRODUCTION

Dye contaminated wastewater originates from a number of industries such as plastic, tannery, textile, packaging to colour their final products. Control of pollution is one of the prime concerns of society today. Many dyes and their degradated products may be toxic to living organisms[1]. Therefore it is necessary to decolourise wastewater before discharge. Colour removal was mostly studied with physiochemical methods such as ultra filtration, electrochemical adsorption, coagulation and photo-oxidation[1-2].

Among these methods, adsorption is widely used for dye adsorption from wastewaters [2-3]. Activated carbon is most commonly used for dye removal[3]. But it is expensive and also causes several problems during regeneration and disposal. Therefore, many researchers have studied the feasibility of using low cost bio sorbents such as coconut shell, ground nut shell, rice husk, bamboo dust and straw [1]; powered activated sludge[2]; neem leaf powder [3] for removal of various dyes from wastewaters.

MB is an important basic dye widely used for dyeing, printing cotton and tannin, printing calcico, dyeing leather, indicating oxidation – reduction. In zinc free form, it is used as an antiseptic and for other medicinal purposes. It causes eye burns. It also may cause methemoglobinemia, cyanosis, and tachycardia, if inhaled. It also causes irritation to the skin. Hence it is necessary to remove MB from wastewater.

Therefore there is a need for the search of low cost and easily available biomaterials as adsorbents for removal of dyes from wastewater. In this paper, we attempt to use MPLP and MPFP as adsorbents. In India, mangrove vegetation is found in coastal areas of Mumbai, Kerala, Bengal and Andaman and Nicobar Island. Mangove plants include Rhizophora, Sonneratia, Avicenia, Salsola etc. In this study, we used Sonneratiaapetala. Mature leaves and fruits of Sonneratiaapetala were collected from coastal area of Alibag (Village Chikhali).

2. MATERIALS AND METHODS

2.1. Sorbate and Chemicals

MB ($C_{16}H_{18}ClN_3S$), the sorbate used in the present study, is a monovalent cationic dye. It has a molecular weight of 373.9 and was supplied by Merck. A stock solution of 1000 mg l^{-1} was prepared and the working solutions were prepared by diluting the stock solution by distilled water as per requirement.

2.2. Sorbent

Mature mangrove plant leaves and fruits were washed thoroughly with distilled water to remove dust and other impurities. Washed leaves and fruits were dried for 5-6 days in sunlight. Dried leaves and fruits were ground in a domestic mixer-grinder. After grinding, the powders were again washed and dried. Different sized MPLP and MPFP were stored in plastic container for further use.

2.3. Sorption Kinetics

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

Also variation in pH, adsorbent dose, particle size, agitation speed, was studied. Comparative studies of both the adsorbents (MPLP and MPFP) were carried out under same experimental conditions.

2.3.1. 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^{-1} 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.

2.3.2. Effect of Adsorbent Dosage and Initial Dye Concentration

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

2.3.3. Effect of pH

Initial pH of MB solutions was adjusted to 3, 4, 5, 6, 7, 8, 9, 10 and 11 for 200 mg l^{-1} concentration. Contact time, adsorbent dose, agitation speed, temperature and particle size of 30 minutes, 1 g l^{-1}, 230 rpm, 303K and ≥ 120 mesh respectively were kept constant.

2.3.4. 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^{-1} MB concentration. Contact time, adsorbent dose, agitation speed, temperature and pH of 30 minutes, 1 g l^{-1}, 230 rpm, 303K and 7 respectively were kept constant.

2.3.5. 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^{-1} MB concentration. Contact time, adsorbent dose, agitation speed, particle size and pH of 30 minutes, 1 g l^{-1}, 230 rpm, ≥ 120 mesh and 7 respectively were kept constant.

2.3.6. Effect of Agitation Speed

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

3. Results and Discussion

3.1. 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(a) and 2(a)** for MPLP, **Figures 1(b) and 2(b)** for MPFP. 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 98.9 to 67.75% for MPLP and 98.2 to 63.25% for MPFP) but amount of MB adsorbed per unit mass of adsorbent increased (From 98.9 to 271 mg g^{-1} for MPLP and 98.2 to 253 mg g^{-1} for MPFP) with increase in MB concentration from 100 to 400 mg l^{-1}.

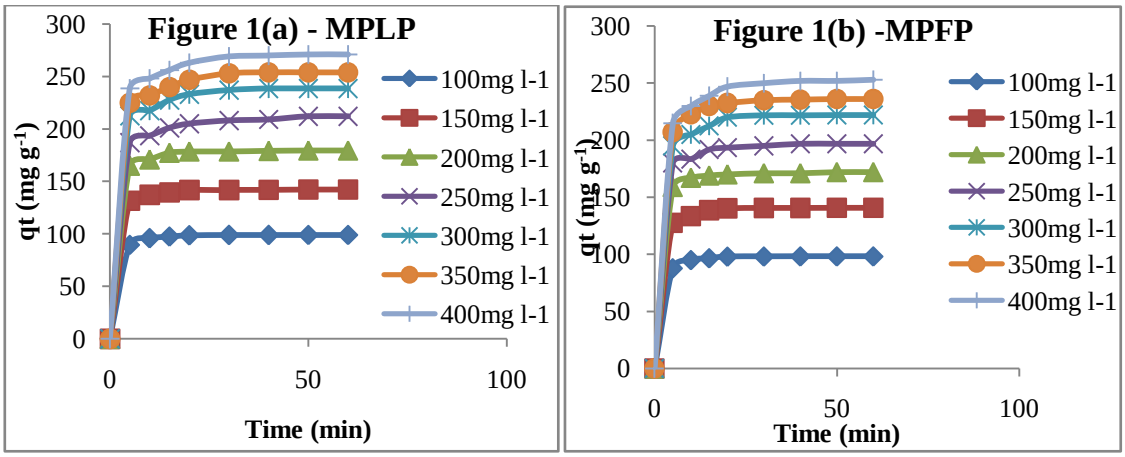

Fig1(a) and 1(b). *Effect of initial dye concentration and contact time on adsorption of MB onto MPLP and MPFP respectively*

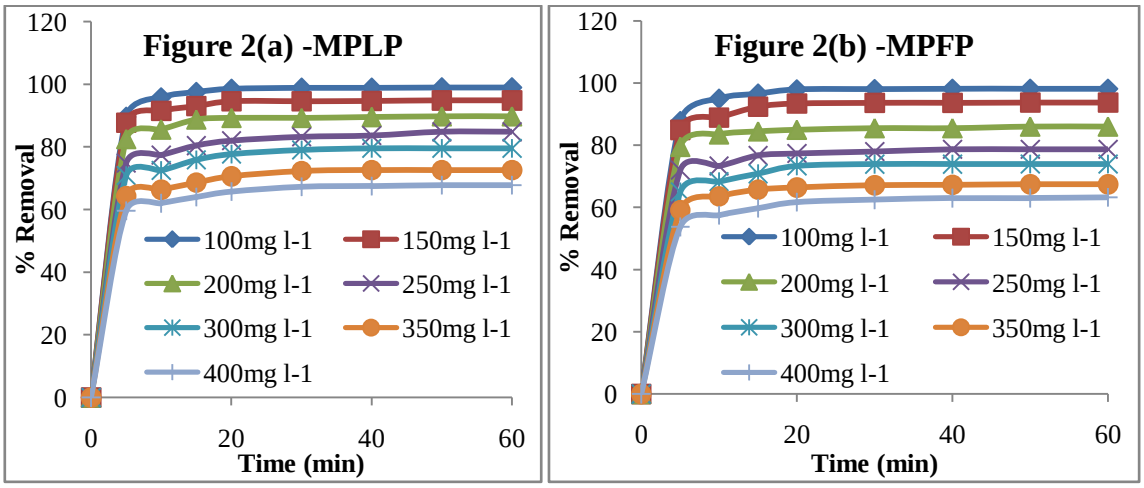

Fig2(a) and 2(b). *Effect of initial dye concentration and contact time on percentage removal of MB onto MPLP and MPFP respectively*

To investigate the mechanism of adsorption, pseudo - first order and pseudo- second order models were used.

