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Low-Cost Non-Conventional Activated Carbon for The Removal Of Reactive Red 4: 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. Langmuir, Freundlich, Tempkin, Dubinin-Radushkevich and Halsey isotherms were also studied. Thermodynamic parameters such as ΔH°, ΔS°, and ΔG° were also calculated. Adsorbent used in this study are characterized by FT-IR, XRD and SEM analysis.

Keywords: Reactive Red 4, AC-MnO_2-NC, adsorption isotherm, Kinetics.

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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 [1]. 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[2]. 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[3].Azo-based chromophores with different types of reactive groups such as vinyl sulfone, chlorotriazine, trichloropyrimidine and difluorocholoropyridimine forms the reactive dyes[4]. These reactive dyes are difficult to get removed from effluent due to their ability of easy passage through conventional treatment systems [5].

For decolourization of dyes general physical-chemical methods namely, chemical coagulation/flocculation, ozonation, oxidation, ion exchange, irradiation, precipitation and adsorption are used [6]. Adsorption has been found to be an efficient and economic process for the treatment of dyeing industry effluent [7].

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 [8], Jackfruit peel [9], Chitosan / Oil palm ash [10], Durian peel [11], Papaya seeds[12], Rattan saw dust [13], Palm ash[14], Pomelo [citrus grandis] peel [15], Sunflower seed hull [16], Oil palm trunk fibre [17], Rice straw-derived charcoal [18], Firmiana simplex wood fiber [19], Seaweed Enteromorpha [20], Sulphuric acid treated marble power [SATMP] [21], Cashew nut Bark [22], Acid activated Nirgudi leaf powder [23], Sugarcane bagasse [24], Pandanus Carbon [25], Hydrilla Verticillata [26], Annona Squmosa seed activated carbon [27], Surface of wool fiber [28], Bannana Pseudo-stem fibers [29], Chemically modified silicagel [30], Terminalia catappa linn carbon [TCC] [31], borassus Bark carbon [32], Jambonut[33] and Borassus flabellifer L[34]. 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 and Methods

2.1 Adsorbate

The Reactive Red employed was RED 4. It is a commercial dye widely used by textiles industries near Tirupur,India.All the chemicals used are reagent grade. A Reactive Red (Reactive Red 4) having molecular formula $C_{32}H_{19}N_8Na_4Cl$ (Mol Wt :995.23) with CI No.18105,(E.Merck,India) (λmax=517nm) was chosen as the adsorbate. The structure of Reactive Red 4 is shown in Figure 1. A stock solution containing 1000mg 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 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 500^0Cand 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 0.25mm was used.

2.3 Preparation of AC-MnO_2-NC

Activated Carbon [3gm] was allowed to swell in 15mL of water-free Alcohol and stirred for 2 hours at 25^0C to get uniform suspension. At the same time, the Maganese dioxide [3gm] was dispersed into water-free Alcohol [15mL]. Then the diluted Maganese dioxide was slowly added into the suspension of activated Carbon and stirred for a further 5 hours at 25^0C.To this, 5mL alcohol and 0.2mL of deionised water was slowly added. The stirring was continued for another 5 hours at 25^0C and the resulting suspension was kept overnight in a vacuum oven for 6 hours at 80^0C.

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, Temkin, Dubinin-Radushkevich and Halsey 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 [35] is represented by the following equation.

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

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.

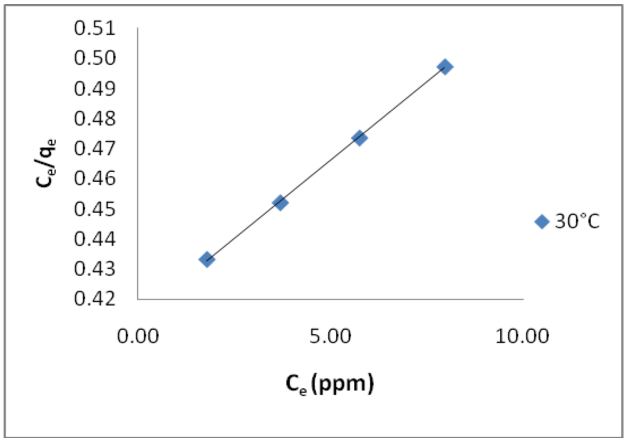

Fig.1: Langmuir plot for the adsorption of Reactive Red 4 onto AC-MnO_2-NC

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

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

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.

