Research Article

A Comparative Study on the Removal of Basic Dye by using Activated Carbon and Activated Carbon-MnO$_2$-Nanocomposite: Different Kinetic Model

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ABSTRACT

The removal of methylene blue by adsorption on Activated carbon (AC) and Activated carbon-MnO$_2$-Nanocomposite (AC-MnO$_2$-NC) under optimized conditions has been studied. The effect of several parameters such as pH, contact time, initial concentration of the adsorbate, adsorbent dosage and temperature has been evaluated. The application of Pseudo first order, Pseudo second order, intra-particle diffusion model and Elovich kinetic models have been calculated. The adsorption on both the Activated carbon and nanocomposite followed Pseudo second order kinetics. The study revealed that nanocomposite is more effective than activated carbon in removing methylene blue by adsorption.

Keywords: Methylene blue; AC; AC-MnO$_2$-NC; Kinetics.

1. INTRODUCTION

The textile dyeing units release large quantities of dyes in their effluents (Nabi *et al.* 2007).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 organisms (Stydini *et al.* 2004). Dye-containing effluents are undesirable wastewaters because they contain high levels of chemicals, suspended solids, and toxic compounds (Valeria *et al.* 2008). Color causing compounds can react with metal ions to form substances which are very toxic to aquatic flora and fauna and cause many water borne diseases (Ohea *et al.* 2004).

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 (Lalitha *et al.* 2008) 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 black tea leaves (Abul Hossain *et al.* 2012), almond shell (Aliabadi *et al.* 2012), mango leaves (Khan *et al.* 2011), Jambonut (Kumar, 1999) and *Borassus flabellifer* L. (Kumar *et al.* 2010).

Hence adsorption is recommended as a viable means for Basic dye removal.

The aim of the present work is to investigate the removal of Basic dye (Methylene Blue) from aqueous solution by adsorption onto activated carbon (AC) and activated carbon-MnO$_2$-nanocomposite (AC-MnO$_2$-NC). Effects of initial dye concentration, contact time, pH and temperature on dye removal have been studied. By using these adsorption data different kinetic models were also evaluated.

2. MATERIALS AND METHODS

2.1. Preparation of Activated Carbon

The Typha Angustata L plant materials were collected from local area situated at Thindal, Erode District, 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 upto 500 °C and kept it for half an h. The carbonized 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 and it was labeled as AC.

2.2. Preparation of AC-MnO$_2$-NC

Activated Carbon (3 gm) 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 gm) 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 h 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. It was labelled as AC-MnO$_2$-NC.

2.3 Preparation of Sorbate

Methylene Blue (C$_{16}$H$_{18}$Cl N$_3$S), 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) (BDH 85 %) 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. The structure of methylene blue is,
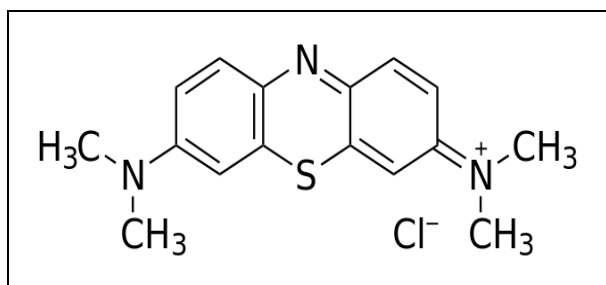
2.4 Batch Experiments

Dye adsorption experiments were carried out by taking 50mL of dye solution with varying concentration (10, 20, 30 and 40 mg/L) and 100mg of both two adsorbents like AC and AC-MnO$_2$-NC. The variables studied were initial dye concentration, agitation time, pH and temperature. The flasks were kept in a shaker and agitated for a predetermined time interval at a constant speed. 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).

