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Kinetic and equilibrium studies of Rhodamine B adsorption by low cost activated carbon

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ABSTRACT

A carbonaceous adsorbent prepared from an indigenous waste Azadirachta indica bark (AIC), by acid treatment was tested for its efficiency in removing Rhodamine B (RDB) dye. The parameters studied include agitation time, initial dye concentration, carbon dose, pH and temperature. The adsorption followed first order reaction equation and the rate is mainly controlled by intra-particle diffusion. Freundlich and Langmuir isotherm models were applied to the equilibrium data. The adsorption capacity (Q_m) obtained from the Langmuir isotherm plots with temperature variation study showed that the Rhodamine B adsorption is endothermic and spontaneous with increased randomness at the solid solution interface. Significant effect on adsorption was observed on varying the pH of the Rhodamine B solutions. Almost 94% removal of Rhodamine B was observed at 50 °C. Thermodynamic parameters such as ΔH° , ΔS° , ΔG° were evaluated. The positive ΔH° value, pH dependent results and desorption of dye in mineral acid suggest that the adsorption of RDB on AIC involves physisorption mechanism. The adsorption of RDB on to the surface of AIC has been confirmed by the analysis of IR spectra, XRD and SEM images before and after RDB adsorption. The adsorbent was found to be both effective and economically viable.

Key words: *Azadirachta Indica*, Rhodamine B, Adsorption isotherm, Equilibrium, Kinetic and Thermodynamic parameters, Intraparticle diffusion, Regeneration pattern.

INTRODUCTION

Color is one of the characteristics of an effluent. This can be easily detected and readily traced back to its source. Most of the dyes are stable to biological degradation. Colored waters are often objectionable on aesthetic grounds for drinking and other agricultural purposes. Wastewaters from dyeing industries are released in to nearby land or rivers without any treatment, because the conventional treatment methods are not cost effective in the Indian context. Adsorption is one of the most effective methods and activated carbon is the preferred adsorbent widely employed to treat wastewater containing different classes of dyes, recognizing the economic drawback of commercial activated carbon [1, 2].

The feasibility of using inexpensive alternative materials like pearl millet husk, date pits, saw dust buffing dust of leather industry, coir pith, crude oil residue, tropical grass, olive stone, almond shells, pine bark, wool waste, coconut shell etc., as carbonaceous precursors for the removal of dyes from water and wastewater has been studied by many investigators [1,2,3].

The present study aims at to evaluate the efficiency of an acid activated carbon prepared from acid activated *Azadirachta indica* bark Carbon (AIC) for the removal of dye from aqueous solutions

MATERIALS AND METHODS

Preparation of Adsorbent and Adsorbate Solution

The dried *Azadirachta indica* bark was carbonized with concentrated sulphuric acid in the weight ratio of 1:1 (w/v). Heating for twelve hours in a furnace at 500°C has completed the carbonization and activation. The resulting carbon was washed with distilled water until a constant pH of the slurry was reached. Then the carbon was dried for four hours at 125°C in a hot air oven. The dried material was ground well to a fine powder and sieved.

Stock RDB dye solution (1000 mg L^{-1}) was prepared by dissolving desired quantity of commercially available RDB in distilled water. By proper dilution of the stock solution, other concentrations for experimentation were obtained.

Adsorption Dynamic Experiments Batch Equilibration Method

Experiments were carried out in a batch process at different temperatures namely, 35, 40, 45 and 50° C. A known weight of AIC was added to 50 ml of the dye solutions with an initial concentration of 10 mg L⁻¹ to 60 mg L⁻¹. The contents were shaken thoroughly using a mechanical shaker rotating with a speed of 125 rpm. The solution was then filtered at preset intervals of time and the residual dye concentration was determined by colorimetry. Experiments were also conducted in order to evaluate the effect of different variables such as dose of the adsorbent, initial dye concentration, contact time, pH and the effect of the presence of other ion such as chloride ions on adsorption process under a given set of optimal conditions.