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$R_L > 1$	**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 66.666mg/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.

3.2 Freundlich Isotherm

The Freundlich isotherm [36] was also applied for the adsorption of the dye. This isotherm is represented by the equation

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

Where q_e is the amount of dye adsorbed (mg) at equilibrium, C_e is the equilibrium dye concentration in solution (mgL^{-1}) and k_f and n are constants incorporating all factors affecting the adsorption process, adsorption capacity and intensity of adsorption. Linear plot of $\log q_e$ vs $\log C_e$ shown in the Fig.2. Values of k_f and n were calculated from the intercept and slope of the plot and are presented in Table.1.

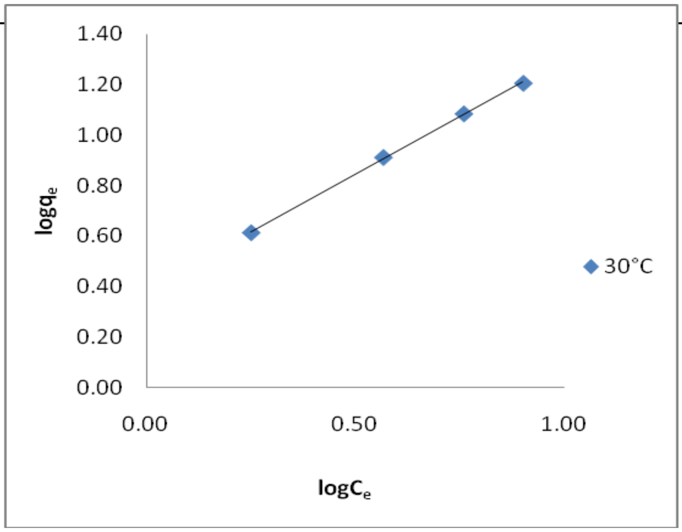

Fig.2. Freundlich plot for the adsorption of Reactive Red 4 onto AC-MnO_2-NC

3.3 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 energy [37] Tempkin isotherm is represented by the following equation:

q_e =RT/b ln(AC_e) ……………..(4)

equation (5) can be expressed in its linear form as:

q_e= RT/b lnA+RT/b lnC_e

q_e=B lnA+BlnC_e …………….(5)

Where B=RT/b

The adsorption data can be analyzed according to equation (5). A plot of q_e versus lnC_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 Reactive Red 4 adsorption on AC-MnO_2-NC and values of the parameters are given in Table.1.

