

Adsorption of Basic Dye, Methylene Blue by a Novel Activated Carbon Prepared from *Typha Angustata* (L.)

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Abstract: This paper presents the feasibility of removal of basic dye methylene blue from aqueous solutions by using a low cost AC-MnO₂-NC. Batch adsorption experiments were carried out as a function of pH, contact time, initial concentration of the adsorbate, adsorbent dosage and temperature. Langmuir, Freundlich and Tempkin isotherms were also studied. Pseudo first order, Pseudo second order, intra-particle diffusion model and Elovich kinetic models were studied. Thermodynamic parameters such as ΔH° , ΔS° and ΔG° were also calculated. Adsorbent used in this study were characterized by FT-IR, XRD and SEM analysis.

Keywords: Methylene blue, AC-MnO₂-NC, Adsorption isotherm, Kinetics

Introduction

During the last few decades the mobility and distribution of dyes in water have been studied extensively due to their toxic effects to humans, animals, plants and the aquatic organisms. Many of the industries, such as dyestuffs, textile, paper, leather, foodstuffs, cosmetics, rubber and plastics are using enormous quantity of synthetic dyes in order to give colour for their products and consume substantial volumes of water. As a result, they generate a considerable amount of coloured waste water. Textile and dyeing industry are among important sources for the continuous pollution of the aquatic environment. Because they produce approximately 5% of them end up in effluents. The textile and dyeing industries effluents are discarded into rivers, ponds and lakes; they affect the biological life various organisms¹⁻³. Dye-containing effluents are undesirable wastewaters because they contain high levels of chemicals, suspended solids, and toxic compounds^{4,5}. Colour causing compounds can react with metal ions to form substances which are very toxic to aquatic flora and fauna and cause many water borne diseases⁶⁻⁸.

Due to the chemical structure of dye, they are act as a resistant to many chemicals, oxidizing agents and heat and are biologically non-degradable. So it is difficult to decolorize the effluents, once released into the aquatic environment. Many of the methods are available for the removable pollutants from water, the most important of which are reverse osmosis, ion exchange, precipitation and adsorption.

Adsorption process has been found to be superior technique for treating dye effluents due to simplicity and insensitivity to toxic substance. Although the activated carbon^{9,10} is most effective for absorption of dye, but it has some disadvantages such as (i) high adsorbent cost, (ii) problems of regeneration and difficulties of separation of powdered activated carbon from waste water for regeneration are expensive and hence increasing need for equally effective but commercially low cost sorbents. A wide variety of materials such as animal bone meal¹¹, black tea leaves¹², cocoa¹³, almond shell¹⁴, mango leaves¹⁵, saw dust¹⁶.

The objective of the present study is, to remove the basic dye methylene blue from aqueous solution by using a low cost natural absorbent AC-MnO₂-NC. In the batch mode studies, the dynamic behaviour of the adsorption was investigated on the effect on initial Dye Concentration, temperature, adsorbent dosage and pH. The thermodynamic parameters were also evaluated from the adsorption measurements. The Langmuir, Freundlich and Tempkin adsorption isotherms, kinetics, FT-IR, XRD and SEM were also studied. Double distilled water was used throughout the experiment.

Experimental

The *Typha Angustata* L. plant materials were collected from local area situated at Thindal, Erode District, and Tamilnadu. They were cut into small pieces and dried for 20 days. Finally it was taken in a steel vessel and heated in muffle furnace. The temperature was raised gradually up to 500 °C and kept it for half an hour. The carbonised material was ground well and sieved to different particle size. It was stored in a plastic container for further studies. In this study particle size of 0.15 to 0.25 mm was used.