The Lagergen pseudo- first order rate expression is given as

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

Where q_e and q_t are amounts of dye adsorbed (mg g^{-1}) 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 plots $\log(q_e - q_t)$ against t , **Figure 3(a)** for MPLP and **3(b)** for MPFP 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.

Table1. *Pseudo -first order model constants for effect of initial dye concentration and contact time on adsorption of MB*

Initial MB Conc. ($mg\ l^{-1}$)	**MPLP**				**MPFP**			
	$q_{e(exp)}$ ($mg\ g^{-1}$)	K_1 (min^{-1})	$q_{e(the)}$ ($mg\ g^{-1}$)	R^2	$q_{e(exp)}$ ($mg\ g^{-1}$)	K_1 (min^{-1})	$q_{e(the)}$ ($mg\ g^{-1}$)	R^2
100	98.9	0.205	26.122	0.993	98.2	0.1934	22.646	0.934
150	142.2	0.2096	37.757	0.926	140.6	0.2073	41.495	0.975
200	179.5	0.1865	42.267	0.972	172	0.0967	15.776	0.947
250	212	0.0852	40.644	0.989	196.8	0.0944	26.669	0.948
300	238.5	0.1059	50.699	0.955	222	0.2027	115.08	0.963
350	254	0.0944	51.404	0.962	236	0.1336	51.404	0.994
400	271	0.0921	55.081	0.981	253	0.1036	62.951	0.98

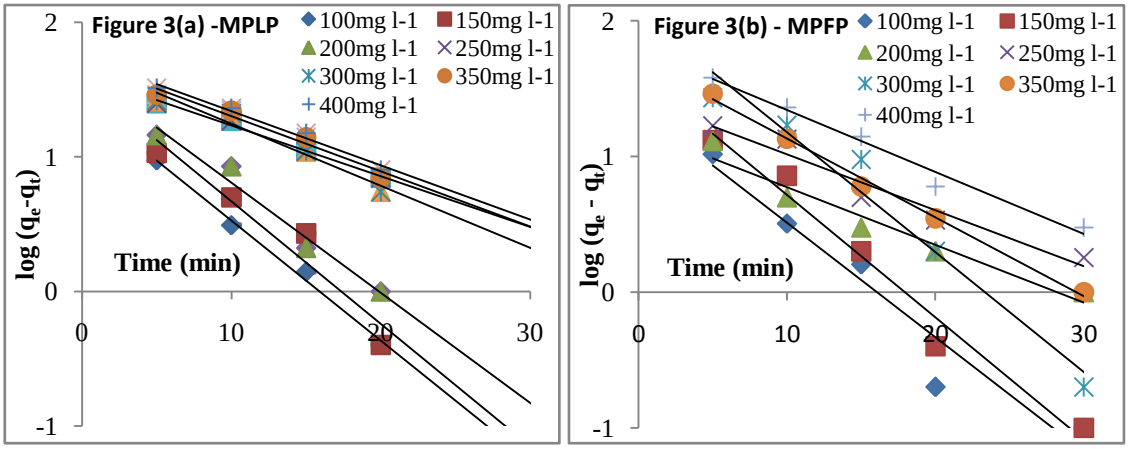

Fig3(a) and 3(b). *Pseudo first order plot of effect of initial dye concentration and contact time on adsorption of MB onto MPLP and MPFP respectively*

The Langergen pseudo- second order kinetic model is given as

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

Where k_2 is rate constant of second order adsorption ($g\ mg^{-1}min^{-1}$). The slopes and intercepts of plots of t/q_t against t, **Figure 4(a)** for MPLP and **4(b)** for MPFP were used to determine $q_{e(the)}$ and k_2 respectively. From highly linear plots it is cleared that there may be a possibility of chemisorptions 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 2**.

Where h is initial adsorption rate ($mg\ g^{-1}$ .min), $h = k_2\ q_e^2$

The correlation coefficient R^2 for second order adsorption model has very high values for both the adsorbents ($R^2 \geq 0.999$) and $q_{e(the)}$ values are consistent with $q_{e(exp)}$ 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.

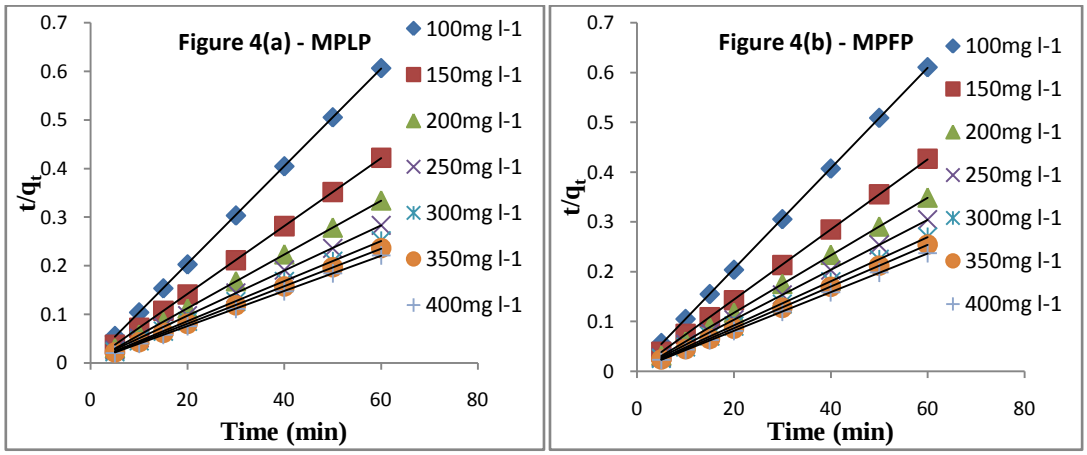

Fig4(a) and 4(b). *Pseudo second order plot of effect of initial dye concentration and contact time on adsorption of MB onto MPLP and MPFP respectively*

Table2. *Pseudo -second order model constants for effect of initial dye concentration and contact time on adsorption of MB*