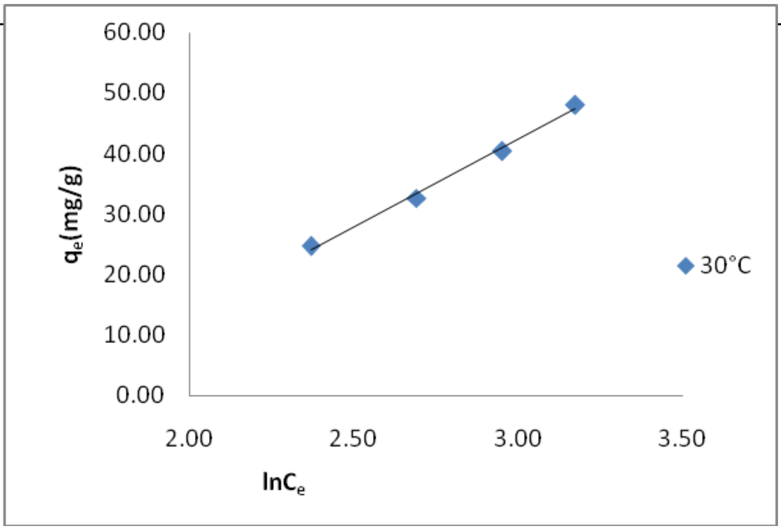

Fig.3. Tempkin plot for the adsorption of Reactive Red 4 onto AC-MnO_2-NC

3.4 Dubinin-Radushkevich (D-R) Isotherm

The (D-R) isotherm this model is generally applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface. This model has often successfully fitted high solute activities and the intermediate range of concentration data well. This model is applied to the data in order to deduce the heterogeneity of the surface energies of adsorption (physical or chemical) and the characteristic porosity of the adsorbent [38]. The linear form of the D-R isotherm is given in

$$\ln q_e = \ln q_D - B_D\varepsilon^2 \text{ --------(6)}$$

Where q_e is the amount of dye adsorbed in the adsorbent at equilibrium (mg/g), q_D is the D-R constant representing theoretical saturation capacity (monolayer adsorption capacity) (mg/g), and B_D is the D-R isotherm constant of the sorption energy (mol^2/ KJ^2), which is related to the (E) average energy of sorption per mole of the sorbate as it is transferred to the surface of the solid from an infinite distance in the solution [39]. The parameter ε is the Polanyi [40] potential, which can be obtained by

$$\varepsilon = RT \ln\left(1+\frac{1}{C_e}\right) \text{ ------- (7)}$$

where T is the solution temperature(K) and

R is the gas constant, which is equal to 8.314 J/mol K.

The average energy, E (kJ/mol), can be calculated by using the D-R parameter B_D:

$$E = \frac{1}{\sqrt{2B_D}} \text{ --------------- (8)}$$

The adsorption data were analyzed according to linear form of the D-R isotherm equation.

The plot of $\ln q_e$ against ε^2 is shown in Fig.4. and the constants q_D and B_D were calculated from the slope and intercept respectively. The D-R isotherm parameters are given in Table.1.This plot also indicated from the regression parameter (R^2). If the value of E lies between 8 and 16kJ/mol the sorption process is a chemisorptions one, while values of below 8kJ/mol indicates a physical adsorption process [41].

The high value q_D show high adsorption capacity. The values of the apparent energy of adsorption also depict physisorption process.

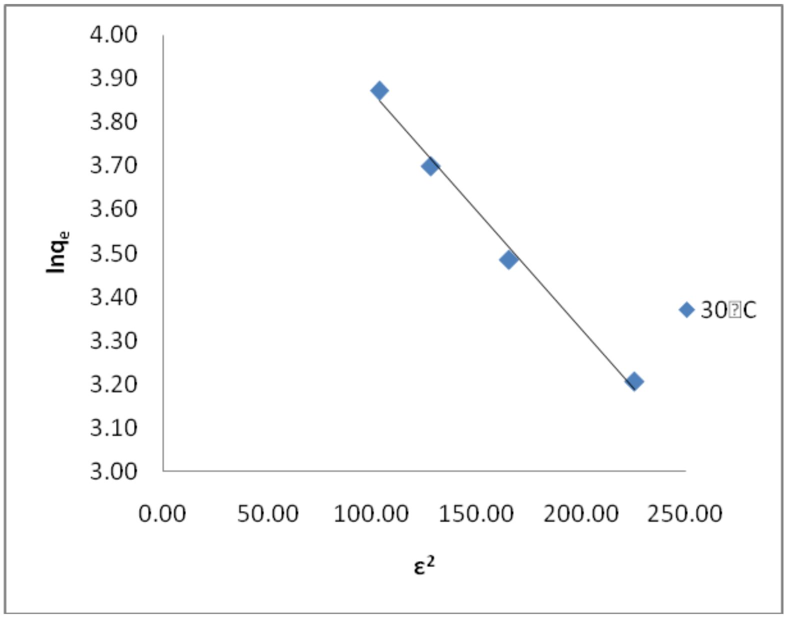

Fig.4. Dubinin-Radushkevich plot for the adsorption of Reactive Red 4 onto AC-MnO_2-NC