Preparation of AC-MnO₂-NC

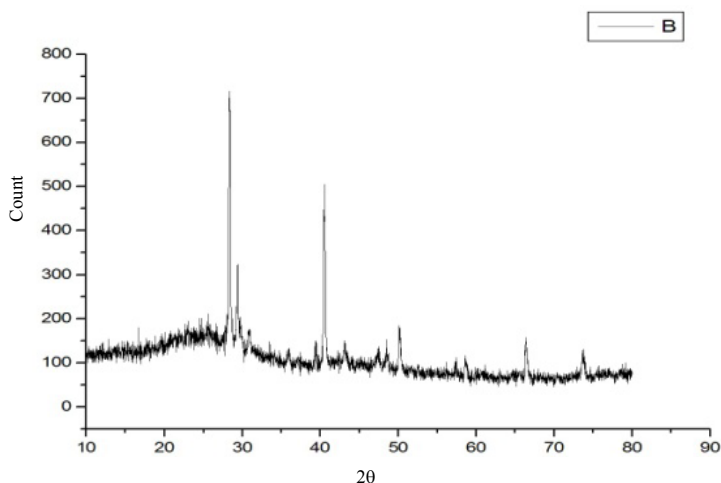
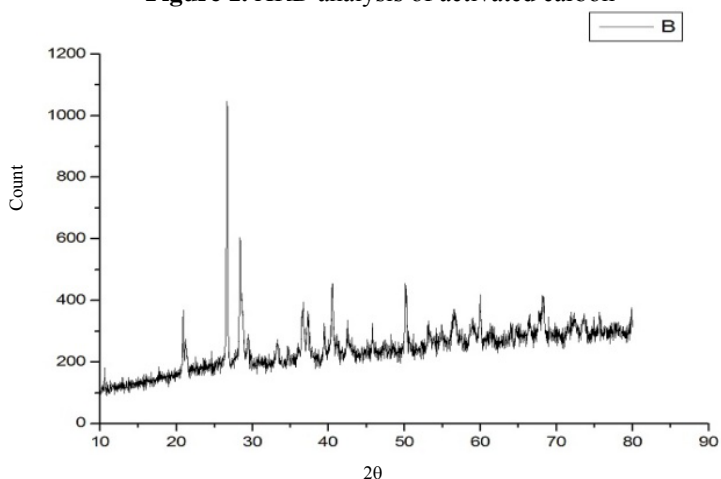
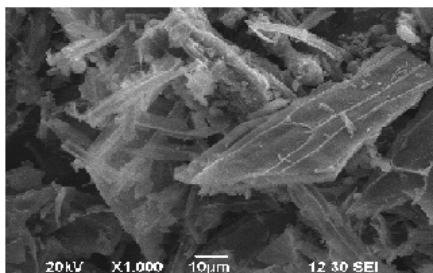
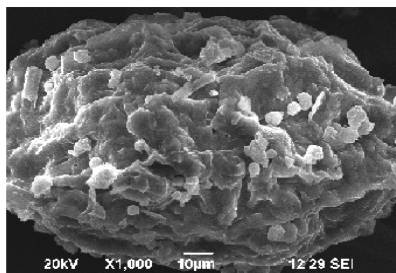
Activated carbon (3 g) was allowed to swell in 15 mL of water-free alcohol and stirred for 2 h at 25 °C to get uniform suspension. At the same time, the maganese dioxide (3 g) was dispersed into water-free alcohol (15 mL). Then the diluted maganese dioxide was slowly added into the suspension of activated carbon and stirred for a further 5 hours at 25 °C. To this, 5 mL alcohol and 0.2 mL of deionised water was slowly added. The stirring was continued for another 5 h at 25 °C and the resulting suspension was kept overnight in a vacuum oven for 6 h at 80 °C.

Preparation of sorbate

Methylene blue (C₁₆H₁₈Cl N₃S), the sorbate used in the present study, is a monovalent cationic dye. It is classified in dye classification as C.I. Basic blue 9, C.I. Solvent blue 8 and C.I. 52015. It has a molecular weight of 373.90 and wavelength (λ_{max}) of 661 nm. The methylene blue (MB)(BDH85%) was used as supplied. A stock solution of 1000 mg/L was prepared and the working solutions were prepared by diluting the stock solution with deionized water as required.