Initial MB Conc. (mg l^{-1})	MPLP					MPFP				
	$q_{e(exp)}$ (mg g^{-1})	K_2 (g mg^{-1} min^{-1})	$q_{e(the)}$ (mg g^{-1})	h (mg g^{-1} .min)	R^2	$q_{e(exp)}$ (mg g^{-1})	K_2 (g mg^{-1} min^{-1})	$q_{e(the)}$ (mg g^{-1})	h (mg g^{-1} .min)	R^2
100	98.9	0.0333	100	333.33	1	98.2	0.025	100	250	1
150	142.2	0.0245	142.86	500	1	140.6	0.0163	142.86	333.33	1
200	179.5	0.0125	200	500	1	172	0.0125	200	500	1
250	212	0.004	250	250	0.999	196.8	0.0083	200	333.33	1
300	238.5	0.0053	250	333.33	0.999	222	0.0053	250	333.33	0.999
350	254	0.003	333.33	333.33	0.999	236	0.008	250	500	1
400	271	0.003	333.33	333.33	0.999	253	0.0023	333.333	250	1

Steps involved in sorption of the dye by adsorbent 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. According to

Weber and Morris, the intra particle diffusion rate constant (K_i) is given by the following equation

$$q_t = K_i t^{1/2} \quad (3)$$

K_i (mg $g^{-1}min^{-1/2}$) values can be determined from the slope of the plots q_t against $t^{1/2}$, **Figure 5(a)** for MPLP and **5(b)** for MPFP showed a linear relationship after certain time but they do not pass through origin. This is 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 in the initial concentration of dye, **Table 3**. Initial portion is attributed to the liquid film mass transfer and linear portion to the intra particle diffusion.

Table3. *Intra particle diffusion model constants for effect of initial dye concentration and contact time on adsorption of MB*

Initial MB Concentration (mg l^{-1})	MPLP		MPFP	
	K_i (mg g-1$min^{-1/2}$)	R^2	K_i (mg g-1$min^{-1/2}$)	R^2
100	1.287	0.592	1.41	0.576
150	1.609	0.682	2.012	0.65
200	2.226	0.674	1.854	0.692
250	4.415	0.892	3.014	0.804
300	4.855	0.837	4.544	0.754
350	5.42	0.855	4.357	0.699
400	5.866	0.864	6.271	0.802

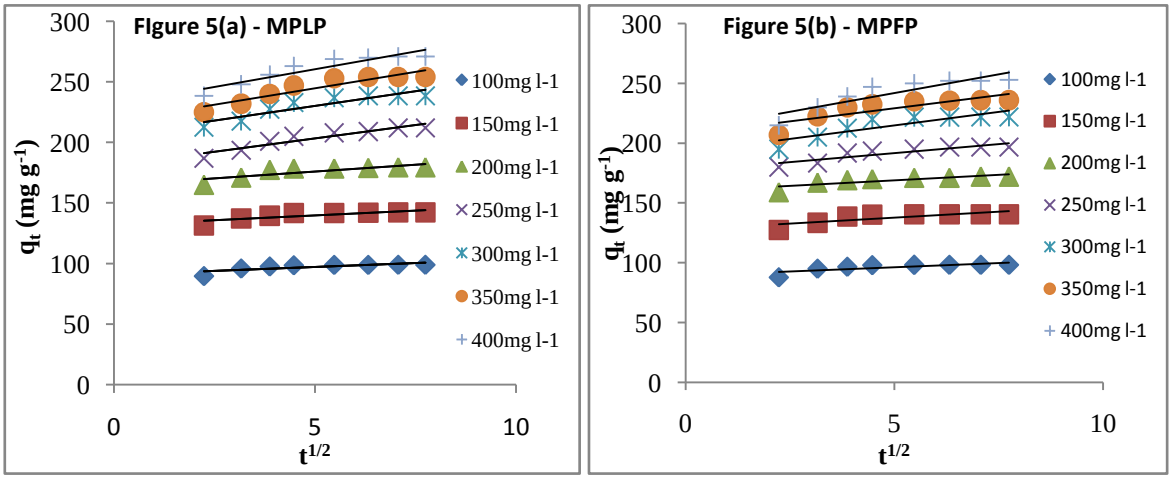

Fig5(a) and 5(b). *Intra particle diffusion plot of effect of initial dye concentration and contact time on adsorption of MB onto MPLP and MPFP respectively*

The linearized form of Elovich kinetic equation is presented as

$$q_t = 1/[\beta \ln(\alpha\beta)] + \ln t / \beta \quad (4)$$

Where α and β are the constants calculated from the intercepts and slopes of plots q_t against ln t, **Figure 6(a)** for MPLP and **6(b)** for MPFP. The values of constant α increases and constant β decreases with increase in initial MB concentration, **Table 4** .This Elovich kinetic model gave quiet satisfactory results for MPLP than MPFP.

Table4. *Elovich model constants for effect of initial dye concentration and contact time on adsorption of MB*

	MPLP			MPFP		
Initial MB Concentration (mg l^{-1})	α	β	R^2	α	β	R^2
100	3.421	0.3036	0.75	3.78	0.276	0.736
150	4.16	0.2481	0.829	5.286	0.1972	0.8
200	5.763	0.1797	0.815	4.759	0.2165	0.832
250	11.095	0.0958	0.967	7.575	0.1378	0.903
300	12.29	0.0863	0.925	11.859	0.0897	0.879
350	13.741	0.0755	0.939	11.49	0.092	0.844
400	14.914	0.0715	0.952	16.482	0.0656	0.918

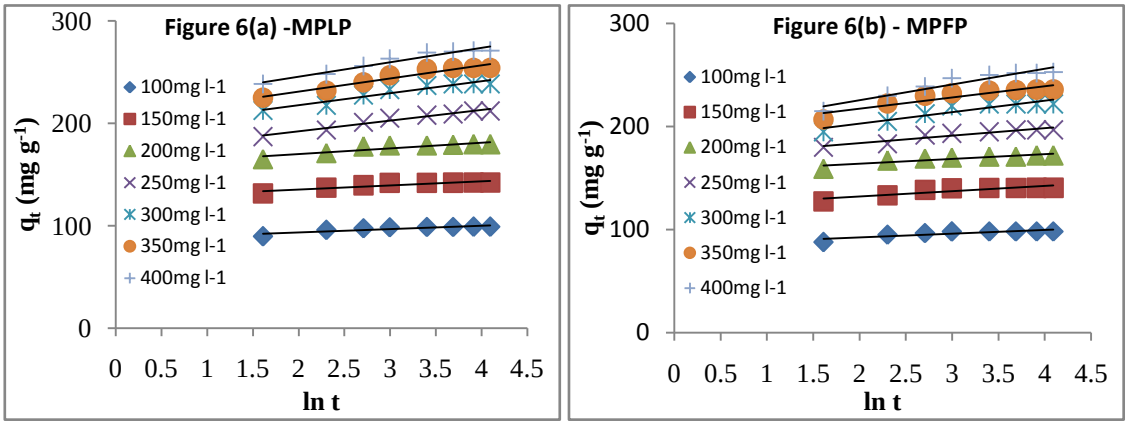

Fig6(a) and 6(b). *Elovich plot of effect of initial dye concentration and contact time on adsorption of MB onto MPLP and MPFP respectively*

