

# A Comparative Study on the Removal of Methylene Blue and Reactive Red 4 Dyes by using AC-MnO<sub>2</sub>-NC Using Typha Angustata L: Different Kinetic Model

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**Abstract** - The potential of using Typha Angustata L modified AC-MnO<sub>2</sub>-NC to remove different types of dyes namely basic and reactive dyes were studied. The application of Pseudo first order, Pseudo second order, intra-particle diffusion model and Elovich kinetic models have been calculated. The adsorption on AC-MnO<sub>2</sub>-NC followed Pseudo second order kinetics. Thermodynamic parameters such as free energy change ( $\Delta G^\circ$ ) enthalpy change ( $\Delta H^\circ$ ), and entropy change ( $\Delta S^\circ$ ) indicate the adsorption process to be endothermic and spontaneous. The study revealed that AC-MnO<sub>2</sub>-NC is suitable to use as a adsorbent to remove Reactive Red 4 than Methylene Blue.

**Key words**- Methylene Blue, Reactive Red 4, AC-MnO<sub>2</sub>-NC and Kinetics.

## I. INTRODUCTION

Colour is considered as the first pollutant to be identified in wastewater and it is mostly caused by the effluents discharged from dyeing industries such as paper, rubber, cosmetics, textile and plastics. Approximately 10,000 different dyes and pigments are used for industries and over  $7 \times 10^5$  tons of these dyes are annually produced worldwide [1]. Textile and dyeing industry are among important sources for the continuous pollution of the aquatic environment [2].

In addition some dyes (or) their metabolites are either toxic (or) mutagenic and carcinogenic[3]. Thus, the discharge of dyes into water has severe environmental impact and therefore the removal of dyes from wastewater has become a challenging and perplexing problem. In order to overcome this problem, various physicochemical and biological techniques have been studied extensively. Adsorption have been found to be an efficient and economical process to treat dyeing industry effluent.

Recently some agricultural wastes and forestry products have been developed as adsorbents. A wide variety of materials such as animal bone [4], black tea leaves [5], cocoa [6], almond shell [7], mango leaves [8], saw dust [9], Jambonut [10], Borassus flabellifer L[11] and Passiflora foetida [12] are used as a low cost adsorbents.

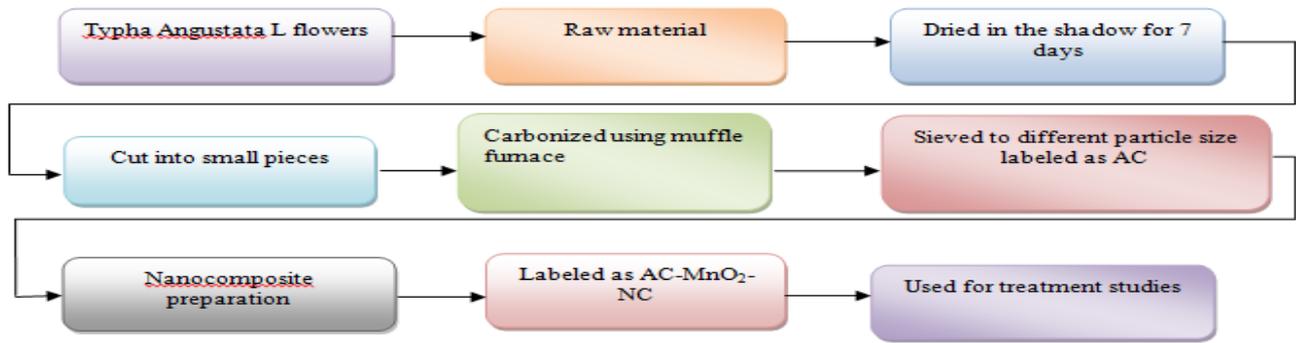
In this present study, Typha Angustata L was chosen as the local low-cost adsorbent and it can be converted into nanocomposite. Most of the studies indicated that the modified adsorbents are efficient in binding either the cationic (or) anionic species but not both. However, a mixture of different types of dyes is usually found in the industrial effluents. In our continued effort to use low-cost materials for the removal of organic pollutants, we have investigated the performance of AC-MnO<sub>2</sub>-NC from Typha Angustata L as a sorbent for basic and reactive dyes.