Characterization of adsorbent

Physicochemical characteristics of the adsorbent were studied as per the standard testing methods. The XRD pattern of pure activated carbon (Figure 1) and that of AC-MnO₂-NC (Figure 2) show characteristic peaks at 28° and 30° which the presence of AC-MnO₂ phase in the nano composite. The surface morphology of the adsorbent were visualised via Scanning Electron Microscopy (SEM) (Figure 3 and 4). The diameter of the composite range was 10 µm.

**Figure 1.** XRD analysis of activated carbon**Figure 2.** XRD analysis of AC-MnO₂-NC**Figure 3.** SEM of Activated Carbon**Figure 4.** SEM of AC-MnO₂-NC

Experimental methods

In each adsorption experiment, 50 mL of dye solution with a known concentration was added to 100 mg of AC-MnO₂-NC in a 250 mL glass-stoppered flask at 30°±0.5 °C and the mixture

was stirred on a mechanical shaker at 150 rpm min⁻¹. The samples were withdrawn during stirring at preset time intervals and the adsorbent was separated from the solution by centrifugation (Research centrifuge, Remi Scientific Works, Mumbai) at 4500 rpm min⁻¹ for 5 min. The absorbance of the supernatant solution was estimated to determine the residual dye concentration and was measured before and after treatment with double beam spectrophotometer (HITACHI U 2000 spectrophotometer). All experiments were carried out twice, and the concentrations given are average values. The initial dye concentration in the test solution and the adsorbent dosage were varied to investigate their effect on the adsorption kinetics. The effect of pH was observed by studying the adsorption of dye over the pH range from 3 to 13. The pH of the dye solution was adjusted by using NaOH or HCl solution and a pH meter. The sorption studies were carried out at different temperatures (30°, 40°, 50° and 60 °C). This is used to determine the effect of temperature on the thermodynamic parameters. The amount of sorption at time t, q_t (mg/g), was calculated using the following formula:

$$q_t = (C_0 - C_t)V / W \quad (1)$$

Where C_t (mg L⁻¹) is the liquid phase concentrations of dye at any time, C_0 (mg L⁻¹) is the initial concentration of the dye in solution. V is the volume of the solution (L) and W is the mass of dry adsorbent (g). The amount of equilibrium adsorption, q_e (mg/g), was calculated using the formula;

$$q_e = (C_0 - C_e) V / W \quad (2)$$

Where, C_0 and C_e (mg L⁻¹) are the liquid-phase concentrations of dye initially and at equilibrium. The dye removal percentage can be calculated as follows:

$$(\%) \text{ of dye removal} = \frac{(C_0 - C_e)}{(C_0)} \times 100 \quad (3)$$

Where, C_0 and C_e (mg L⁻¹) are the initial and equilibrium concentrations of the dye in solution.

Results and Discussion

Effects of agitation time vs. initial dye concentration

Effects of agitation time and initial dye concentration (10, 20, 30 and 40 mg/L) on removal of MB are presented in Figure 5. The percent removal of MB increased with increase in agitation time and reached equilibrium at 210 min. The percent dye removal at equilibrium decreased from 73.12 to 35.24 as the dye concentration was increased from 10 to 40 mg/L. It is clear that the removal of dye depends on the initial concentration of the dye. The removal curves are single, smooth and continuous leading to saturation.

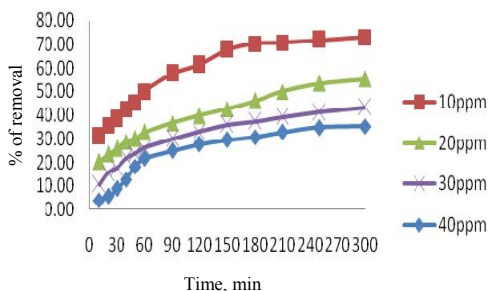


Figure 5. Effects of agitation time vs. initial dye concentration MB by AC-MnO₂-NC