Zero Point Charge

The pH at the potential of zero charge of the carbon (pH_{zpc}) was measured using the pH drift method [4]. The pH of the solution was adjusted by using 0.01 M sodium hydroxide or hydrochloric acid. Nitrogen was bubbled through the solution at 25 °C to remove the dissolved carbon dioxide. 50 mg of the activated carbon was added to 50 ml of the solution. After stabilization, the final pH was recorded. The plot of final pH versus initial pH was used to determine the zero point charge of the activated carbon.

Titration Studies

Literature survey has revealed that [4], only strong acidic carboxylic acid groups are neutralized by sodium bicarbonate, whereas those neutralized by sodium carbonate are thought to be lactones, lactol and carboxyl group. Only the weakly acidic phenolic groups react with sodium hydroxide. Therefore, by selective neutralization using bases of different strength, the surface acidic functional groups in AIC can be characterized both quantitatively and qualitatively. Neutralization with hydrochloric acid characterizes the amount of surface basic groups such as pyrones and chromenes. The results indicate that the activated carbon used may possess acidic oxygen functional group on their surface and this is supported well by their respective zero point charge values. The results obtained from the above characterization studies are given in the Table-1.

Desorption Studies

Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the dye. The effect of various reagents used for desorption are studied.

Analytical Measurements

The IR spectra, SEM images and XRD diagrams of the adsorbent before and after adsorption were recorded at the CECRI, Karaikudi, South India.

RESULTS AND DISCUSSION

Characterization of the Adsorbent

The physico-chemical properties of the chosen adsorbent, AIC, were carried out by standard methods [5-7] and are listed in the following Table-1.

Effect of Dosage of AIC

The adsorption of RDB on AIC was studied by varying the carbon concentration (10-100 mg/50ml) for 30 mg L^{-1} of dye concentration. The percent adsorption increased with increase in the carbon concentration (Figure 1). This may be due to the increased carbon surface area and availability of more adsorption sites [5,6]. Hence the remaining parts of the experiments were carried out with an optimum dose of the adsorbent (50 mg/50 ml).

Effect of contact time and initial dye concentration

The experimental results for the adsorption at various concentrations (10 to 60 mg L^{-1}) with contact time are shown in Figure 2. The respective data are presented in Table-2, revealing that, percent adsorption decreased with increase in initial dye concentration, but the actual amount of dye adsorbed per unit mass of carbon increased with increase in dye concentration. It means that the adsorption is highly dependent on initial concentration of dye. It is because of the reason that at lower concentration, the ratio of the initial number of dye molecules to the available surface area is low. Subsequently the fractional adsorption becomes independent of initial concentration. However, at high concentrations, the available sites of adsorption becomes fewer and hence the percentage removal of dye is dependent upon initial concentration [5,6]. An equilibrium has been established at 60 minutes for all concentrations. Figure-2 reveals that the curve is single, smooth, and continuous, leading to saturation, suggesting the possibility of monolayer coverage of the dyes on the carbon surface.

Adsorption Isotherm

The experimental data were analyzed according to the linear form of the Langmuir and Freundlich isotherms [7,8]. The Langmuir isotherm is:

$$C_e/Q_e = 1/Q_m b + C_e/Q_m$$

Where C_e is the equilibrium concentration (mg/L), Q_e is the amount adsorbed at equilibrium (mg/g) and Q_m and b are Langmuir constants related to adsorption efficiency and energy of

adsorption, respectively. The linear plots of C_e/Q_e versus C_e suggest the applicability of the Langmuir isotherms (Figure-3). The values of Q_m and b were determined from slope and intercepts of the plots and are presented in Table 3. From the results, it is clear that the value of adsorption efficiency Q_m and adsorption energy b of the carbon increases on increasing the temperature. From the values, we can conclude that the maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on adsorbent surface with constant energy and no transmission of adsorbate in the plane of the adsorbent surface. The observed b values show that the adsorbent prefers to bind acidic ions and that speciation predominates on sorbent characteristics. When ion exchange is the predominant mechanism taking place in the adsorption of RDB, it confirms the endothermic nature of the process involved in the system [9,10,11]. To confirm the favourability of the adsorption process, the separation factor (R_L) was calculated and presented in Table-4. The values were found to be between 0 and 1 and confirm that the ongoing adsorption process is favorable [12].