3.2. Effect of Adsorbent Dosage and Initial Dye Concentration

The adsorption of MB onto MPLP and MPFP was studied by varying the adsorbent dosage. The percentage of adsorption increased with increase in dosage of adsorbent, **Figure7(a)** for MPLP and **7(b)** for MPFP. Percentage removal of MB decreased with increase in concentration. For above 95% removal of MB, adsorbent dosage of 3, 4, 5, 5 g l^{-1} for MPLP and 3, 4, 6, 6 g l^{-1} MPFP were needed for initial MB concentrations 400, 500, 600 and 700 mg l-1 respectively

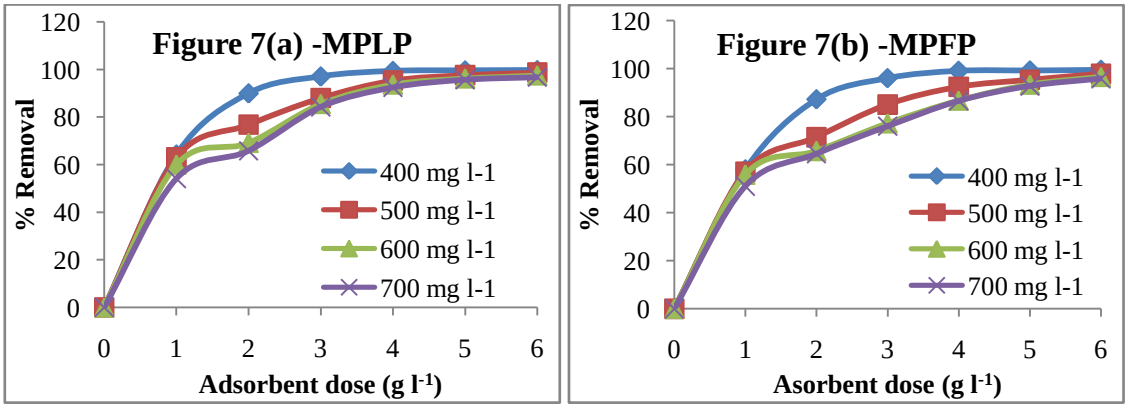

Fig7(a) and 7(b). *Effect of adsorbent dosage and initial dye concentration on adsorption of MB onto MPLP and MPFP respectively*

3.3. Effect of pH

pH is an important factor in controlling the adsorption of dye onto adsorbent. The adsorption of MB from 200mg l^{-1} concentration onto MPLP and MPFP 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 50 to 192.2 mg g^{-1} for MPLP and 57 to 191.6 mg g^{-1} for MPFP by variation in pH from 3 to 11, **Figure 8**.

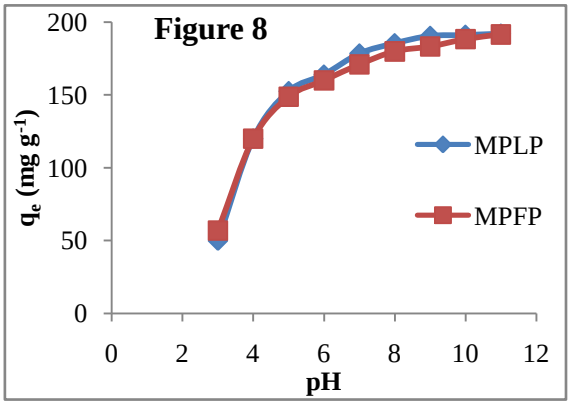

Fig8. *Effect of pH on adsorption of MB From initial concentration 200 mg l^{-1} MB solution onto MPLP and MPFP*

3.4. Effect of Particle Size and Initial Dye Concentration

Adsorption of MB on three sized particles ≥ 120, 120 ≤ 85 and 85 ≤ 60 mesh of MPLP and MPFP was studied for 100 to 350 mg l^{-1} concentrations of MB. The results of variation of these particle sizes on dye adsorption are shown in **Figure 9(a)** for MPLP and **9(b)** for MPFP. It can be observed that as the particle size increases the adsorption of dye decreases and hence the percentage removal of dye also decreases. 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.

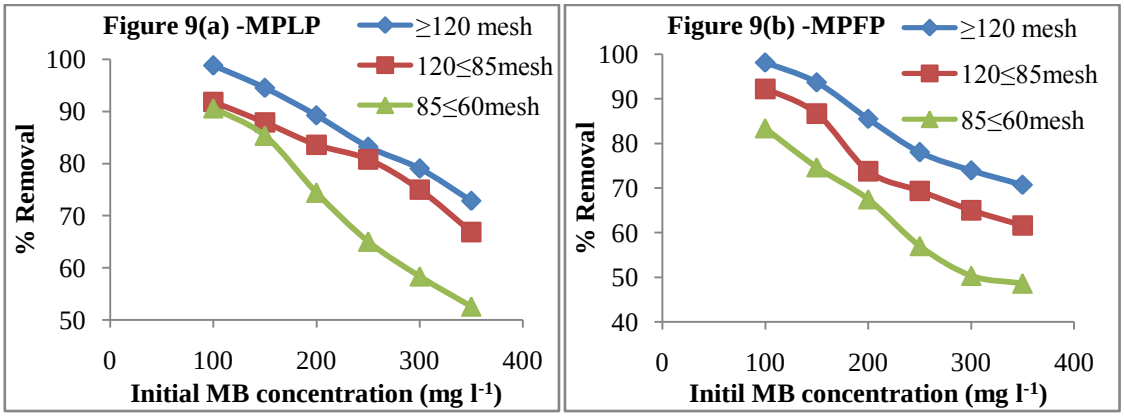

Fig9(a) and 9(b). *Effect of particle size and initial dye concentration on % removal of MB on MPLP and MPFP respectively*

The Freundlich equation was employed for the adsorption of MB onto the adsorbent. The isotherm was represented by

$$\log q_e = \log K_f + 1/n \log C_e \quad (4)$$

Table5. *Freundlich isotherm parameters for effect of particle size and initial dye concentration on adsorption of MB*

Mesh	MPLP			MPFP		
	K_f	n	R^2	K_f	n	R^2
≥ 120	92.47	4.546	0.994	84.14	4.525	0.988
120 ≤ 85	44.67	2.717	0.967	52.72	3.584	0.973
85 ≤ 60	57.41	4.348	0.962	39.81	3.623	0.969

Where q_e is amount of MB adsorbed at equilibrium (mg g^{-1}), C_e is the equilibrium concentration of MB in solution (mg l^{-1}), K_f and n are constant incorporating factors affecting the adsorption capacity and intensity of adsorption respectively. The plots of log q_e against log C_e (R^2= 0.962 to 0.994 for MPLP and0.969 to 0.988 for MPFP) indicating the adsorption of MB obeys the Freundlich adsorption isotherm, **Figure 10(a)** for MPLP and **10(b)** for MPFP. The values of K_f and n are given in the **Table 5**. Values of n between 1 and 10 indicate an effective adsorption while higher values of K_f represent an easy uptake of adsorbate from the solution.

