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For the Removal of Reactive Red 4 by using Activated Carbon – MnO_2-Nano Composite: Different Isotherm Studies

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ABSTRACT

This paper presents the feasibility of removal of Reactive dye Reactive Red 4 from aqueous solutions by using a low cost AC-MnO_2-NC. The effects of agitation time, adsorbent dose, initial dye concentration, pH and temperature were examined. Langmuir, Freundlich and Tempkin isotherms were also studied. Adsorbent used in this study are characterized by FT-IR, XRD and SEM analysis.

Keywords: Adsorption isotherm; AC-MnO_2-NC; Reactive red 4.

1. INTRODUCTION

A high volume of colored waste water is generated by textile industries. Textile, Printing and dyeing industry effluent possess reactive dyes which induce a strong color to the effluent and are then discharged to many water resources. Hence it becomes a major contributor for water pollution causing toxic and carcinogenic effects including, cut-off of sunlight passage into water underneath blocking photosynthesis of aquatic system, reduction in dissolved oxygen content, etc (Mohamed *et al.* 2012). Usually reactive dyes which have complex aromatic molecular structure are mainly used dyes in these industries and so its removal prior to effluent discharge to environment is necessary (Hadibarata *et al.* 2012).

Favourable characteristics of reactive dyes like bright colour, water-fastness,and simple application techniques with low energy consumption enhanced the common usage of these dyes in textile industries (Daneshvar *et al.* 2006). Azo-based chromophores with different types of reactive groups such as vinyl sulfone, chlorotriazine, trichloropyrimidine and difluorocholoropyridimine forms the reactive dyes (Aksu, 2005). These reactive dyes are difficult to get removed from effluent due to their ability of easy passage through conventional treatment systems (Zhao *et al.* 2005).

For decolourization of dyes general physical-chemical methods namely, chemical coagulation/flocculation, ozonation, oxidation, ion exchange, irradiation, precipitation and adsorption are used (Ayed *et al.* 2011). Adsorption has been found to be an efficient and economic process for the treatment of dyeing industry effluent (Hassler, 1963).

Many researchers have been working for the preparation of low-cost adsorbents. Exploration of good low cost adsorbent may contribute to the sustainability of the environment and offer promising benefits for the commercial purpose in future. Abundance and low cost of agricultural by products and useless plant materials makes plant materials makes them good precursor for the preparation of activated carbon.

Activated carbon was already prepared from agricultural waste and waste plant materials like Grass-waste (Hameed, 2009), Jambonut (Kumar, 1991), and *Borassus flabellifer* L (Kumar *et al.* 2010). The efficiency of the adsorption process mainly depends on the cost and removal capacity of adsorbents used. The purpose of the present work is to evaluate the sorption of Reactive Red 4 (Anionic-Reactive dye) from its aqueous solution using *Typha angustata* L.

2. MATERIALS & METHODS

2.1 Adsorbate

The Reactive Red employed was RED 4. It is a commercial dye widely used by textiles industries near Tiruppur, India. All the chemicals used are reagent grade. A stock solution containing 1000 mg of the dye per litre was prepared by dissolving the dye in double distilled water and was used to prepare the adsorbate solutions by appropriate dilution required. In order to simplify the discussion the prepared activated carbon is designated as AC-MnO_2-NC and the dye Reactive Red 4 is designated as RR4.

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 ^{0}C to get uniform suspension. At the same time, the Manganese dioxide [3 gm] was dispersed into water-free Alcohol [15mL]. Then the diluted Manganese dioxide was slowly added into the suspension of activated Carbon and stirred for a further 5 h at 25 ^{0}C. To this, 5 mL alcohol and 0.2 mL of de-ionised water was slowly added. The stirring was continued for another 5 h at 25 ^{0}C and the resulting suspension was kept overnight in a vacuum oven for 6 hr at 80 ^{0}C.

3. ADSORPTION ISOTHERM

The adsorption isotherm was obtained from the data deduced from the effect on initial dye concentration. These isotherms are generally used to establish the relationship between the amount of dye adsorbed and its equilibrium concentration in solution. The degree of the adsorbent (AC-MnO_2-NC) affinity for the adsorbate (RR4) determines its distribution between the solid and liquid phases. These adsorption isotherms are used as functional expressions capable of simulating favourable adsorption uptake capacity as long as environmental parameters such as pH, initial dye concentration and contact time are carefully controlled during experiments. The Langmuir, Freundlich and Temkin, isotherm were applied in this study. Although these isotherms shed no light on the mechanism of adsorption, they are useful for comparing results from different sources on a quantitative basis, providing information on the adsorption potential of a material with easily interpretable constants.