3. RESULTS & DISCUSSION

3.1 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 by both AC and AC-MnO$_2$-NC are presented in fig.1a & 1b. The percent removal of MB increased with increase in agitation time and reached equilibrium at 90 min. In the case of AC the percent dye removal at equilibrium decreased from 55.92 to 27.78 as in the case

of AC-MnO$_2$-NC it is 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.
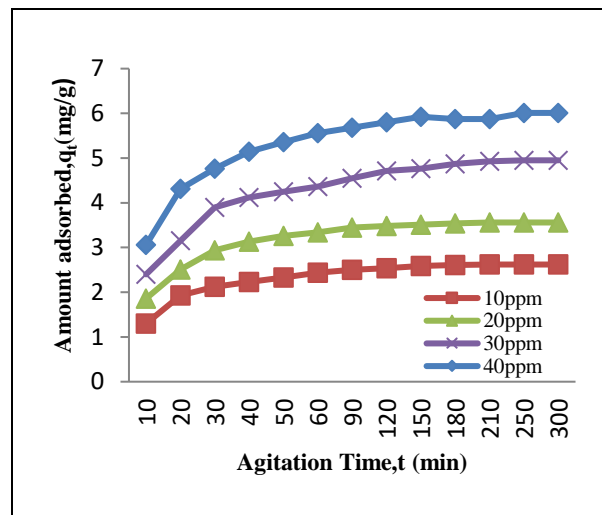

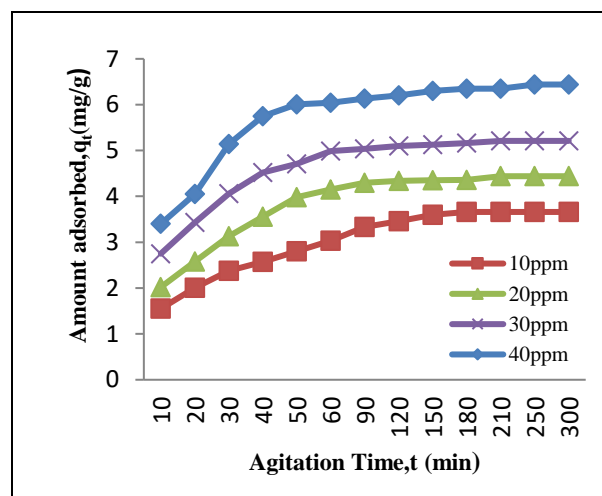**Fig. 1a: Effects of agitation time vs. initial dye concentration MB by AC**

Fig. 1b: Effects of agitation time Vs initial dye concentration MB by AC-MnO$_2$-NC

3.2. Effect of Adsorbent Dose

The removal of MB by both AC and AC-MnO$_2$-NC at different adsorbent doses is presented in fig. 2a & 2b. (10 mg to 600 mg/50 ml) was tested for the dye concentrations 10, 20, 30 and 40 mg/L. With both AC and AC-MnO$_2$-NC 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.
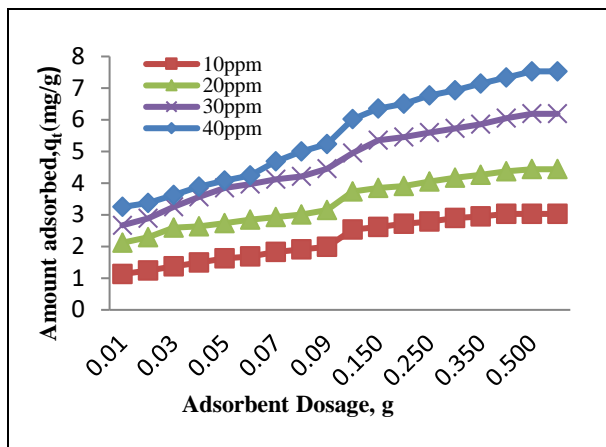
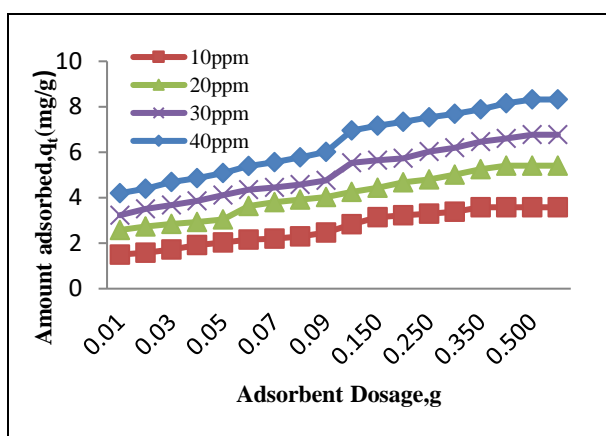**Fig. 2a: Effect of adsorbent dosage for MB by AC**