## II. MATERIALS AND METHODS

### Preparation of sorbate

**Methylene Blue**(C<sub>16</sub>H<sub>18</sub>Cl N<sub>3</sub>S), the sorbate used in the present study, is a monovalent cationic dye and C.I. 52015. It has a molecular weight of 373.90 and wavelength ( $\lambda_{\max}$ ) of 661 nm.

A **Reactive Red 4** having molecular formula C<sub>32</sub>H<sub>19</sub>N<sub>8</sub>Na<sub>4</sub>Cl, Mol Wt of 995.23 with CI No.18105 and wavelength ( $\lambda_{\max}$ ) of 517 nm was chosen as the adsorbate. 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.



Flow chart for the preparation of AC-MnO<sub>2</sub>-NC from *Typha Angustata L*

### III. EXPERIMENTAL METHODS

In each adsorption experiment, 50mL of dye solution with a known concentration was added to 100mg of AC-MnO<sub>2</sub>-NC in a 250ml glass-stoppered flask at 30 ± 0.5 °C, and the mixture was stirred on a mechanical shaker at 150 rpm min<sup>-1</sup>. 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<sup>-1</sup> for 5min. 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 p<sup>H</sup> was observed by studying the adsorption of dye over the p<sup>H</sup> range from 3 to 13. The p<sup>H</sup> of the dye solution was adjusted by using NaOH or HCl solution and a p<sup>H</sup> meter. The sorption studies were carried out at different temperatures (30°,40°, 50°,60 °C). This is used to determine the effect of temperature on the thermodynamic parameters. The amount of sorption at time t, q<sub>t</sub>(mg/g), was calculated using the following the formula:

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

Where C<sub>t</sub>(mgL<sup>-1</sup>) is the liquid phase concentrations of dye at any time, C<sub>0</sub>(mgL<sup>-1</sup>) 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<sub>e</sub>(mg/g), was calculated using the formula

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

where C<sub>0</sub> and C<sub>e</sub>(mgL<sup>-1</sup>) are the liquid-phase concentrations of dye initially and at equilibrium.

The dye removal percentage can be calculated as follows:

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

Where C<sub>0</sub> and C<sub>e</sub>(mgL<sup>-1</sup>) are the initial and equilibrium concentrations of the dye in solution.

### IV. RESULTS AND DISCUSSION

#### 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 and RR4 adsorption on the AC-MnO<sub>2</sub>-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<sup>2</sup>) value, the R<sup>2</sup> values close or equal to 1. A relatively high R<sup>2</sup> value indicates that the model successfully describes the kinetics of MB and RR4 dye adsorption.

#### Pseudo first order kinetic model

The first-order rate expression of Langergren [13] equation is given as:

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.203} t \quad \dots\dots\dots (4)$$

Where q<sub>e</sub> and q<sub>t</sub> are the amounts of dye adsorbed on adsorbent at equilibrium and at time t, respectively (mg/g) and k<sub>1</sub> is the rate constant of first order adsorption (min<sup>-1</sup>). The slope and intercept of plot of log (q<sub>e</sub>-q<sub>t</sub>) vs t were used to determine k<sub>1</sub> and q<sub>e</sub>. These values are given in Figure 1.(a&b) and Table 1and 2. From the table the q<sub>e</sub> values calculated from the Pseudo first order model is less than that of the experimental value for AC-MnO<sub>2</sub>-NC of MB and RR4 . It is does not fit for pseudo first order kinetics.

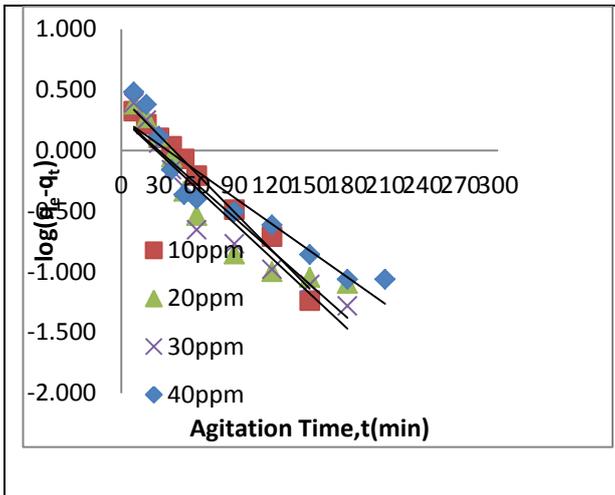


Figure 1a. Plots of the pseudo-first order kinetic model of Methylene Blue onto AC-MnO<sub>2</sub>-NC

