Scholars Journal of Engineering and Technology (SJET) **ISSN 2321-435X (Online)**
Sch. J. Eng. Tech., 2014; 2(2B):258-263 **ISSN 2347-9523 (Print)**

(An International Publisher for Academic and Scientific Resources)
www.saspublisher.com

Research Article

Kinetic and Thermodynamic Studies on the Adsorption behavior of RhodamineB dye using Prosopis Juliflora Bark Carbon.

M. Thilagavathi[1], S. Arivoli[2*] and V.Vijayakumaran[3]
[1] Department of Chemistry, Pattukkottai Polytechnic College, Pattukkottai - 614 601,India.
[2*] Department of Chemistry, Thiru Vi Ka Govt. Arts College, Thiruvarur- 610 003, India.
[3] Anna university, University college of Engineering, Pattukkottai - 614 701, India.

***Corresponding author**
S. Arivoli
Email: arivu3636@yahoo.com

Abstract: The adsorption behavior of Rhodamine B dye from aqueous solution was investigated using prosopis juliflora bark carbon. The effects of various experimental factors such as contact time, adsorbent dose, initial dye concentration, pH and temperature were studied by using the batch technique. The adsorption capacities were evaluated by using Freundlich and Langmuir adsorption isotherm models. Thermodynamic parameters were calculated and it was found that the adsorption of Rhodamine B dye using prosopis juliflora bark carbon was an exothermic and spontaneous process. Pseudo second order and intraparticle diffusion model shows good applicability with very high correlation coefficient values.
Keywords: Adsorption, Kinetic, PJBC, RhoB dye, Thermodynamic

INTRODUCTION

The increase in population and rapid industrial growth in India has resulted in high demand for dyes and pigments [1]. Dyes are important pollutants in the effluents of textile, leather, food processing, cosmetics and paper manufacturing industries. The discharge of these dye wastes into receiving streams not only affects the aesthetic nature but also reduces photo-synthetic activity [2]. Waste waters offer considerable resistance for their biodegradation [4] and also a several commonly used dyes have been reported to be carcinogenic and mutagenic for aquatic organisms [3]. Pollution caused by industrial waste water has become a common problem for many countries [5]. Therefore, it is necessary to reduce dyes concentration in the waste water. Adsorption is an attractive and alternative for the treatment of waste water, especially if the adsorbent is inexpensive and does not require an additional pre-treatment step before its application. Currently, the most commonly used adsorbent is activated carbon that was successfully remove the dyes from waste water [6, 7]. However, the activated carbon is considered to be an expensive and problems with regeneration of the spent activated carbon in its large scale application. In order to decrease the cost of water treatment, attempts have been made to find inexpensive low-cost adsorbents [8]. Therefore, new, economical, easily available and highly effective adsorbents still need to be found. The present study is used to find out the suitability of PJBC adsorbent to remove the Rhodamine B from aqueous solution.

MATERIALS AND METHODS

Adsorbate

Rhodamine-B (RhoB) dye used in this study is purchased from Sigma-Aldrich Company. RhoB has molecular formula $C_{28}H_{31}N_{20}Cl_3$.The dye stock solution was prepared by dissolving accurate weight of dye in distilled water to the concentration of 1 g/L.

Preparation of Prosopis Juliflora Bark Carbon (PJBC) adsorbent

Prosopis Juliflora Bark Carbon (PJBC) was collected from local market. The collected PJBC materials were finely powdered with grinding machine. Then the powder was treated with con. sulphuric acid for 2 hours, filtered and then washed with water. The black product was kept in a furnace for about 24 hours and the temperature was maintained at 800^{o}C. The resulting powder was used for adsorption experiment.

Batch method

The batch adsorption and kinetic [9] experiments were carried out by adding a fixed amount of adsorbent (25 mg/50ml) into a number of 250 ml stopper glass flasks containing a definite volume (50 ml in each case) of different initial concentration (50,100,150,200 and 250 mg/L) of dye solutions without changing pH and at temperatures 30, 40, 50 and

60°C. The flasks were placed in a thermostatic water bath shaker to ensure equilibrium was reached. At time "t" and at equilibrium condition, the RhoB dye concentration were measured by using spectrophotometer at 555 nm. The amount of adsorption q_t (mg/g) at time "t", amount of adsorption at equilibrium q_e(mg/g), and % removal of RhoB dye were calculated by

$$q_t = \frac{(C_O - C_t)V}{W} \quad (1)$$

$$q_e = \frac{(C_O - C_e)V}{W} \quad (2)$$

$$\% \text{ Removal} = \frac{C_o - C_t}{C_o} X100 \quad (3)$$

Where C_o (mg/L), C_t (mg/L) and C_e (mg/L) are the liquid phase concentrations of RhoB dye at initial, at particular time and equilibrium respectively .V (Litre) is the volume of the solution. W (gram) is the mass of dry adsorbent used.