Fig. 2b: Effect of adsorbent dosage for MB by AC-MnO$_2$-NC

3.3 Effect of pH

Effect of pH on the removal of MB by both AC and AC-MnO$_2$-NC are presented in fig. 3. 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 upto 7.25 the percentage removal is upto 24.31 for AC and 28.73 in the case of AC-MnO$_2$-NC 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 13.54 to 36.55 for AC and 14.41 to 43.66 in the case of AC-MnO$_2$-NC. when the pH was increased from 2 to 14 and the percent removal remained almost the same above pH 8.
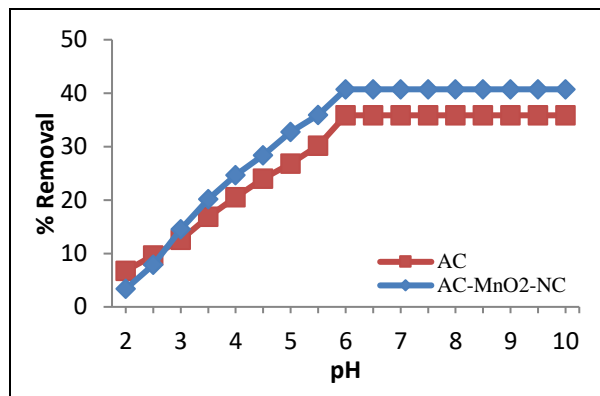

Fig. 3: Effect of pH for MB by AC & AC-MnO$_2$-NC

3.4 Effect of Temperature

The effect of temperature of adsorption of MB by both AC and AC-MnO$_2$-NC is presented in fig. 4a &4b. For concentration 40 mg/L adsorbent was carried out at 30 °C, 40 °C, 50 °C and 60 °C. The percent removal of dye increased from 46.01 to 83.85 for AC and 49.39 to 85.76 as in the case of AC-MnO$_2$-NC. 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.
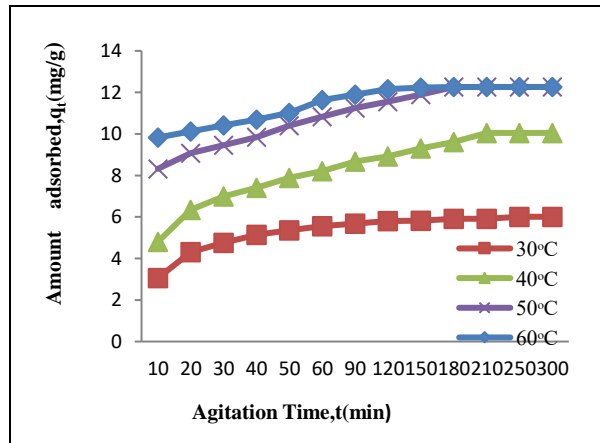

Fig. 4a: Effect of temperature for MB by AC

4. 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 and AC-MnO$_2$ –NC were 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.
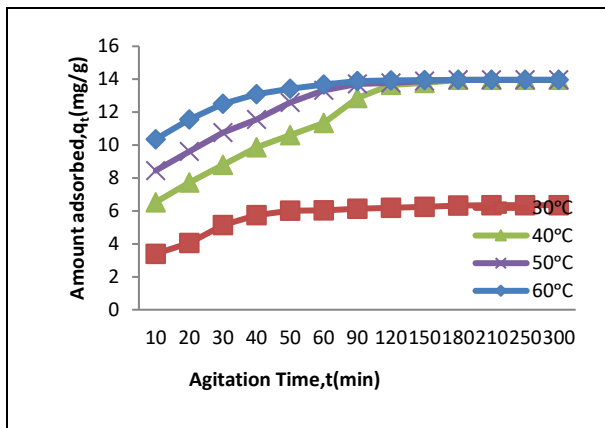