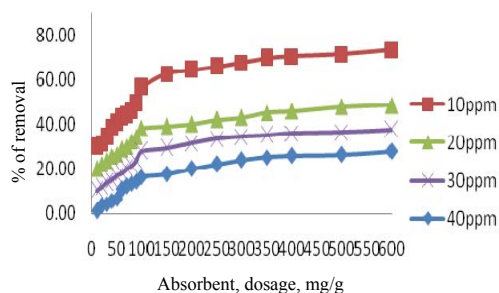


Figure 6. Effect of adsorbent dosage for MB by AC-MnO₂-NC

Effect of adsorbent dose

The removal of MB by AC-MnO₂-NC at different adsorbent doses are presented in Figure 6. (10 mg to 600 mg / 50 mL) was tested for the dye concentrations 10, 20, 30 and 40 mg/L. The adsorption increases with increase in adsorbent concentration; this is due to the increase in surface area and availability of more adsorption site. The percentage removal of MB is greatly increases in the range of 10-600 mg / 50 mL after that small change occur. So the optimum adsorbent carbon doses for the experiments were carried out using 100 mg / 50 mL.

Effect of pH

Effect of pH on the removal of MB is presented in Figure 7. The solution pH is one of the most important factors that control the adsorption of MB on the adsorbent material. Therefore an increase in pH may cause an increase or decrease in the adsorption capacity. The adsorption capacity can be attributed to the chemical form of MB in a solution at the specific pH or due to different functional groups on the adsorbent surface. To examine the effect of pH on the percentage removal of MB gradually increases as the pH increases. The pH value up to 7.25 the percentage removal is up to 28.73 after that suddenly increases. At the solution pH the adsorbent surface negatively charged and favours uptake of cationic dyes due to increased electrostatic force of attraction. Therefore, all the experiments were carried out at the pH 7.25. For 40 mg/L dye concentration the percent removal increased from 14.41 to 43.75 when the pH was increased from 2 to 14 and the percent removal remained almost the same above pH 9.

Effect of temperature

The effect of temperature of adsorption of MB is presented in Figure 8. For concentration 40 mg/L adsorbent was carried out at 30°, 40°, 50° and 60 °C. The percent removal of dye increased from 49.39 to 85.76. This indicates that increase in adsorption with increase in temperature may be due to increase in the mobility of the large dye ions. Moreover, increasing temperature may produce a swelling effect within the internal structure of the adsorbent, penetrating the large dye molecule further.

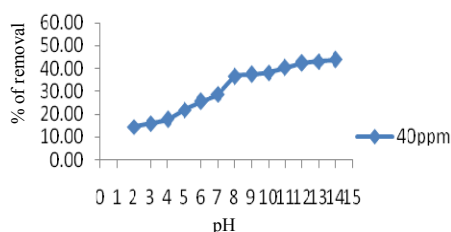


Figure 7. Effect of pH for MB by AC-MnO₂-NC

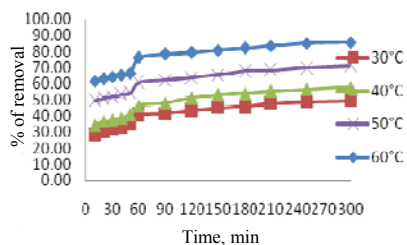


Figure 8. Effect of temperature for MB by AC-MnO₂-NC

Adsorption isotherms

To quantify the adsorption capacity of the adsorbent for the removal of dyes, the most commonly used isotherm, namely Freundlich and Langmuir have been adopted.

Langmuir isotherm

Langmuir isotherm model¹⁷ is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface. The linear form of the Langmuir isotherm equation can be described by

$$\frac{C_e}{q_e} = \frac{1}{Q_0 K_L} + \frac{C_e}{Q_0} \quad (4)$$

Where, C_e is the concentration of dye solution (mg L^{-1}) at equilibrium. The constant Q_0 signifies the adsorption capacity (mg g^{-1}) and $K_L(\text{L/mg})$ is the Langmuir isotherm constant that relates to the energy of adsorption or rate of adsorption. The linear plot of C_e/q_e vs. C_e are presented in Figure 9.