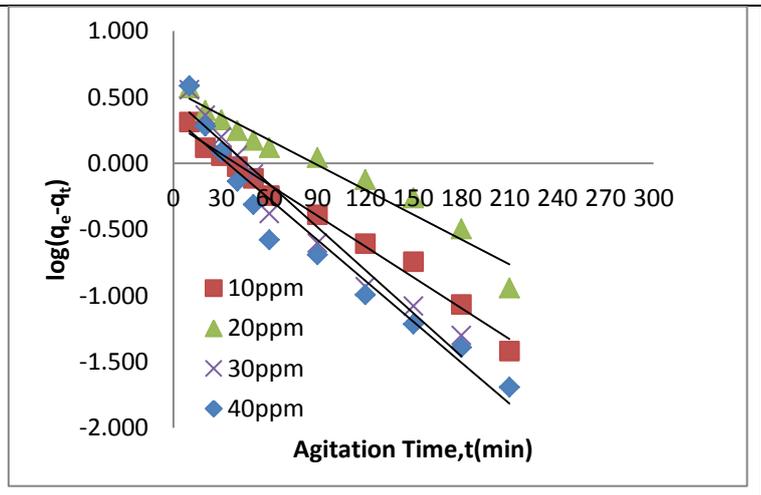


Figure 1b. Plots of the pseudo-first order kinetic model of Reactive Red 4 onto AC-MnO<sub>2</sub>-NC

**Pseudo-second order kinetic model**

The second-order kinetic rate equation [14] is given as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \dots\dots\dots(5)$$

Where  $k_2$  is the rate constant of Pseudo-second order adsorption ( $\text{mg}^{-1} \text{min}^{-1}$ ) and  $q_e$  is the maximum adsorption capacity ( $\text{mgg}^{-1}$ ). 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 and RR4 on AC-MnO<sub>2</sub>-NC are presented in Figure 2(a&b) and Table 1 and 2 for the initial dye concentrations of 10, 20, 30 and 40ppm.

For pseudo second order model, the  $q_e$  calculated values agreed very well with the  $q_e$  experimental values and the correlation coefficient  $R^2$  values were also near to one. Therefore the adsorption of dyes AC-MnO<sub>2</sub>-NC can be well described by pseudo second order model.

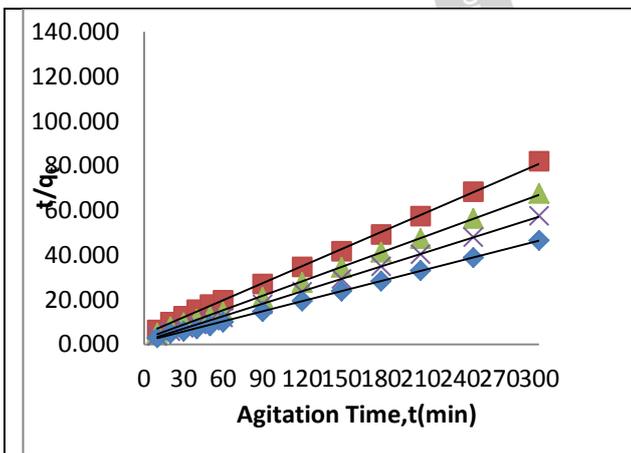


Figure 2a. Plots of the pseudo-second order kinetic model of Methylene Blue onto AC-MnO<sub>2</sub>-NC

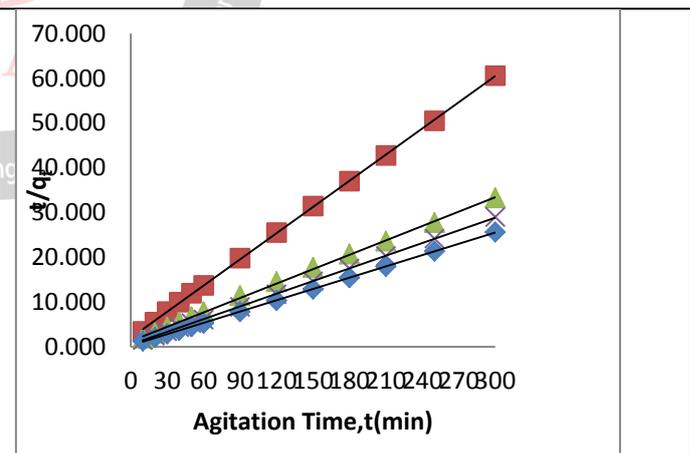


Figure 2b. Plots of the pseudo second - order kinetic model of Reactive Red 4 onto AC-MnO<sub>2</sub>-NC