Fig. 4b: Effect of temperature for MB by AC-MnO₂-NC

4.1. Pseudo First Order Kinetic Model

The first-order rate expression of Langergren (Langergren, 1898) equation is given as:

$$\log (q_e\text{-}q_t) = \log q_e - \frac{k_1}{2.203}t \qquad (1)$$

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 fig. 5a & 5b and Table 1 & 2. From the table the q_e values calculated from the Pseudo first order model is less than that of the experimental value for both AC and AC-MnO₂-NC. It is does not fit for pseudo first order kinetics.
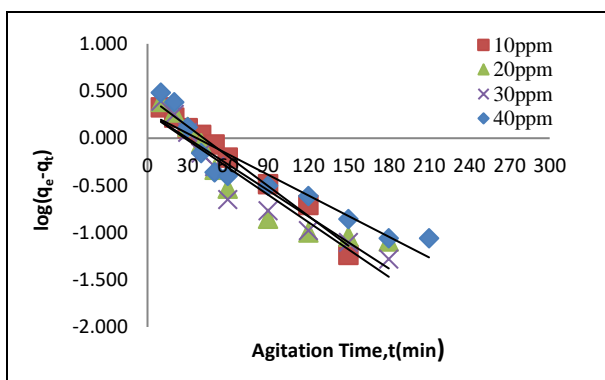

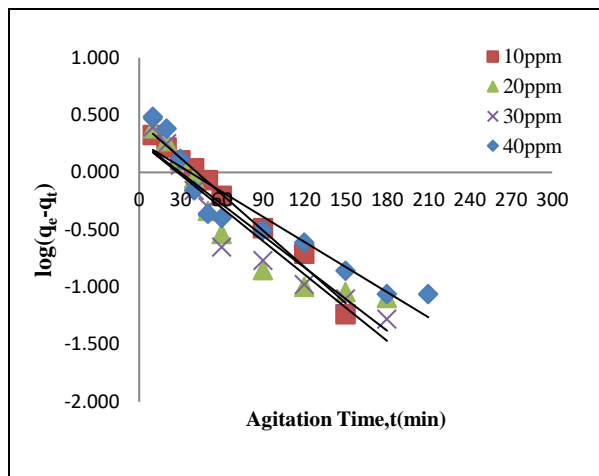**Fig. 5a: Pseudo first order kinetics of MB by AC**

Fig. 5b: Pseudo first order kinetics of MB by AC-MnO₂-NC

4.2. Psuedo Second Order Kinetic Model

The second-order kinetic rate equation (Ho *et al.* 2000) is given as:

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

where k_2 is the rate constant of Pseudo-second order adsorption (gmg⁻¹ min⁻¹) and q_e is the maximum adsorption capacity (mgg⁻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 and AC-MnO₂-NC are presented in fig.6a & 6b and table 1 & 2.
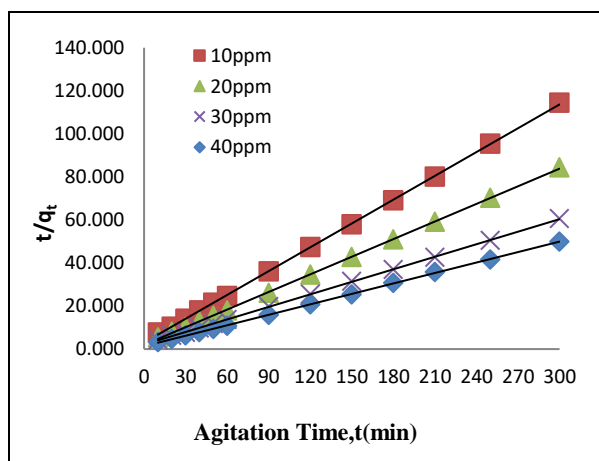

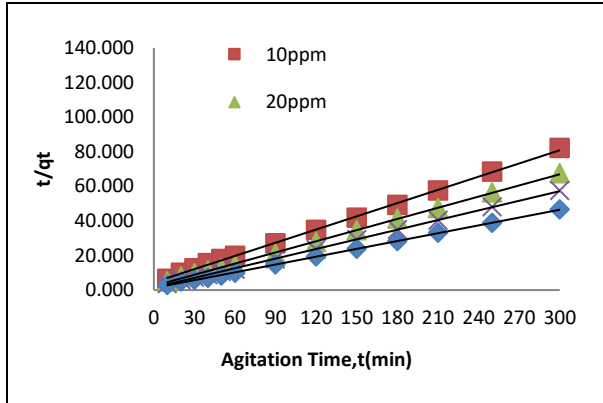**Fig. 6a: Pseudo Second order kinetics of MB by AC**

Fig. 6b: 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 by both AC and AC-MnO₂-NC is to follow the Pseudo second order kinetic model.