The Freundlich equation was employed for the adsorption of Rhodamine B dye on the adsorbent. The Freundlich isotherm was represented by

$$\log Q_e = \log K_F + 1/n \log C_e$$

where Q_e is the amount of Rhodamine B dye adsorbed (mg g⁻¹), C_e is the equilibrium concentration of dye in solution (mg L⁻¹) and K_F and n are constants incorporating the factors affecting the adsorption capacity and intensity of adsorption, respectively. Linear plots of log Q_e versus log C_e show that the adsorption of Rhodamine B dye obeys the Freundlich adsorption isotherm (Figure-4). The values of K_F and n are given in the Table-5 which indicate that the increase in negative charges on the adsorbent surface that makes electrostatic force like van der Waal's between the carbon surface and dye. The molecular weight, size and radii either limit or increase the possibility of the adsorption of the dye onto adsorbent. However, the values clearly show the dominance in adsorption capacity. The intensity of adsorption is an indicative of the bond energies between dye and adsorbent and the possibility of slight chemisorptions rather than physisorption [10,11]. However, the multilayer adsorption of RDB through the percolation process may be possible. The values of n are greater than one, indicating the adsorption is much more favorable [12].

Effect of temperature

The adsorption capacity of the carbon increased with increase in the temperature of the system from 30-60 °C. Thermodynamic parameters such as change in free energy (ΔG° , kJ mol⁻¹), enthalpy (ΔH° , kJ mol⁻¹) and entropy (ΔS° , J K⁻¹mol⁻¹) were determined using the following equations

 $\begin{array}{rcl} K_{o} & = & C_{solid}/C_{liquid} \\ \Delta G^{\circ} & = & -RT \ lnK_{0} \\ log \ K_{o} & = & \Delta S^{\circ/} \left(2.303 RT \right) - \Delta H^{\circ}/(2.303 RT) \end{array}$

Where K_o is the equilibrium constant, C_{solid} is the solid phase concentration at equilibrium (mg L⁻¹), C_{liquid} is the liquid phase concentration at equilibrium (mg L⁻¹), T is the temperature in Kelvin and R is the gas constant. The ΔH° and ΔS° values obtained from the slope and intercept of van't Hoff plots have presented in Table 6. The values ΔH° is with in the range of 1 to 93 kJ mol⁻¹ indicates the physisorption. From the results we could make out that physisorption is much more favorable for the adsorption of RDB. The positive values of ΔH° show the endothermic nature of adsorption and it governs the possibility of physical adsorption [11,13]. Because in the case of physical adsorption, while increasing the temperature of the system, the extent of dye adsorption

increases, this rules out the possibility of chemisorption [13,14]. The low ΔH° value depicts dye is physisorbed onto adsorbent TPC.

The negative values of ΔG° (Table-6) shows the adsorption is highly favorable and spontaneous. The positive values of ΔS° (Table-6) show the increased disorder and randomness at the solid solution interface of RDB with AIC adsorbent, while the adsorption there are some structural changes in the dye and the adsorbent occur. The adsorbed water molecules, which have displaced by the adsorbate species, gain more translational entropy than is lost by the adsorbate molecules, thus allowing the prevalence of randomness in the system. The enhancement of adsorption capacity of the activated carbon at higher temperatures was attributed to the enlargement of pore size and activation of the adsorbent surface [12,13,14].

Kinetics of adsorption

The kinetics of sorption describes the solute uptake rate, which in turn governs residence time or sorption reaction. It is one of the important characteristics in defining the efficiency or sorption. In the present study, the kinetics of the dye removal was carried out to understand the behaviour of these low cost carbon adsorbents. The adsorption of dye from an aqueous follows reversible first order kinetics, when a single species are considered on a heterogeneous surface. The heterogeneous equilibrium between the dye solutions and the activated carbon are expressed as

$$A \xrightarrow{k_1} B$$

Where k_1 is the forward rate constant and k_2 is the backward rate constant. A represents dyes remaining in the aqueous solution and B represent dye adsorbed on the surface of activated carbon. The equilibrium constant (K₀) is the ration of the concentration adsorbate in adsorbent and in aqueous solution (K₀=k₁/k₂).