**Elovich model**

A simplified linearized form of Elovich kinetic equation [15] is presented as follows:

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

where  $\alpha$  is the initial adsorption rate ( $\text{mg/g/ min}$ ),  $\beta$  is the desorption constant ( $\text{g/mg}$ ) 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 3(a&b). The elovich model parameters  $\alpha$ ,  $\beta$  and correlation coefficient  $R^2$  are summarized in Table 1 and 2 for the initial dye

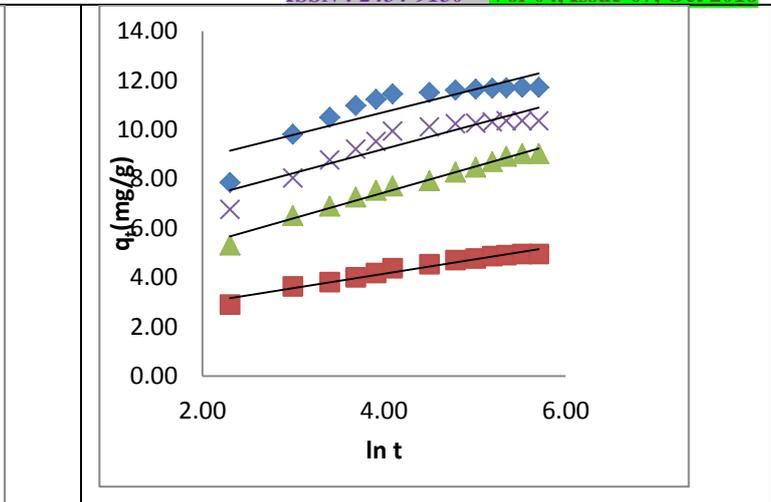
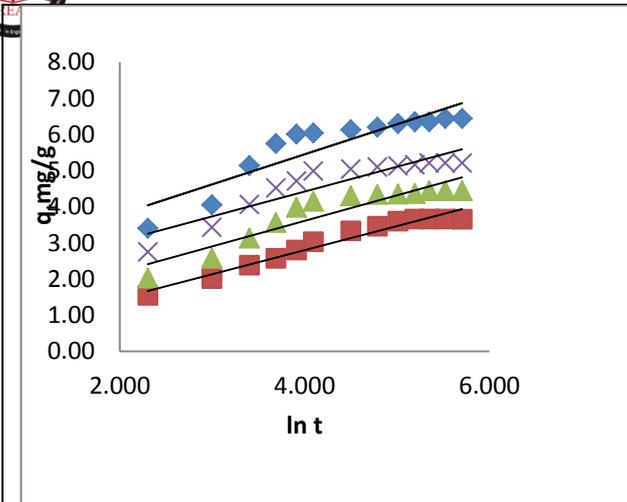


Figure 3a. Plots of the Elovich kinetic model of Methylene Blue onto AC-MnO<sub>2</sub>-NC

Figure 3b. Plots of the Elovich kinetic model of Reactive Red 4 onto AC-MnO<sub>2</sub>-NC

concentrations of 10, 20, 30 and 40 ppm. Lowering of β values with increase in initial dye concentrations and justification of  $t \gg t_0$  predict the behavior of adsorption of dyes over the whole range of variables studied strongly supports the validity of the Elovich equation.

**Intraparticle Diffusion Model**

The intra particle diffusion model is used here refers to the theory proposed by Weber and Morris [16] based on the following equation for the rate constant:

$$q_t = k_{id}t^{0.5} + C \dots\dots\dots (7)$$

Where  $K_{id}$  is the intra particle diffusion rate constant (mg/g min<sup>-1/2</sup>) 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 Figure 4(a&b) and Table 1 and 2 for the initial dye concentration of 10, 20, 30 and 40ppm of all the dyes studied.