4.3 Elovich Kinetic Model

A simplified linearized form of Elovich kinetic equation (Sparks, 1986) is presented as follows:

$$q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln(t) \qquad (3)$$

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 Fig. 7a & 7b . The elovich model parameters α, β and correlation coefficient R^2 are summarized in Table 1 and 2. From the table the initial adsorption rate (α), desorption constant (β) and the correlation coefficient (R^2) are calculated.
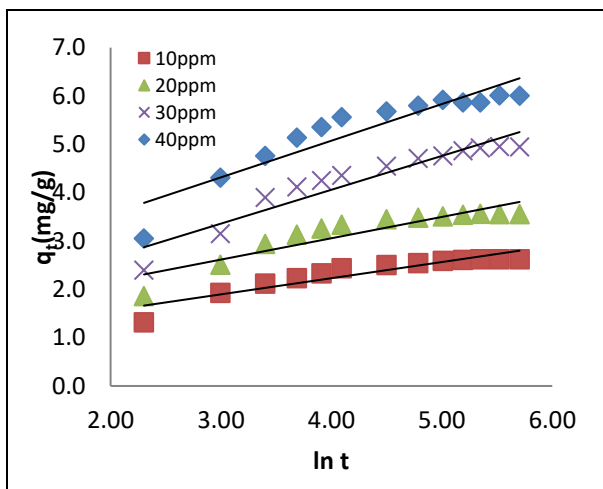

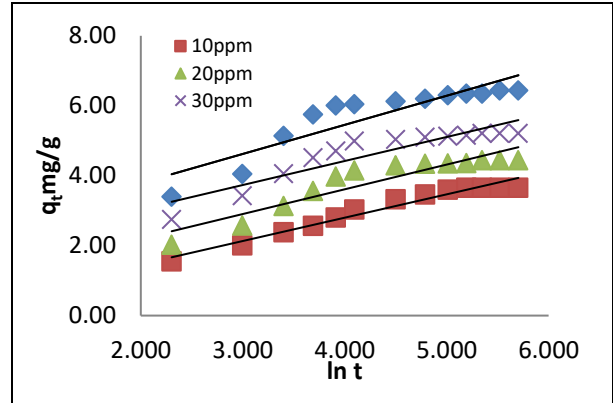**Fig. 7a: Elovich kinetic model of MB by AC**

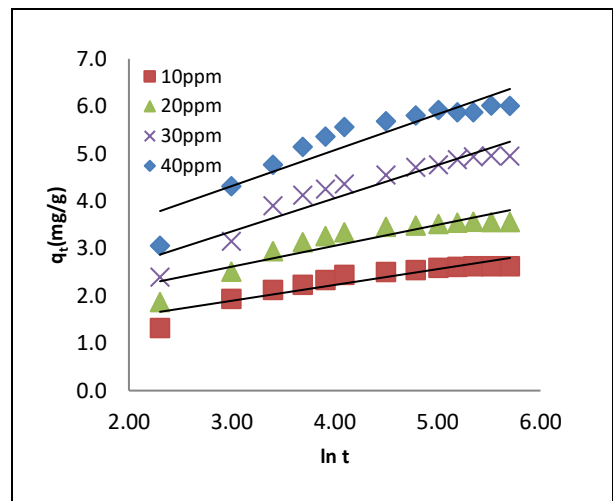

Fig. 7b: Elovich kinetic model of MB by AC-MnO₂-NC

Fig. 8a: Intraparticle diffusion model kinetic model of MB by a) AC
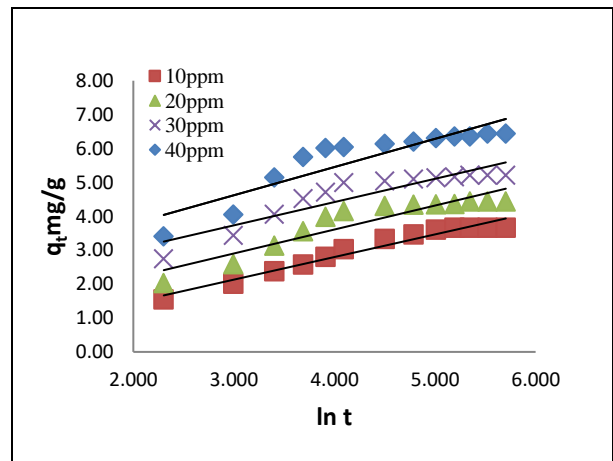