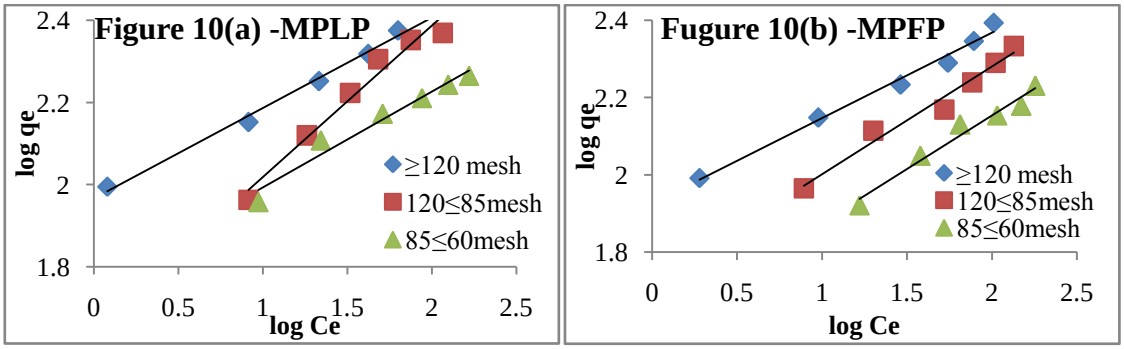

Fig10(a) and 10(b). *Freundlich isotherm plots of effect of particle size and initial dye co centration on adsorption of MB on MPLP and MPFP respectively.*

The Langmuir isotherm was represented by the following equation

$$C_e / q_e = 1/ (q_m b) + C_e /q_m \quad (5)$$

Where q_m is monolayer (maximum) adsorption capacity (mg g^{-1}) 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 11(a)** for MPLP and **11(b)** for MPFP (R^2= 0.989 to 0.997 for MPLP and 0.974 to 0.989 for MPFP). The values of q_m and b were determined slope and intercepts of the plots, **Table 6**. Monolayer adsorption capacity (q_m) decreased from 333.333 mg g^{-1} to 200 mg g^{-1} with decreased in particle size from ≥ 120 to 85 ≤ 60 mesh for both the adsorbents.

Table6. *Langmuir isotherm parameters for effect of particle size and initial dye concentration on adsorption of MB*

Mesh	MPLP			MPFP		
	q_m	b	R^2	q_m	b	R^2
≥ 120	333.3	0.111	0.989	333.3	0.083	0.979
120 ≤ 85	333.3	0.046	0.997	250	0.048	0.974
85 ≤ 60	200	0.074	0.997	200	0.038	0.989

The essential features of the Langmuir isotherm can be expressed in terms of dimensionless constant separation factor,

$$R_L = 1/ (1+bC_o) \quad (6)$$

Where C_o is initial MB concentration (mg l^{-1})

The nature of adsorption If,

R_L> 1 Unfavourable, R_L = 1 Linear

R_L = 0 Irreversible , 0 < R_L< 1 Favourable .

R_L values lies between 0 and 1 for both the adsorbents (0.0178 to 0.1779 for MPLP and 0.0205 to 0.2075 for MPFP) indicates favourable adsorption for MPLP and MPFP, **Table 11 and 12**.

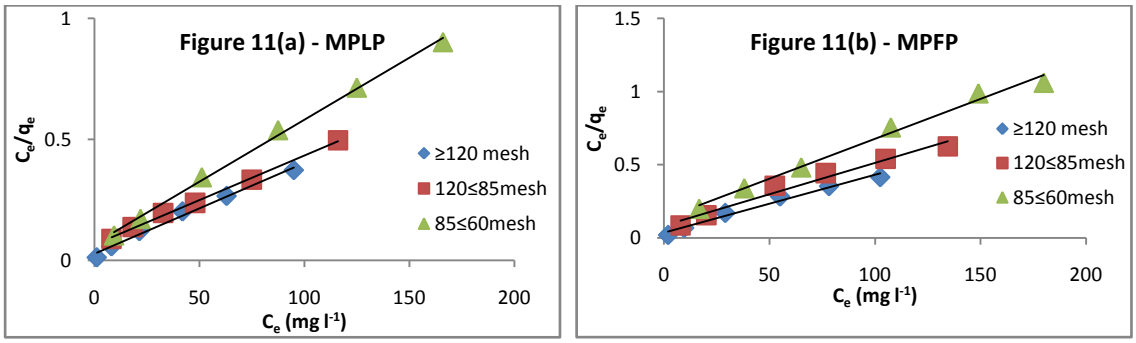

Fig11(a) and 11(b). *Langmuir isotherm plots of effect of particle size and initial dye concentration on adsorption of MB on MPLP and MPFP respectively.*

The Temkin isotherm is given as

$$q_e = B \ln A + b \ln C_e \quad (7)$$

Where A (1/g) is the equilibrium binding constant, corresponding to the maximum binding energy and constant B is related to heat of adsorption. A linear plots of q_e against $\ln C_e$, **Figure 12(a)** for MPLP and **12(b)** for MPFP enables the determination of the constants B and A from the slope and intercept. The results of the plots are given in **Table 7**.

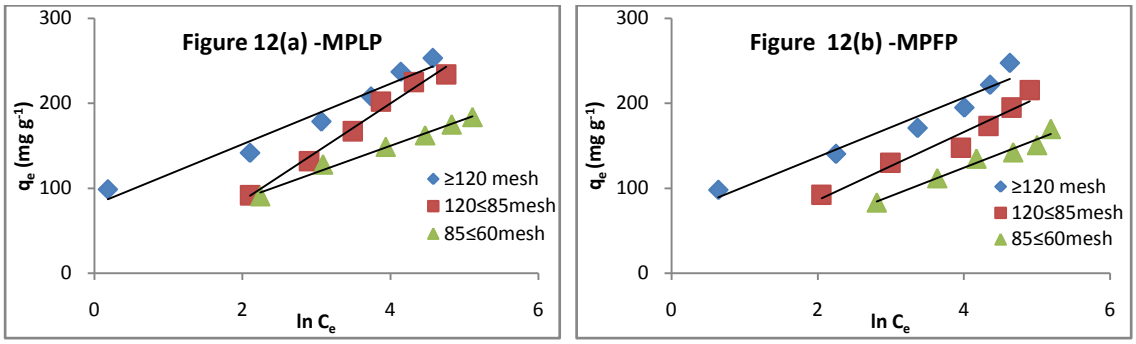

Fig12(a) and 12(b). *Temkin isotherm plots of effect of particle size and initial dye concentration on adsorption of MB on MPLP and MPFP respectively.*

Table7. *Temkin isotherm parameters for effect of particle size and initial dye concentration on adsorption of MB*

Mesh	MPLP			MPFP		
	A	B	R^2	A	B	R^2
≥ 120	9.328	35.88	0.959	6.741	34.97	0.946
120 ≤ 85	0.597	57.34	0.983	1.154	40.13	0.946
85 ≤ 60	2.256	31.12	0.983	0.753	33.36	0.973

3.5. 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 MPLP and MPFP was studied for 100 to 350 mg l^{-1} initial MB concentrations. The results variation in temperatures on dye adsorption is shown in **Figure 13(a)** for MPLP and **13(b)** for MPFP. 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 . Changing the temperature will change the equilibrium capacity of the adsorbent for particular adsorbate.