3.1 Langmuir Isotherm

Langmuir isotherm (Langmuir, 1918) is represented by the following equation.

$$\frac{C_e}{q_e} = \frac{1}{Q_o K_L} + \frac{C_e}{Q_o} \qquad (1)$$

Where C_e is the concentration of dye solution (mgl^{-1}) at equilibrium. The constant Q_0 signifies the adsorption capacity (mgg^{-1}) and b is related to the energy of adsorption (Lmg^{-1}). The linear plot of C_e/q_e vs C_e shows that adsorption follows a Langmuir isotherm (fig.1). Values of Q_0 and K_L were calculated from the slope and intercept of the linear plot and are presented in table 1.

The essential characteristics of Langmuir isotherm can be expressed by a dimensionless constant called equilibrium parameter, R_L defined by

$$R_L = \frac{1}{1 + K_L C_0} \qquad (2)$$

Where K_L is the Langmuir constant and C_0 is the initial dye concentration (mgL^{-1}). R_L value between 0 to 1 indicates favourable adsorption.

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

The RL values between 0 to 1 which indicates favourable adsorption. Values of Q0 and KL 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 (Q0) is 66.666 mg/g. The Langmuir isotherm can also be expressed in terms of a dimensionless constant separation factor (RL). The RL values lies in between 0 to 1 indicate the adsorption is favourable for all the initial dye concentration.

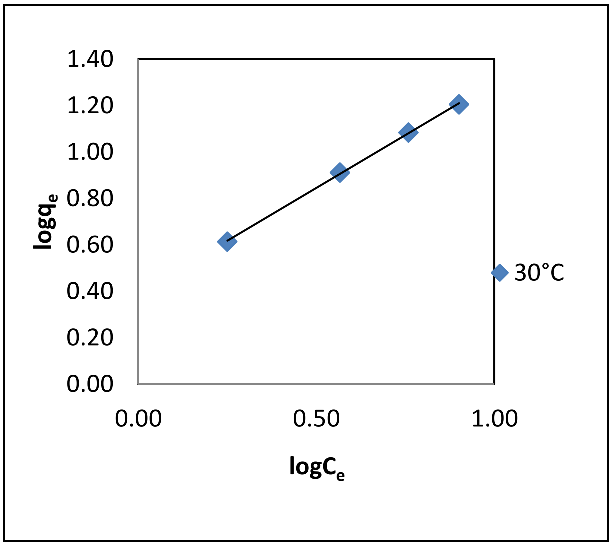

Fig. 1: Langmuir plot for the adsorption of Reactive Red 4 onto AC-MnO_2-NC

3.2 Freundlich Isotherm

The Freundlich isotherm (Freundlich, 1906) was also applied for the adsorption of the dye. This isotherm is represented by the equation

$$\log q_e = \left(\frac{1}{n}\right)\log C_e + \log k_f \qquad (3)$$

Where qe is the amount of dye adsorbed (mg) at equilibrium, Ce is the equilibrium dye concentration in solution (mgL-1) and kf and n are constants incorporating all factors affecting the adsorption process, adsorption capacity and intensity of adsorption. Linear plot of logqe vs log Ce shown in the fig.2. Values of kf and n were calculated from the intercept and slope of the plot and are presented in Table.1.

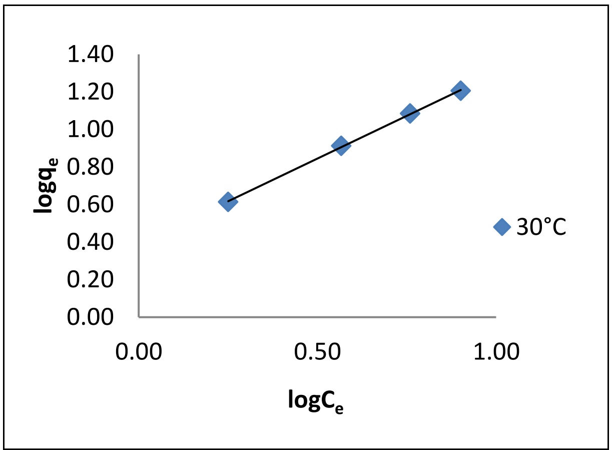

Fig. 2: Freundlich plot for the adsorption of Reactive Red 4 onto AC-MnO_2-NC

3.3 Temkin Isotherm

Tempkin isotherm contains a factor that explicitly takes into account adsorbing species-adsorbate interactions. This isotherm assumes that:

- 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 energy (Temkin *et al.* 1940) Temkin isotherm is represented by the following equation:

$$q_e = RT/b \ln(AC_e) \qquad (4)$$

equation (4) can be expressed in its linear form as:

$$q_e = RT/b \ln A + RT/b \ln C_e$$
$$q_e = B \ln A + B \ln C_e \qquad (5)$$

where B=RT/b

The adsorption data can be analyzed according to equation (5). A plot of q_e versus $\ln C_e$ enables the determination of the isotherm constants A and B and it is shown in fig. 3. 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 fig. 3 for Bismarck Brown Y adsorption on AC-MnO_2-NC and values of the parameters are given in Table.1.

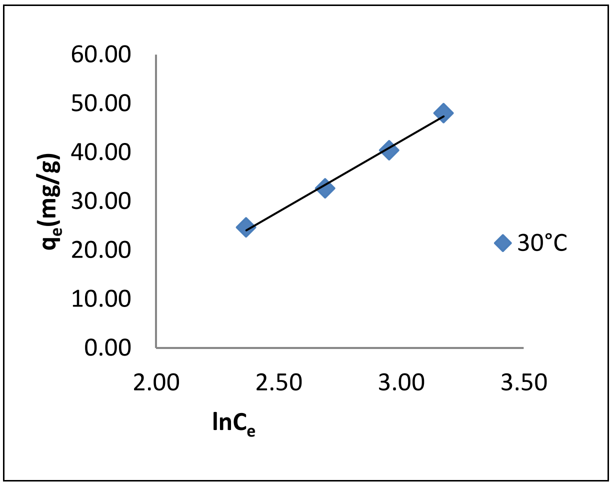

Fig. 3: Tempkin plot for the adsorption of Reactive Red 4 onto AC-MnO_2-NC

Table 1. Results of various isotherms plots for the adsorption of RR4 onto AC-MnO_2-NC

Isotherm Models	Initial dye conc.	Parameters and their results			
		R_L	b	Q_o(mg/g)	R^2
Langmuir	60	0.4088	0.0241	100.00	0.999
	80	0.3424			
	100	0.2932			
	120	0.2569			
Freundlich	Initial dye conc.	n	K_F(mg/g(L/mg)$^{1/n}$)		R^2
	60	1.0989	2.4490		0.999
	80				
	100				
	120				
Temkin	Initial dye conc.	B_T	A_T	b_T	R^2
	60	28.95	4.5643	85.5810	0.994
	80				
	100				
	120				

4. ANALYSIS OF ISOTHERM

4.1 Langmuir Isotherm

In the present study Q_o value is 100.00. The separation factor R_L values in between 0 to 1 indicates the favourable adsorption. The R^2 value is close to unity which reached to good fitting into Langmuir isotherm.

4.2 Freundlich Isotherm

The values of n were between 1 to 10 indicates cooperative adsorption. The R^2 value is is close to unity which reached to good fitting into Freundlich isotherm.

4.3 Temkin Isotherm

B_T – Temkin constant is related to the heat of adsorption. This B_T value is 28.95 indicates temperature of adsorption increased. The Temkin parameter A_T value give on idea about nature of adsorption. In our present study the A_T value is 4.5643 which indicate the adsorption is physical nature. The R^2 value is low compared to Langmuir and Freundlich isotherm.

In general the fitting data in isotherm equation were in the following order: Langmuir> Freundlich > Temkin.

5. CONCLUSION

This study shows that AC-MnO_2-NC can be used effectively for the removal of RR 4 dye from aqueous solution. The adsorption equilibrium data well described by the following order: Langmuir> Freundlich> Temkin. This isotherm constant predicted that the high level mono layer adsorption and low level multi layer adsorption.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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