Fig. 8b: Intraparticle diffusion model kinetic model of MB by AC-MnO₂-NC

4.4. Intraparticle Diffusion Model

The intra particle diffusion model is used here refers to the theory proposed by Weber and Morris

(Weber *et al.* 1964) based on the following equation for the rate constant:

$$q_t = k_{id}t^{0.5} + C \quad \ldots\ldots\ldots\ldots \quad (4)$$

Where K_{id} is the intra particle diffusion rate constant (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 coefficient (R^2) is indicated in Fig. 8.

The intra-particle parameters K_{id}, C and correlation co-efficients R^2 are summarized in Table 1 and 2. From these data inter set value indicate that the line are not passing through origin, therefore some other process that may affect the adsorption.

Table 1. Consolidated table for kinetics of adsorption of Basic dyes - Methylene blue onto AC

| | | Methylene blue- AC | | | | | | | | | | | | | | | | | |
| Initial dye conc. (ppm) | q_e exp (m g/g) | Pseudo first-order | | | | Pseudo second-order | | | | Elovich kinetic model | | | | | Intra particle diffusion model | | | | |
		q_e cal mg/g	k_1x 10^{-2} min^{-1}	R^2	SSE	q_e cal mg/g	k_2x 10^{-2} g mg^{-1} min^{-1}	R^2	SSE	α	β	R^2	q_e cal mg/g	SSE	K_{id}	C	R^2	q_e cal mg/g	SSE
10	2.62	1.09	2.303	0.972	0.245	2.71	4.46	0.999	0.081	4.214	2.994	0.855	2.67	0.165	0.068	1.674	0.674	2.65	0.015
20	3.56	1.30	2.303	0.956	0.440	3.67	3.74	0.999	0.081	4.840	2.267	0.829	3.64	0.021	0.088	2.333	0.637	3.61	0.014
30	4.95	2.49	2.070	0.939	0.590	5.15	1.92	0.999	0.114	8.237	1.428	0.903	5.12	0.035	0.145	2.864	0.742	5.15	0.010
40	6.01	1.74	1.380	0.848	0.724	6.21	1.766	0.999	0.127	11.251	1.321	0.857	6.22	0.098	0.154	3.812	0.676	6.24	0.065

Table 2. Consolidated table for kinetics of adsorption of Basic dyes- Methylene blue onto AC-MnO$_2$-NC

| | | Methylene blue- AC-MnO$_2$-NC | | | | | | | | | | | | | | | | | |
| Initial dye conc. (ppm) | q_e exp (mg/g) | Pseudo first-order | | | | Pseudo second-order | | | | Elovich kinetic model | | | | | Intra particle diffusion model | | | | |
		q_e cal mg/g	k_1x 10^{-2} min^{-1}	R^2	SSE	q_e cal mg/g	k_2x 10^{-2} g mg^{-1} min^{-1}	R^2	SSE	α	β	R^2	q_e cal mg/g	SSE	K_{id}	C	R^2	q_e cal mg/g	SSE
10	3.66	2.76	2.303	0.987	0.329	3.93	2.295	0.999	0.112	0.561	1.499	0.960	4.02	0.094	0.139	1.616	0.840	3.53	0.105
20	4.44	1.87	2.303	0.869	0.295	4.65	2.150	0.999	0.132	0.809	1.457	0.860	4.55	0.029	0.143	2.420	0.690	4.53	0.022
30	5.21	1.85	2.072	0.906	0.416	5.40	1.835	0.999	0.142	2.140	1.416	0.843	5.34	0.026	0.146	3.282	0.659	5.29	0.018
40	6.44	1.85	1.612	0.876	0.314	6.66	1.435	0.999	0.159	7.853	0.191	0.943	4.05	0.026	0.168	4.082	0.628	6.73	0.071

5. CONCLUSION

The present investigation showed that AC and AC-MnO$_2$-NC can be used as adsorbent for removal of methylene blue. The amount of dye adsorbed varied with initial concentration, adsorbent dose, p^H and temperature. The kinetic parameters fit for Pseudo second order model. The study reveals that AC-MnO$_2$- NC is more efficient than the AC in removing the methylene blue.

FUNDING

CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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