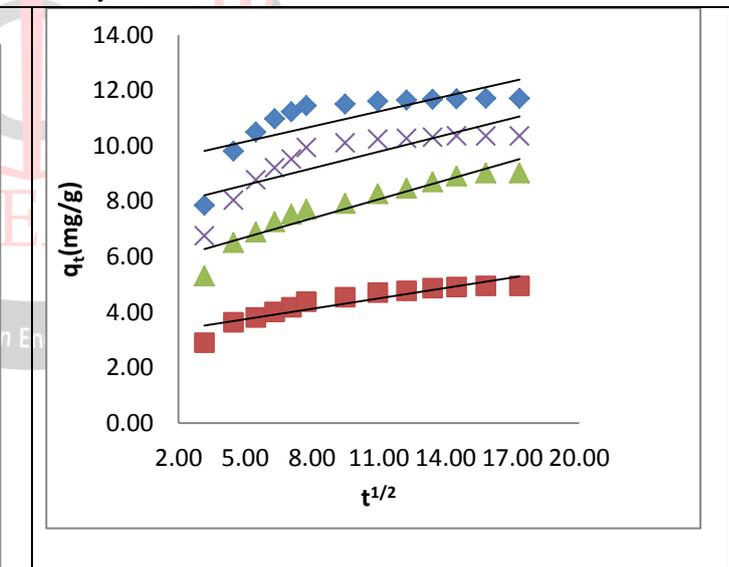
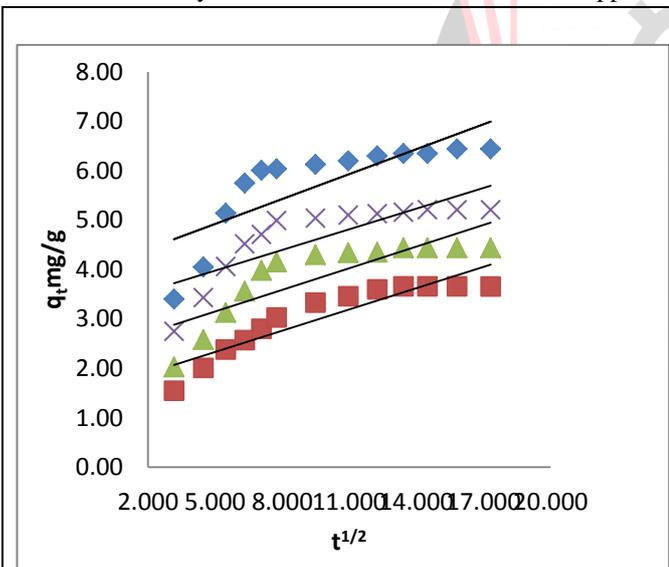


Figure 4a. Plots of the Intra particle diffusion kinetic model of Methylene Blue onto AC-MnO<sub>2</sub>-NC

Figure 4b. Plots of the Intra particle diffusion kinetic model of Reactive Red 4 onto AC-MnO<sub>2</sub>-NC

Table 1. Consolidated table for kinetics of adsorption of Basic dyes- Methylene Blue onto AC-MnO<sub>2</sub>-NC

Methylene Blue- AC-MnO <sub>2</sub> -NC																			
Initial dye concentration (ppm)	C <sub>e</sub> (mg/g)	Pseudo first-order				Pseudo second-order				Elovich kinetic model				Intra particle diffusion model					
		q <sub>e</sub> cal (mg/g)	k <sub>1</sub> × 10 <sup>-2</sup> (min <sup>-1</sup> )	R <sup>2</sup>	SSE	q <sub>e</sub> cal (mg/g)	k <sub>2</sub> × 10 <sup>-2</sup> (g mg <sup>-1</sup> min <sup>-1</sup> )	R <sup>2</sup>	SSE	α	β	R <sup>2</sup>	q <sub>e</sub> cal (mg/g)	SSE	K <sub>id</sub>	C	R <sup>2</sup>	q <sub>e</sub> 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

Reactive Red 4- AC-MnO <sub>2</sub> -NC																			
Initial dye concentration (ppm)	q <sub>e</sub> exp (mg/g)	Pseudo first-order				Pseudo second-order				Elovich kinetic model				Intra particle diffusion model					
		q <sub>e</sub> cal mg/g	k <sub>1</sub> x 10 <sup>-2</sup> min <sup>-1</sup>	R <sup>2</sup>	SSE	q <sub>e</sub> cal mg/g	k <sub>2</sub> x 10 <sup>-2</sup> g mg <sup>-1</sup> min <sup>-1</sup>	R <sup>2</sup>	SSE	α	β	R <sup>2</sup>	q <sub>e</sub> cal mg/g	SSE	K <sub>id</sub>	C	R <sup>2</sup>	q <sub>e</sub> cal mg/g	SS E
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