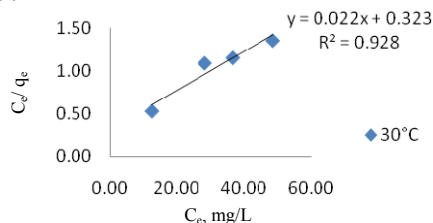


Figure 9. Plot of Langmuir adsorption isotherm

In order to find out the feasibility of the isotherm, the essential characteristics of the Langmuir isotherm can be expressed in terms dimensionless constant separation factor (R_L)^{18,19} is given by the equation;

$$R_L = \frac{1}{1 + K_L C_0} \quad (5)$$

Where K_L is the Langmuir isotherm constant and C_0 is the initial dye concentration (mg L^{-1}). The parameter R_L indicate the nature of the adsorption isotherm.

$R_L > 1$	Unfavourable adsorption
$0 < R_L < 1$	Favourable adsorption
$R_L = 0$	Irreversible adsorption
$R_L = 1$	Linear adsorption

The R_L values between 0 to 1 which indicates favourable adsorption. Values of Q_0 and K_L were calculated from the slope and intercept of the linear plot and are presented in Table 1. From the Table 1 it is clear that the Langmuir isotherm constant value indicate the maximum adsorption capacity (Q_0) is 45.454 mg/g. The Langmuir isotherm can also be expressed in terms of a dimensionless constant separation factor (R_L). The R_L values lies in between 0 to 1 indicate the adsorption is favourable for all the initial dye concentration.

Freundlich isotherm

The Freundlich isotherm²⁰ was also applied for the adsorption of the dye. This isotherm is represented by the equation;

$$\log q_e = \left(\frac{1}{n} \right) \log C_e + \log k_f \quad (6)$$

Where q_e is the amount of dye adsorbed (mg/g) at equilibrium, C_e is the equilibrium dye concentration in solution (mg L^{-1}), k_f is (mg/g(L/mg)) measure of adsorption capacity and $1/n$ is the adsorption intensity. The magnitude of the exponent $1/n$ gives an indication of the favourability of adsorption. The value of $n > 1$ represents favourable adsorption condition^{21,22} or the value of $1/n$ lying in the range of 1 to 10 confirms the favourable condition for adsorption. Linear plot of $\log q_e$ vs. $\log C_e$ are presented in Figure 10.

The Values of k_f and n were calculated from the intercept and slope of the plot and are presented in Table 1. The Freundlich isotherm parameter indicates that the adsorption capacity is 10.7398 and the n value indicates the adsorption is favourable process.

Table 1. Langmuir, Freundlich and Tempkin constants for adsorption of MB by AC-MnO₂-NC

Initial dye Concentration mg/L	Langmuir				Freundlich			Temkin			
	Q_0 , mg/g	K_L , L/g	R^2	R_L	K_f , Mg/g/ L/g	n	R^2	A	b	B	R^2
60	45.454	0.068	0.928	0.1966	10.7398	3.3898	0.839	1.0917	290.487	8.529	0.814
80				0.1550							
100				0.1280							
120				0.1090							

Tempkin isotherm

Tempkin isotherm contains a factor that explicitly takes into account adsorbing species-adsorbate interactions. This isotherm assumes that: (1) The heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbate-adsorbate interactions and (2) Adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy²³. Tempkin isotherm is represented by the following equation:

$$q_e = RT/b \ln(AC_e) \quad (7)$$

equation (7) can be expressed in its linear form as:

$$q_e = RT/b \ln A + RT/b \ln C_e, q_e = B \ln A + B \ln C_e \quad (8)$$

Where $B = RT/b$

The adsorption data can be analysed according to equation (8). A plot of q_e versus $\ln C_e$ enables the determination of the isotherm constants A and B and is shown in Figure 11. A is the equilibrium binding constant (1/mol) corresponding to the maximum binding energy and constant B, is related to the heat of adsorption. This isotherm is plotted in Figure 11 for MB adsorption on AC-MnO₂-NC and values of the parameters are given in Table 1.