In order to study the kinetics of the adsorption process under consideration the following kinetic equation proposed by Natarajan and Khalaf as cited in literature has been employed [1].

$$\log C_o/C_t = (k_{ad}/2.303)t$$

Where C_o and C_t are the concentrations of the dye in mg/L at time zero and at time t, respectively. The rate constants, k_{ad} , for the adsorption processes have been calculated from the slope of the linear plots of log C_0/C_t versus t for different concentrations and temperatures. The determination of rate constants as described in literature given by:

$$k_{ad} = k_1 + k_2 = k_1 + (k_1/K_o) = k_1[1+1/K_o]$$

The overall rate constant k_{ad} for the adsorption of dye at different temperatures were calculated from the slopes of the linear Natarajan-Khalaf plots. The rate constant values are presented in Table-7 indicating that the rate constant (k_{ad}) increases with increase in temperature suggesting that the adsorption process is endothermic in nature. Further, k_{ad} values decrease with increase in initial concentration of the dye. In cases of strict surface adsorption a variation of rate should be proportional to the first power of concentration. However, when pore diffusion limits the adsorption process, the relationship between initial dye concentration and rate of reaction will not be linear. Thus, in the present study pore diffusion limits the overall rate of dye adsorption. The over all rate of adsorption is separated into the rate of forward and reverse reactions using the above equation. The rate constants for the forward and reverse processes are also given in Table-7 which indicate that, at all initial concentrations and temperatures, the forward rate constant is much higher than the reverse rate constant suggesting that the rate of adsorption is clearly dominant [1,11,13].

Intraparticle diffusion

The most commonly used technique for identifying the mechanism involved in the sorption process is by fitting the experimental data in an intraparticle diffusion plot. Previous studies by various researchers showed that the plot of Q versus $t^{0.5}$ represents multi linearity, which characterizes the two or more steps involved in the sorption process. According to Weber and Morris, an intraparticle diffusion coefficient K_p is defined by the equation:

$$K_p = Q/t^{0.5} + C$$

The K_p (mg g⁻¹ min^{-0.5}) value can be obtained from the slope of the plot of Q_t (mg/g) versus t^{0.5} for Rhodamine B. From figure 5, it was noted that the sorption process tends to be followed by two phases. The two phases in the intraparticle diffusion plot suggest that the sorption process proceeds by surface sorption and intraparticle diffusion [15,16]. The initial curved portion of the plot indicates a boundary layer effect while the second linear portion is due to intraparticle or pore diffusion. The slope of the second linear portion of the plot has been defined as the intraparticle diffusion parameter K_p (mg g⁻¹ min^{-0.5}). On the other hand, the intercept of the plot reflects the boundary layer effect. Larger the intercept, greater the contribution of the surface sorption in the rate limiting step. The calculated intraparticle diffusion coefficient K_p values are 0.274, 0.353, 0.588, 0.635, 0.705 and 0.917 mg g⁻¹ min^{-0.5} for different initial dye concentrations of 10, 20, 30, 40, 50 and 60 mg L⁻¹ at 35 °C.

Effect of pH

One of the most important parameters controlling the adsorption process is pH. The effect of pH of the solution on the adsorption of RDB on AIC was determined. The result is shown in Figure. 6. The pH of the solution was controlled by the addition of HCl or NaOH. The uptake of RDB at pH 7.5 was the minimum and a maximum uptake was obtained at pH 3.0 - 6.0. However, when the pH of the solution was increased (more than pH 7.5), the uptake of RDB was increased. It appears that a change in pH of the solution results in the formation of different ionic species, and different carbon surface charge. At pH values lower than 6, the RDB dye can enter into the pore structure. At a pH value higher than 6, the zwitterions form of RDB in water may increase the aggregation of RDB to form a bigger molecular form (dimer) and become unable to enter into the pore structure of the carbon surface. The greater aggregation of the zwitterions form is due to the attractive electrostatic interaction between the carboxyl and xanthane groups of the monomer.