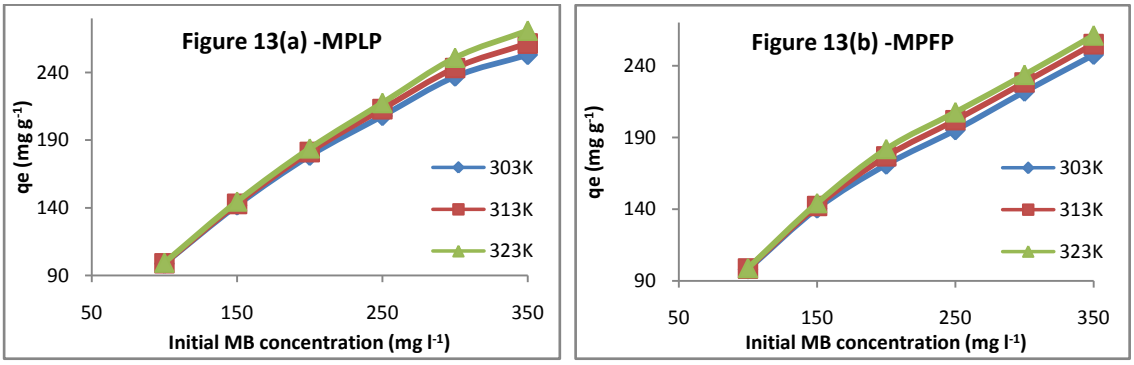

Fig13(a) and 13(b). *Effect of temperature and initial dye concentration on adsorption of MB on MPLP and MPFP respectively.*

Freundlich and Langmuir adsorption isotherms were employed for 303K, 313K and 323K temperatures. Plot of log q_e against log C_e, **Figure 14(a)** for MPLP and **14(b)** for MPFP and plots of C_e / q_e against C_e,**Figure 15(a)** for MPLP and **15(b)** for MPFP showed good linearity with regression coefficients ($R^2 \approx 0.99$). Freundlich constants K_f and n as well as Langmuir constants qm and b are given in **Table 8** and **Table 9** respectively. Dimensionless constant separation factor (R_L) values lie between 0 and 1 for both the adsorbents. Monolayer (maximum) adsorption capacity (q_m) obtained from Langmuir plots for MPLP as well as for MPFP for all temperature conditions remains 333.333 mg g^{-1}. Both Langmuir as well as Freundlich adsorption isotherms fits well for 303 to 323K temperature range.

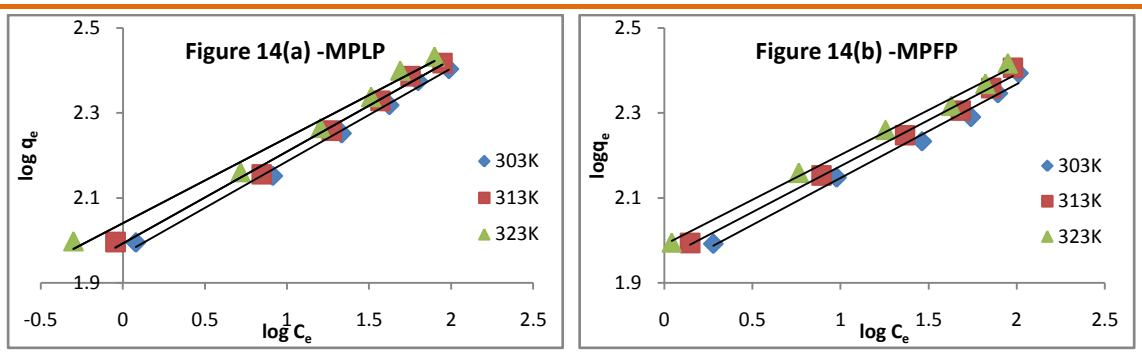

Fig14(a) and 14(b). *Freundlich isotherm plots of effect of temperature and initial dye concentration on adsorption of MB on MPLP and MPFP respectively*

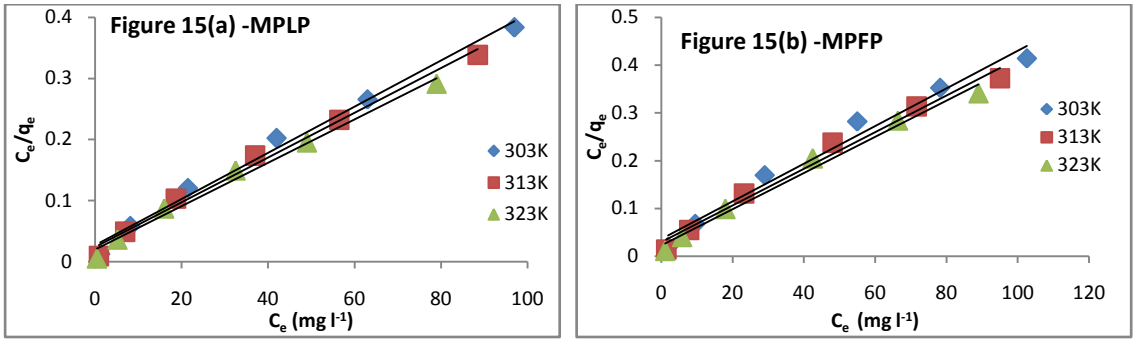

Fig15(a) and 15(b). *Langmuir isotherm plots of effect of temperature and initial dye concentration on adsorption of MB on MPLP and MPFP respectively.*

Table8. *Freundlich isotherm parameters for effect of temperature and initial dye concentration on adsorption of MB*

Temp. in Kelvin	**MPLP**			**MPFP**		
	K_f	n	R^2	K_f	n	R^2
303	92.68	4.587	0.994	84.14	4.525	0.988
313	98.17	4.63	0.992	90.78	4.63	0.995
323	109.6	5	0.987	97.5	4.739	0.994

Table9. *Langmuir isotherm parameters for effect of temperature and initial dye concentration on adsorption of MB*

Temp. in Kelvin	**MPLP**			**MPFP**		
	q_m	b	R^2	q_m	b	R^2
303	333.3	0.115	0.99	333.3	0.083	0.979
313	333.3	0.13	0.99	333.3	0.103	0.983
323	333.3	0.158	0.988	333.3	0.136	0.986

Temkin plot q_e against lnC_e , Figures 16(a) for MPLP and 16(b) for MPFP also showed linearity (R^2 = 0.937 to 0.961 for MPLP and 0.946 to 0.97 for MPFP). Temkin constants A and B are given in Table (11).