Table 2. Consolidated table for kinetics of adsorption of Reactive dye- Reactive Red 4 onto AC-MnO<sub>2</sub>-NC

**Evaluation of thermodynamic parameters**

The adsorption thermodynamic parameters namely change in Gibbs free energy, ΔG°, change in Enthalpy of adsorption, ΔH° and change in entropy of adsorption ΔS° are determined from adsorption affinity, ln(q<sub>e</sub>\*m/C<sub>e</sub>). ΔH° and ΔS° were determined from the slope and intercept of linear plot of ln(q<sub>e</sub>\*m/C<sub>e</sub>) vs 1/T using Eyring's equation for Figure 5(a&b),

$$\ln\left(q_e * \frac{m}{C_e}\right) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \text{-----(8)}$$

Where, q<sub>e</sub> is the amount of dye adsorbed at equilibrium(mg/g); C<sub>e</sub> is the equilibrium concentration of the dye solution (ppm); m is the adsorbent dosage in gm/litre; m=2; R is the universal gas constant 8.314 J/mole/K; T is the temperature in Kelvin.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \text{-----(9)}$$

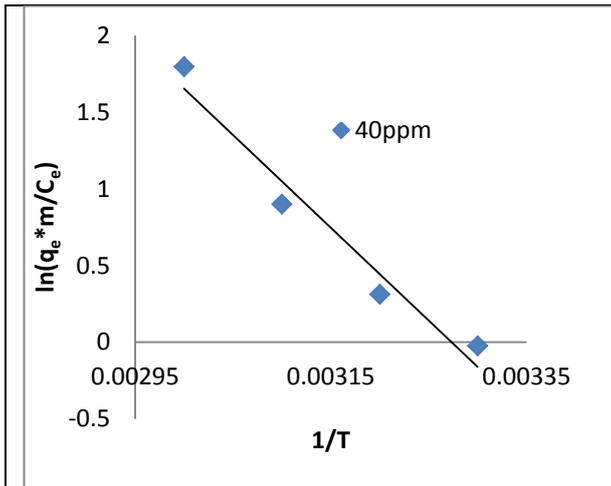
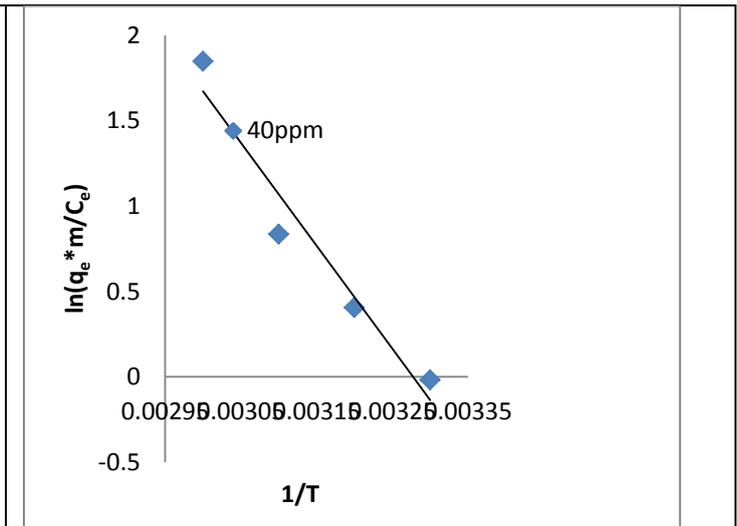
Where, ΔS° is the standard entropy change; ΔH° is the standard enthalpy change; ΔG° is the Gibbs free energy change. The calculated ΔS° and ΔH° values for different temperatures 30°C to 60°C using equations 8 and 9 are presented in Table 3.

For adsorption on AC-MnO<sub>2</sub>-NC the negative values of free energy change (ΔG°) indicate the feasibility of the process and the spontaneous nature of the adsorption, with respect to all the five dyes used in this study as indicated by [17]. For value of ΔH° indicates the heat change associated with the overall adsorption process. The positive ΔH° value, observed for the process indicates that the adsorption of all dyes the adsorbent is an endothermic process. A similar endothermic process has been reported by Namasivayam et al.,[18]. The magnitude of ΔH° may give an idea about the type of adsorption. From Table 3, the absolute values of ΔH° for adsorption of MB and RR 4 are 54.1407 and 63.8681KJ/mol respectively on AC-MnO<sub>2</sub>-NC, which therefore indicates that adsorption of these dyes would be attributed to chemisorptions on both the adsorbents. The positive values of ΔS° indicate the affinity of the adsorbent for dyes. The positive ΔS° values observed for the adsorption of all the five dyes studied suggest a higher degree of disorderliness in the displacement of adsorbed water molecules.