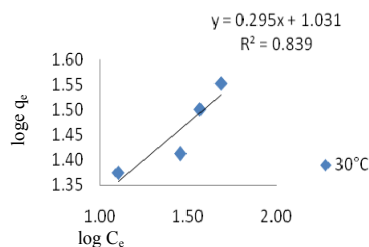


Figure 10. Plot of Freundlich adsorption isotherm

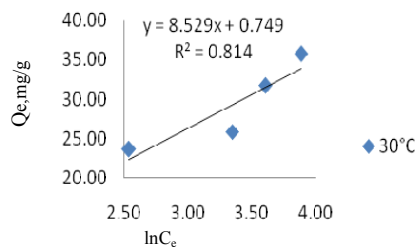


Figure 11. Plot of Tempkin adsorption isotherm

Compared to the correlation coefficient (R^2) values from Table 1 shows that Langmuir isotherm is found to be best.

Adsorption kinetics

The study of adsorption kinetics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid – solution interface. The kinetics of MB adsorption on the AC-MnO₂ –NC was analysed using Pseudo first order, Pseudo second order, Elovich and Intraparticle diffusion kinetics models. The conformity between experimental data and the kinetics models was expressed by the correlation coefficients (R^2) value, the R^2 values close or equal to 1. A relatively high R^2 value indicates that the model successfully describes the kinetics of MB dye adsorption.

Pseudo first order kinetic model

The first-order rate expression of Lagergren²⁴ equation is given as:

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.203} t \quad (9)$$

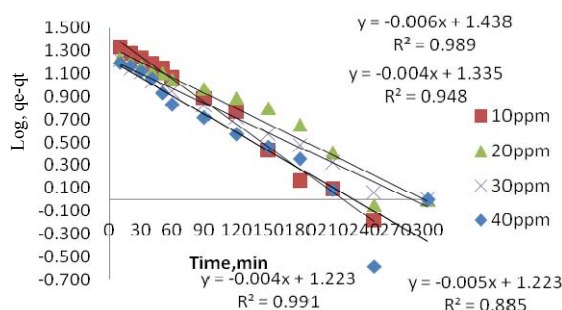


Figure 12. Pseudo first order kinetics of MB by AC-MnO₂-NC

Where q_e and q_t are the amounts of dye adsorbed on adsorbent at equilibrium and at time t , respectively (mg/g) and k_1 is the rate constant of first order adsorption (min^{-1}). The slope and intercept of plot of $\log (q_e - q_t)$ vs. t were used to determine k_1 and q_e . These values are given in Figure 12 and Table 2. From the table the q_e values calculated from the Pseudo first order model is less than that of the experimental value. It does not fit for pseudo first order kinetics.

Table 2. Pseudo First order Kinetic Parameters for the adsorption of MB by AC-MnO₂-NC at various concentrations

Initial Concentration of dye, mg/L	q_e expt., mg/g	Pseudo First-order Kinetics		
		q_e cal., mg/g	K_1 , mg min^{-1}	R^2
10	73.12	27.415	1.381×10^{-2}	0.989
20	55.21	21.627	9.212×10^{-3}	0.948
30	43.46	16.710	9.212×10^{-3}	0.991
40	35.24	16.710	1.151×10^{-2}	0.885

Pseudo second order kinetic model

The second-order kinetic rate equation²⁵ is given as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (10)$$

Where k_2 is the rate constant of Pseudo-second order adsorption ($\text{gm g}^{-1} \text{min}^{-1}$) and q_e is the maximum adsorption capacity (mg g^{-1}). The plot of t/q_t vs. t should give a linear relationship from which K_2 and q_e can be determined from slope and intercept of the plot, respectively. The plot and parameter of Pseudo second order of MB on AC-MnO₂-NC are presented in Figure 13 and Table 3.