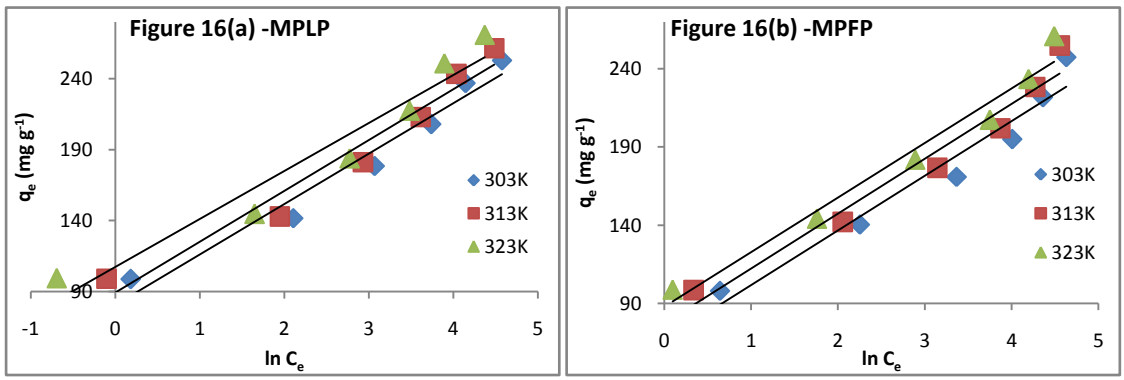

Fig16(a) and 16(b). *Temkin isotherm plots of effect of temperature and initial dye concentration on adsorption of MB on MPLP and MPFP respectively.*

Table10. *Temkin isotherm parameters for effect of temperature and initial dye concentration on adsorption of MB*

Temp. in Kelvin	MPLP			MPFP		
	A	B	R^2	A	B	R^2
303	12.18	35.78	0.954	6.741	34.97	0.946
313	9.649	35.56	0.961	9.066	35.06	0.957
323	23.94	33.82	0.937	12.44	34.89	0.97

Table11. *Dimensionless separation factor (R_L) calculated from Langmuir constant (b) for MPLP*

Initial MB Conc. (mg l^{-1})	Mesh			Temperature		
	≥ 120	120 ≤ 85	85 ≤ 60	303K	313K	323K
100	0.083	0.178	0.119	0.08	0.071	0.06
150	0.057	0.126	0.083	0.055	0.049	0.041
200	0 .043	0.098	0.064	0.042	0.037	0.031
250	0.035	0.08	0.054	0.034	0.03	0.025
300	0.029	0.067	0.043	0.028	0.025	0.021
350	0.025	0.058	0.037	0.024	0.021	0.018

Table12. *Dimensionless separation factor (R_L) calculated from Langmuir constant (b) for MPFP*

Initial MB Conc. (mg l^{-1})	Mesh			Temperature		
	≥ 120	120 ≤ 85	85 ≤ 60	303K	313K	323K
100	0.107	0.172	0.208	0.107	0.088	0.068
150	0.074	0.121	0.149	0.074	0.061	0.047
200	0.057	0.094	0.116	0.057	0.046	0.035
250	0.046	0.077	0.095	0.046	0.037	0.029
300	0.039	0.065	0.08	0.039	0.031	0.024
350	0.033	0.056	0.07	0.033	0.027	0.021

3.5.1. Thermodynamic Analysis

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

$$K_o = C_{solid} / C_{liquid} \quad (8)$$

$$\Delta G = -RT\ln K_o \quad (9)$$

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

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

$$\ln K_o = \Delta S/R - \Delta H/RT \quad (10)$$

Where K_o is equilibrium constant, C_{solid} is solid phase concentration at equilibrium (mg l^{-1}), C_{solid} is liquid phase concentration at equilibrium (mg l^{-1}), T is absolute temperature in Kelvin and R is gas constant.

ΔG values obtained from equation (9), ΔH and ΔS values obtained from the slope and intercept of Von't Hoff plot, $\ln K_o$ against 1/T , **Figure 17(a)** for MPLP and **17(b)** for MPFP, presented in **Table 13** and **Table 14** respectively.. 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 indicatephysisorption and endothermic nature of adsorption [12-14]. ΔH values decreases from 22.58 to 7.91 KJ/mole for MPLP and 35.758 to 11.132 kJ/mole for MPFP with increase in initial MB concentration from 100 to 350 mg l^{-1}. 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 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.

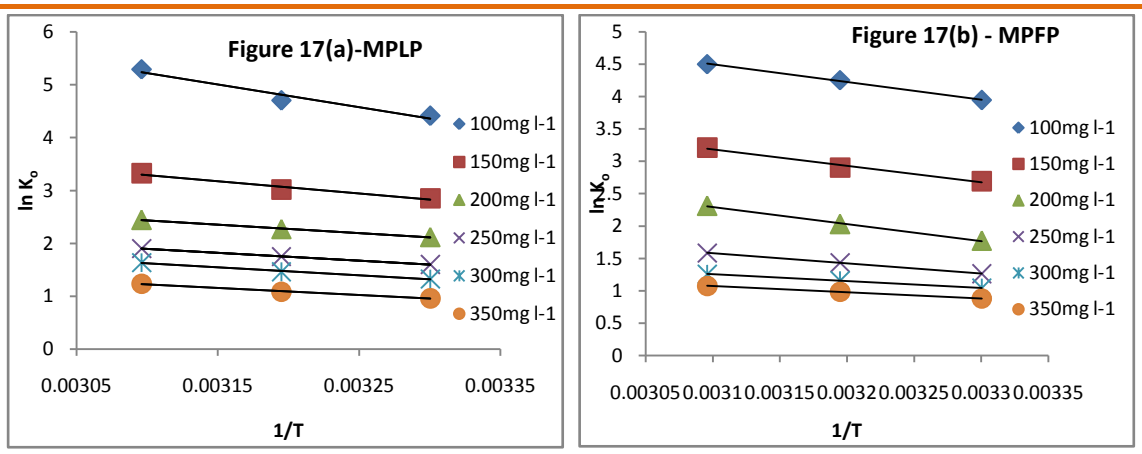

Fig17(a) and 17(b). *Von't Hoff plots of effect of temperature and initial dye concentration on adsorption of MB on MPLP and MPFP respectively.*

Table13. *Equilibrium constants and thermodynamic parameters for the adsorption of MB on MPLP*

Initial MB Conc.(mg l^{-1})	**Ko**			**ΔG (kJ/mole)**			**ΔH (kJ/mole)**	**ΔS (J/K/mole)**
	303K	313K	323K	303K	313K	323K		
100	82.3	110	199	-11.111	-12.235	-14.215	22.580	107.334
150	17.3	20.4	27.8	-7.180	-7.851	-8.934	21.076	91.7866
200	8.3	9.7	11.5	-5.332	-5.911	-.6559	219.15	86.9644
250	4.95	5.76	6.69	-4.030	-4.555	-5.105	13.019	53.5172
300	3.76	4.31	5.12	-3.338	-3.802	-4.387	8.762	37.6209
350	2.61	2.95	3.43	-2.415	-2.819	-3.310	7.910	33.4472

Table14. *Equilibrium constants and thermodynamic parameters for the adsorption of MB on MPFP*

Initial MB Conc.(mg l^{-1})	**Ko**			**ΔG (J/mole)**			**ΔH (J/mole)**	**ΔS (J/K/mole)**
	303K	313K	323K	303K	313K	323K		
100	51.6	70.4	89.9	-9.936	-11.072	-12.081	35.758	154.225
150	14.8	18.2	24.9	-6.786	-7.555	-8.629	19.313	87.2139
200	5.9	7.62	10.1	-4.470	-5.285	-6.213	13.244	61.2659
250	3.55	4.21	4.88	-3.188	-3.740	-4.258	12.238	53.7001
300	2.84	3.19	3.52	-2.626	-3.019	-3.378	12.537	52.3366
350	2.41	2.68	2.93	-2.221	-2.569	-2.889	11.132	44.6628