Table 3. Thermodynamic data for removal of dyes studied for AC-MnO<sub>2</sub>-NC

Name of the Adsorbate	Temperature (°C)	1/T (K <sup>-1</sup> )	ln(q <sub>e</sub> *m/ C <sub>e</sub> )	ΔG° (KJ mole <sup>-1</sup> )	ΔH° (KJ mole <sup>-1</sup> )	ΔS° (J/mole <sup>-1</sup> K <sup>-1</sup> )
Methylene Blue	30	0.003300	-0.024	-52.9737	54.1407	175.0097
	40	0.003194	0.3119	-54.7238		
	50	0.003095	0.9002	-56.4739		
	60	0.003003	1.7964	-58.2240		
Reactive Red 4	30	0.003300	-0.018	-61.6802	63.8764	203.7761
	40	0.003194	0.4054	-63.7180		
	50	0.003095	0.8354	-65.7558		

	60	0.003003	1.8489	-67.7935	
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 Figure 5a: Eyring plot for Methylene Blue for AC-MnO<sub>2</sub>-NC

 Figure 5b: Eyring plot for Reactive Red 4 for AC-MnO<sub>2</sub>-NC

## V. CONCLUSIONS

The present investigation showed that AC-MnO<sub>2</sub>-NC can be used as adsorbent for removal of Methylene Blue and Reactive Red 4. The kinetic parameters fit for Pseudo second order model. Evaluation of thermodynamic parameters showed the process as endothermic and spontaneous. The study reveals that AC-MnO<sub>2</sub>-NC is more efficient adsorbent for removing the Reactive Red 4 than Methylene Blue.

## REFERENCES

- [1] V.S. Mane, I.D. Mall, V.C. Srivastava, J. Environ. Manage., 84, 390-400, (2007).
- [2] M.Santhi, P.E. Kumar, IJSR., 4 (5),1968-1971, (2015).
- [3] F.A.Pavan, E.C. Lima, S.L.P. Dias, A.C. Mazzocato, J. Hazard. Mater., 150, 703-712, (2007).
- [4] M. El Haddad, R. Mamouni, N. Saffaj, S. Lazar, Global J.Human Soc. Sci.
- [5] M.Abul Hossain , R.M. Afiqu, Orbital Elec. J. Chem. Campo Grande., 4(3),187-201, (2012).
- [6] C.Theivarasu, S. Mysamy, Int. J. Eng .Sci.Technol., 2(11), 6284-6292, (2010).
- [7] M. Aliabadi, I. Khazari, M. Hajiabadi, F. J. Shahrzad, Bio & Env. Sci., 2(9,39-44 (2012).
- [8] T.A. Khan, S. Sharma, I. Ali, J. Toxicol. Environ. Health Sci., 3(10),286-297(2011).
- [9] A. Wttek-Krowiak, M. Mittek, K. Pokomeda, R. G. Szafran, S. Modelski , Chem.Process Eng., 31, 409-420 (2010).
- [10] P. E. Kumar, M.Phil., Disseration: Bharathiar University, Coimbatore, Tamilnadu, India (1991).
- [11] P.E. Kumar, V. Perumal, Nature Environment and Pollution., 9 [3], 513-518 (2010).
- [12] M.Sathya, P.E. Kumar, M. Santhi, IOSR Journal of Applied Chemistry (IOSR-JAC)., 10[1],8-14 (2017).
- [13] S. Lagergren, Handlingar., 24 ,1-39(1998).
- [14] M.Ungarish, C.Aharoni, J.Chem.Soc.FaradayTransacations., 77,975-985(1991).
- [15] M.J.D. Low, Chem. Rev., 60 , 267-312 (1960).
- [16] W.J. Weber, J.C. , J. Sanit. Eng. Div. Am. Soc. Civ. Eng., 89 , 31-39 (1963).
- [17] T.S. Anirudhan, M. K. Sreedharv, Ind. J. Chem. Tech., 5 ,41-47 (1998).
- [18] C.Namasivayam, K. Kadirvelu, Bioresour. Technol., 38 , 79-81 (1994).