At a pH value higher than 7.5, the existence of OH^- creates a competition between $-N^+$ and COO^- and it will decrease the aggregation of RDB, which causes an increase in the adsorption of RDB on the carbon surface [12,17].

Effect of the Ionic Strength on the Adsorption of RDB on AIC

The effect of sodium chloride on the adsorption of RDB on AIC is shown in Figure-7. In a low solution concentration NaCl had little influence on the adsorption capacity. At higher ionic strength the adsorption of RDB will be increased due to the partial neutralization of the positive charge on the carbon surface and a consequent compression of the electrical double layer by the CI^{-} anion. The chloride ion can also enhances adsorption of RDB onto AIC by pairing of their

charges and hence reducing the repulsion between the RDB molecules adsorbed on the surface. This initiates carbon to adsorb more of positive RDB ions [1,17].

Desorption studies

Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the dye. If the adsorbed dye can be desorbed using neutral pH water, then the attachment of the dye of the adsorbent is by weak bonds. If sulphuric acid or alkaline water desorb the dye, then the adsorption is by ion exchange. If organic acids, like acetic acid can desorb the dye, then the dye has been held by the adsorbent through chemisorption. The effect of various reagents used for desorption studies indicate that hydrochloric acid is a better reagent for desorption, because we could get more than 68 % removal of adsorbed dye. The reversibility of adsorbed dye in mineral acid or base is in agreement with the pH dependent results obtained. The desorption of dye by mineral acids and alkaline medium indicates that the dyes were adsorbed onto the activated carbon through physisorption [12,18].

Properties	AIC
Particle size (mm)	0.030
Density (g/cc)	0.2856
Moisture content (%)	1.55
Loss on ignition (%)	78
Acid insoluble matter (%)	2.5
Water soluble matter (%)	0.52
pH of aqueous solution	6.5
pH_{zpc}	5.75
Surface groups (m equiv/g)	
i) Carboxylic acid	0.528
ii) Lactone, lactol	0.085
iii) Phenolic	0.079
iv) Basic (pyrones and chromenes)	0.018

Table-1	Characteristics	of	the	adsorbent

Table 2 : equilibrium parameters for the adsorption of dye onto AIC

[RDB] ₀ mg L ⁻¹		C _e (n	ng /L)			Dye Removed (%)						
	35°	40°	45°	50°	35°	40°	45°	50°	35°	40 °	45 °	50°
10	1.336	1.208	0.982	0.640	8.6638	8.7919	9.0171	9.3598	86.63	87.91	90.17	93.59
20	2.793	2.473	2.208	1.994	17.2062	17.5262	17.7915	18.0053	86.03	87.63	88.95	90.02
30	4.828	4.347	3.889	3.330	25.1718	25.6570	26.1109	26.6695	83.90	85.50	87.03	88.89
40	8.595	7.811	7.153	6.399	31.4404	32.1888	32.8467	39.0995	78.60	80.47	82.11	84.00
50	12.699	11.901	11.115	10.900	37.3007	38.0985	38.8841	39.0995	74.60	76.19	77.76	58.48
60	17.411	16.351	15.401	14.529	42.5890	43.6488	44.5983	45.4706	70.98	72.74	74.33	75.78

Table 3-Langmuir Constants And Statistical Parameter

S.No.	Temp., °C	Qm	b	\mathbf{R}^2
1	35	60.09	0.1197	0.9964
2	40	59.77	0.1356	0.9963
3	45	59.17	0.1639	0.9978
4	50	55.24	0.2132	0.9946