3.5.2. Kinetics of Equilibrium (Reverse and Forward) Adsorption Processes

The adsorption of dye from aqueous solution follows first order kinetics when a single species is considered on a heterogeneous surface. The heterogeneous equilibrium between the dye solutions and adsorbent (MPLP/MPFP) are represented as

$$A \underset{K_2}{\overset{K_1}{\rightleftharpoons}} B$$

Where K_1 is forward rate constant and K_2 is the backward rate constant. A and B represents dye remaining in the aqueous solution and dye adsorbed on the surface of adsorbent respectively. The equilibrium constant (K_o) is the ratio of concentration of dye on adsorbent and in aqueous solution

$K_o = K_1 / K_2$

To study the kinetics of the adsorption process the kinetic equation proposed by Natarajan and Khalaf has been employed

$$\log (C_o/C_t) = (K_{ad}/2.303)\, t \qquad (11)$$

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

against t for different concentrations and temperatures. The rate constants are determined by the following equation,

$$K_{ad} = K_1+K_2 = K_1+(K_1/K_o)= K_1 (1+ 1/ K_o) \quad (12)$$

The overall rate constant K_{ad} for adsorption of dye increases with increase in temperature suggesting adsorption was endothermic in nature. K_{ad} is separated into rate of forward (K_1) and reverse reactions (K_2) using equation (12). K_{ad}, K_1, K_2 are given in Table 14 for MPLP as well as for MPFP clearly indicate that, at all temperatures, the forward rate constant was much higher than the reverse rate constant suggesting that the rate of adsorption was dominant.

Table15. *First order adsorption rate constant, forward and backward rate constants for the adsorption of MB from 200 mg l^{-1} MB conc.*

	303K			**313K**			**323K**		
Adsorbent	K_{ad} (min^{-1})	K_1 (min^{-1})	K_2 (min^{-1})	K_{ad} (min^{-1})	K_1 (min^{-1})	K_2 (min^{-1})	K_{ad} (min^{-1})	K_1 (min^{-1})	K_2 (min^{-1})
MPLP	0.0184	0.01642	0.00198	0.0195	0.0177	0.00182	0.0207	0.01904	0.00166
MPFP	0.01152	0.00985	0.00167	0.0138	0.01222	0.0016	0.0161	0.01465	0.00145

3.6. Effect of Agitation Speed

The sorption is influenced by mass transfer parameters. **Figure 18(a)** for MPLP and **18(b)** for MPFP illustrates the sorption kinetics of MB by for different agitation speeds ranging from 100 to 230 rpm. The amount adsorbed at equilibrium was found to increased from 189, 205 and 212 mg g^{-1} of MPLP and 172.5 189 and 196.8 mg/g of MPFP with increased in agitation speed from 100, 170 and 230 rpm of an oscillator from 250 mg l^{-1} initial MB solution. This is because with low agitation speed the greater contact time is required to attend the equilibrium. With increasing 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. Under such conditions, the value of external diffusion coefficient becomes larger and finally boundary layer becomes thin and approach to laminar sub layer at high agitation speeds. So, the external diffusion resistance coefficient are constant or can be neglected. Thus, it can be noticed that adsorption increases slightly with increase in sped of agitation.

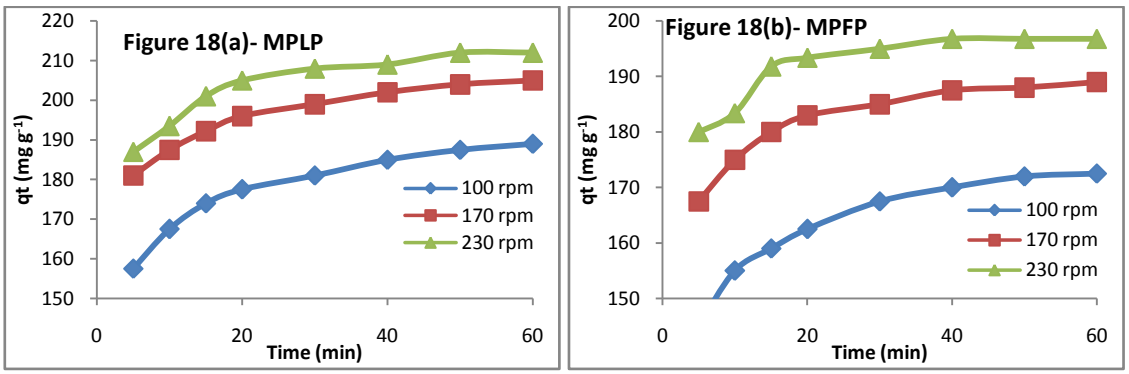

Fig18(a) and 18(b). *Effect of agitation speed on adsorption of MB on MPLP and MPFP respectively*

4. CONCLUSION

In this work, two different adsorbents, mangrove plant leaf powder (MPLP) and mangrove plant fruit powder (MPFP) have been used for the removal of MB from aqueous solutions. The amount of MB adsorbed at equilibrium increased from 98.9 to 271 and 98.2 to 253 mg g^{-1} for MPLP and MPFP respectively with increased in initial MB concentration from 100 to 400 mg l^{-1}.

The best fitting isotherm model was found to be Langmuir (R^2 = 0.988 to 0.997 for MPLP and 0.974 to 0.989 for MPFP). Langmuir and Freundlich isotherm parameters (n = 2.71 to 5 for MPLP and 3.584 to 4.739 for MPFP, R_L = 0.0178 to 0.1779 for MPLP and 0.0205 to 0.2075 for MPFP) confirmed that the adsorption of MB on both adsorbents was favourable. Monolayer adsorption capacity (q_m) decreased from 333.333 mg g^{-1} to 200 mg g^{-1} with decreased in particle size from ≥ 120 to 85 ≤ 60 mesh for both the adsorbents.

Lagergen pseudo -second order model best fits the kinetics of adsorption ($R^2 \geq 0.99$). The values amount of MB adsorbed per unit mass of MPLP as well as of MPFP obtained by Lagergen pseudo - second order Model, $q_{e(the)}$ were in consistent with the experimental $q_{e(exp)}$.

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, temperature, agitation speed and decreasing particle size.

Thermodynamic analysis showed that adsorption of MB on MPLP and MPFP was:

- Favourable and spontaneous (negative values of ΔG, -14.215 to -2.415 kJ/mole for MPLP and -12.281 to -2.221kJ/mole for MPFP).
- Endothermic (positive values of ΔH, 7.91 to 22.58 kJ/mole for MPLP and 11.132 to 35.758 kJ/mole for MPFP)
- Physisorption (small ΔH values)
- Increased disorder and randomness at the solid- solution interface (positive values of ΔS, 0.0334 to 0.1073 KJ/mole for MPLP and 0.0446 to 0.154 KJ/mole).

The overall rate constant K_{ad} for adsorption of MB increased with increase in temperature suggesting adsorption was endothermic in nature. At all temperatures, the forward rate constant were much higher than the reverse rate constant suggesting that the rate of adsorption was dominant for MPLP as well as MPFP.

It was observed that MPLP and MPFP both showed same type of behaviour towards isotherm and kinetic models but MPLP was found to be slightly better adsorbent than MPFP.

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