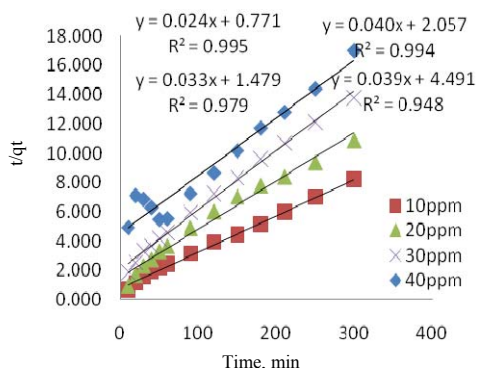


Figure13. Pseudo Second order kinetics of MB by AC-MnO₂-NC

From the table q_e values calculated from the Pseudo second order model are nearly equal to the experimental value and correlation coefficient (R^2) value are high compared with Pseudo first order model. So that the adsorption of MB on AC-MnO₂-NC is to follow the Pseudo second order kinetic model.

Table 3. Pseudo second order Kinetic Parameters for the adsorption of MB by AC-MnO₂-NC at various concentrations

Initial Concentration of dye, mg/L	q_e expt., mg/g	Pseudo Second-order Kinetics		
		q_e calcd., mg/g	k_2 , mg min^{-1}	R^2
10	73.12	41.666	0.747×10^{-3}	0.995
20	55.21	30.303	0.736×10^{-3}	0.979
30	43.46	25.000	0.778×10^{-3}	0.994
40	35.24	25.641	0.338×10^{-4}	0.948

Elovich kinetic model

A simplified linearized form of Elovich kinetic equation^{26,27} is presented as follows:

$$q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln(t) \quad (11)$$

Where α is the initial adsorption rate (mg/g min), β is the desorption constant (g/mg) during any one experiment. A plot of q_t versus $\ln(t)$ with a straight line, as expected, with a slope of $(1/\beta)$ and an intercept of $(1/\beta)\ln(\alpha\beta)$ can be calculated in Figure 14. The Elovich model parameters α , β and correlation coefficient R^2 are summarized in Table 4. From the table the initial adsorption rate (α), desorption constant (β) and the correlation coefficient (R^2) are calculated. The correlation coefficient is (R^2) is less than that of Pseudo second order model.

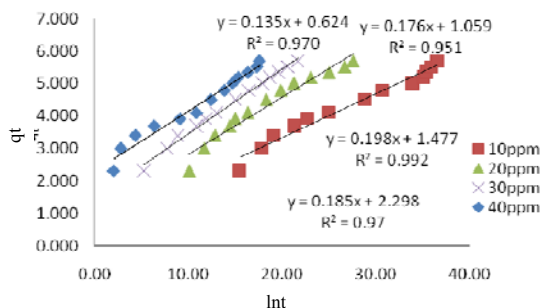


Figure 14. Elovich kinetic model of MB by AC-MnO₂-NC

Intraparticle diffusion model

The intra-particle diffusion model is used here refers to the theory proposed by Weber and Morris²⁸ based on the following equation for the rate constant:

$$q_t = k_{id}t^{0.5} + C \quad (12)$$

Where K_{id} is the intra particle diffusion rate constant ($\text{mg/g min}^{-1/2}$) and C is constant. If that rate limiting step is intra particle diffusion, the graphical representation of adsorbed dye q_t versus $t^{0.5}$ yield straight lines passing through the origin and the slope gives the intra particle diffusion rate constant k_{id} and correlation co-efficient (R^2) is indicated in Figure 15.