3.5 Halsey Isotherm

Halsey proposed an expression for condensation of a multi layer at a relatively large distance from the surface [42],

$$q_e=\left[\frac{K_H}{C_e}\right]^{1/n} H \text{ --------------------(9)}$$

This can be linearised as:

$$\ln q_e = \frac{1}{n_H \ln K_H} - \frac{1}{n_H \ln C_e} \text{ --------(10)}$$

This equation is suitable for multilayer adsorption. Especially, the fitting of the experimental data to this equation attests to the hetero porous nature of the adsorbent.

The plot of $\ln q_e$ vs $\ln C_e$ is shown in Fig.5. and the constants K_H and n_H were calculated from the slope and intercept respectively.

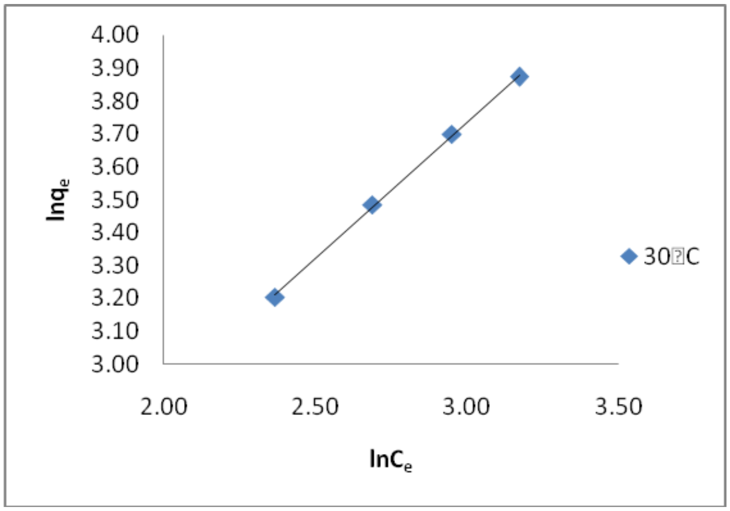

Fig.5. Halsey plot for the adsorption of Reactive Red 4 onto AC-MnO_2-NC

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

Isotherm Models	Initial dye concentration	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 concentration	n	K_F (mg/g(L/mg)$^{1/n}$)		R^2
	60	1.0989	2.4490		0.999
	80				
	100				
	120				
Temkin	Initial dye concentration	B_T	A_T	b_T	R^2
	60	28.95	4.5643	85.5810	0.994
	80				
	100				
	120				
Dubinin-Radushkevich	Initial dye concentration	B_D	q_D	E	R^2
	60	$5X10^{-3}$	81.8591	10.000	0.992
	80				
	100				
	120				
Halsey	Initial dye concentration	n_H	K_H		R^2

	60	1.2062	0.5138	0.999
	80			
	100			
	120			

4 Analysis of Isotherm

4.1 Halsey Isotherm

In the present study Q_o value is 100.00. The separation factor R_L values in between 0 to 1 indicate 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 [43]. 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 [37]. 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.

4.4 Dubinin-Radushkevich isotherm

The activation energy E value is 10.000 and B_D value is $5X10^{-3}$ indicates the chemisorption. The R^2 value is low compared to other three isotherms.

4.5 Halsey isotherm

The R^2 value is close to unity which reached to good fitting into Halsey isotherm.

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

5. Conclusions

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> Halsey > Temkin > Dubinin-Radushkevich. This isotherm constant predicted that the high level mono layer adsorption and low level multi layer adsorption.

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