[RDB] ₀ ,	Temp., °C							
mg L ⁻¹	35	40	45	50				
10	0.456	0.425	0.380	0.359				
20	0.294	0.270	0.234	0.190				
30	0.217	0.198	0.169	0.135				
40	0.172	0.156	0.132	0.105				
50	0.142	0.129	0.109	0.085				
60	0.121	0.109	0.092	0.073				

Table 4-dimensionless separation factor, R_L

Table 5-Freundlich Constants And Statistical Parameter

S.No.	Temp., ⁰C	K _F	n	\mathbf{R}^2
1	35	1.8199	1.6701	0.9818
2	40	1.8018	1.6983	0.9789
3	45	1.7533	1.7812	0.9826
4	50	1.6465	2.0052	0.9890

Table 6-equilibrium constant and thermodynamic parameters for the adsorption of dye onto AIC

	Temp., °C									
$[\mathbf{K}\mathbf{D}\mathbf{B}]_0$	35°	40 °	45 °	50 °	35°	40 °	45 °	50 °		
Ing L		J	Ko			Δ	ΔH°	ΔS°		
10	6.48	7.72	9.17	14.32	-4.78	-5.14	-5.84	-7.20	28.84	109.02
20	6.15	7.08	8.05	9.15	-4.65	-5.09	-5.52	-5.94	22.31	87.41
30	5.21	5.90	4.71	8.01	-4.22	-4.61	-5.02	-5.58	21.01	81.80
40	3.65	4.12	4.59	5.25	-3.31	-3.68	-4.02	-4.45	19.95	7691
50	2.93	3.20	3.49	3.58	-2.75	-3.02	-3.30	-3.43	14.51	55.99
60	2.44	2.66	2.89	3.12	-2.28	-2.54	-2.80	-3.06	14.05	52.95



Fig.1-Effect of adsorbent dose on the adsorption of RDB by AIC [RDB]=30 mg/L;Contact time=60 min;Temp=35^oC

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Fig.3-Linear Langmuir isotherm for the adsorption of rhodamine-B by AIC



Fig.5-Intra-particle diffusion effect on the adsorption of RDB {RDB]=30 mg/L;Contact time=60 min; Adsorbent dose=50 mg/50 ml;Temp=35^oC





IDDD1		k	ad	k ₁	k ₂	k ₁	k ₂	k ₁	k ₂	k ₁	k ₂		
$[\mathbf{K}\mathbf{D}\mathbf{D}]_0$	Temp., °C												
Ing L	35 °	40 °	45 °	50 °	35°		40 °		45 °		50 °		
5	13.54	15.89	18.51	20.74	11.73	1.81	13.96	1.93	16.69	1.82	19.41	1.33	
10	9.10	11.46	13.57	15.92	7.83	1.27	10.04	1.42	12.07	1.50	14.35	1.57	
15	7.81	8.66	9.69	11.43	6.55	1.26	7.40	1.26	8.43	1.26	10.16	1.27	
20	5.62	6.21	6.93	7.57	4.41	1.21	4.99	1.22	5.69	1.24	6.36	1.21	
25	4.54	4.90	5.42	5.85	3.39	1.15	3.74	1.16	4.21	1.21	4.57	1.28	
30	3.92	4.79	5.25	5.56	2.78	1.14	3.48	1.31	3.90	1.35	4.21	1.36	

Table 7-rate constants for the adsorption of dye $(10^3 k_{ad}, min^{-1})$ and the rate constants for FORWARD $(10^3 k_1, min^{-1})$ and reverse $(10^3 k_2, min^{-1})$ process

CONCLUSION

The experimental data were very well correlated by the Langmuir and Freundlich adsorption isotherms and the isotherm parameters were reported. The low as well high pH value pays the way to the optimum amount of adsorption of the dye. The amount of Rhodamine B adsorbed increased with increasing ionic strength and increased with increase in temperature. The dimensionless separation factor (R_L) showed that the activated carbon prepared from *Azadiracta indica* bark could be used for the effective removal of Rhodamine B from aqueous solutions. The values of ΔH° , ΔS° and ΔG° show that the carbon employed has a considerable potential as an adsorbent for the removal of Rhodamine B.

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