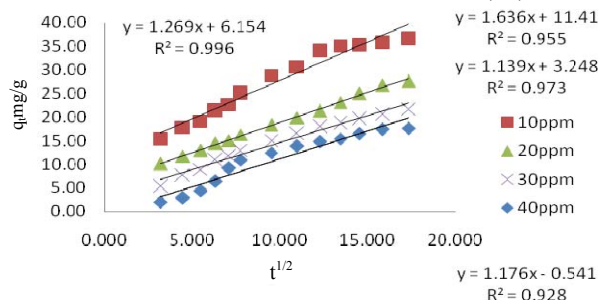


Figure 15. Intraparticle diffusion model kinetic model of MB by AC-MnO₂-NC

The intra-particle parameters K_{id} , C and correlation co-efficient R^2 are summarized in Table 4. From these data inter set value indicate that the line are not passing through origin, therefore some other process that may affect the adsorption. The correlation coefficient (R^2) value is high compared with Elovich model, so that the intra particle diffusion takes place along with other process that may affect the adsorption process.

Table 4. Elovich and Intraparticle diffusion Model of MB by AC-MnO₂-NC

Initial Dye Concentration, mg /L	Elovich Model			Intraparticle diffusion Model		
	α	β	R^2	K_{id}	C	R^2
10	4.313	0.139	0.970	1.636	11.41	0.955
20	4.942	0.185	0.951	1.269	6.154	0.996
30	1.167	0.199	0.992	1.139	3.248	0.973
40	0.561	0.190	0.970	1.176	0.541	0.928

Thermodynamic parameter

Thermodynamic parameters like ΔH° and ΔS° were evaluated using Van't Hoff's equation:

$$\ln K_c = \Delta S^\circ / R - \Delta H^\circ / RT \quad (13)$$

Where K_c is the Langmuir equilibrium constant, ΔH° and ΔS° , are the standard enthalpy and entropy changes of adsorption respectively and their values are calculated from the slopes and intercepts respectively of the linear plot of $\ln K_c$ vs. $1/T$. The free energy change for the adsorption process ΔG° (kJ/mol) is derived in equation 14.

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (14)$$

The values of these parameters were calculated using equation 13 and 14 at various initial concentrations and are shown in Table 5.

Table 5. Thermodynamic parameters for the adsorption of MB by AC-MnO₂-NC

ΔG° , kJ/mol		ΔS° , J/mol/K		ΔH° , kJ/mol	
303K	313K	323 K	333 K	170.270	50.274
-51.541	-53.244	-54.947	-56.649		

The adsorption data indicates that ΔG° were negative at all temperatures. The negative ΔG° confirms the spontaneous nature of adsorption of MB with AC-MnO₂-NC. The magnitude of ΔG° suggests that adsorption is physical adsorption process. The positive value of ΔH° were further confirms the endothermic nature of adsorption process. The positive ΔS° showed increased randomness at the solid-solution interface during the adsorption of MB dye on AC-MnO₂-NC. This was also further supported by the positive values of ΔS° , which suggest that the freedom of MB is not too restricted in the adsorbent, confirming a physical adsorption. The ΔG° value increases with increase in temperature is the increase in enhancement of the adsorption capacity of adsorbent may be due to increase or enlargement of pore size and/or activation of the adsorbent surface.

Desorption studies

After activated carbon is saturated with dye molecules, different solvents could be used to regenerate the activated carbon to restore its dye adsorptive capability²⁹. Desorption with acetic acid revealed that the regeneration of adsorbent was satisfactory, which confirms the physisorptive nature of adsorption.

Conclusion

The present study shows that AC-MnO₂-NC is an effective adsorbent for the removal of MB from aqueous solution. Adsorption followed the Langmuir isotherms. The adsorption capacity was found to be 45.454 mgg⁻¹. The thermodynamic parameters were found to be thermodynamically favourable physical adsorption process. Evaluation of thermodynamic parameters showed the process as endothermic and spontaneous. The kinetic parameters fit for Pseudo second order model. Desorption studies reveals that satisfactory desorption taking place confirming physisorptive nature of adsorption. Complete removal of the dye can be achieved using an appropriate dosage of the adsorbent and pH for waste waters. The results would be useful for the fabrication and designing of waste water treatment plants for the removal of dye. Since the raw material is freely available in large quantities the treatment method, seems to be economical.

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