RESULT AND DISCUSSION

Effect of contact time

The effect of contact time between adsorbent PJBC and adsorbate (RhoB) were determined by keeping RhoB dye concentration, adsorbent dosage, pH and temperature were constant. In the present study, the adsorption process of RhoB using PJBC was studied for various time interval such as 10,20, 30,40,50,60,70,80 and 90 minutes. The results were presented in Fig. 1. It was observed that initially increase in time enhances the rate of adsorption and its equilibrium was almost attained and 94% dye removal takes place within 60 minutes. Hereafter there was no appreciable changes in adsorption. So 60 minutes was the sufficient time for the maximum adsorption of dye.

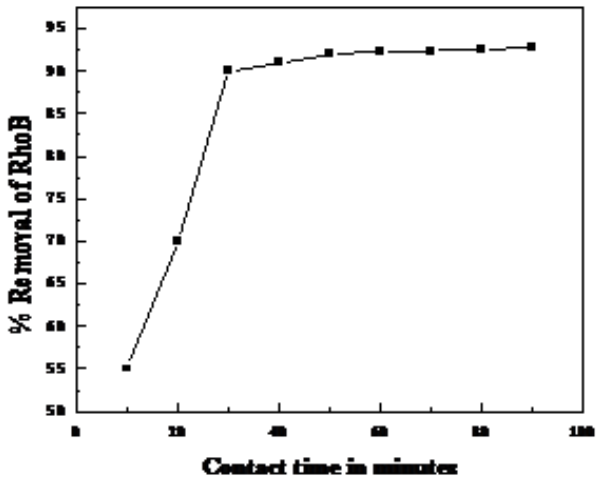

Fig. 1. Effect of contact time for the adsorption of Rhodamine B dye

[RhoB]=50mg/L; pH=7.0; Temp=30°C; Adsorbent dose=25mg/50ml.

Effect of PJBC adsorbent dose

To study the effect of PJBC dose on the RhoB adsorption, different amounts of PJBC powder (5-500 mg) were added into a 250 ml stopper glass containing a definite volume (50ml in each-flask) of fixed initial concentration (50mg/L) of dye solution without changing the pH of solution at 30°C as shown in Fig. 2. The flasks were placed in a thermostatic water bath shaker for 60 minutes and the RhoB dye concentrations were measured at equilibrium.

From the figure, it was observed that the % removal increases initially up to 25mg/50 ml and reaches limiting value with fractional difference. Thus adsorption increases with an increase in the dose of adsorbent due to availability of more active sites for adsorption. However, a further increase in the dose of adsorbent did not affect the % removal of dye because of the unavailability of adsorbate due to saturation. So the experiments were carried out by using 25mg/50 ml of adsorbent dose.

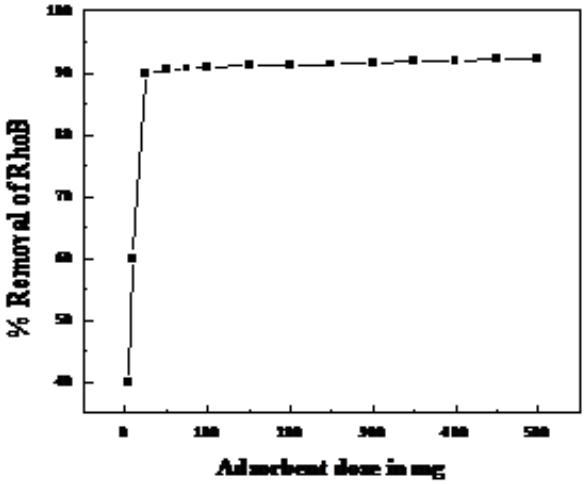

Fig. 2. Effect of adsorbent dose for the adsorption of Rhodamine B dye

[RhoB]=50 mg/L; pH=7.0; Temp=30°C; Contact time=60 minutes.

Effect of solution pH

The effect of solution pH for the adsorption of RhoB using PJBC was studied by mixing 50 mg/L of RhoB dye concentration and 25 mg/50ml of adsorbent with different pH values (2 to10) at 30°C as shown in figure 3. The pH was adjusted with 0.1N NaOH and 0.1N HCl solutions and pH of the solution was measured by pH meter. Agitation was made for 60 minutes.

The adsorption of the dye depends on the solution pH and (pH_{zpc}) zero point charge of the adsorbent. The zero point charge of the PJBC is 4.The adsorption of dye was higher at a solution pH > pH_{zpc}. This could be due to more negative charges at the PJBC adsorbent surface, resulting in the higher % removal of the dye occur. But in the pH< pH_{zpc} the positive charges

on the adsorbent surface, which may decrease the % removal of the dye. The % removal of RhoB increases from pH 2 to 7.5 and suddenly decreases. The pH range of 2 to 4 more hydrogen surrounding the adsorbent surface, this may compete with cationic dye molecule. The pH range of 5 to 7.5, i.e., weakly acidic and neutral medium the cationic dyes easily reaches adsorbent surface. So that more than 90% adsorption takes place with in this pH range. The pH above 8, the adsorbent surface active functional group is anionic and also surrounded by anions which prevents cationic dye adsorption. These anions form complex with cationic dye, so it decreases the % removal of dye. Hence maximum adsorption takes place in the pH range of 5 to 7.5.

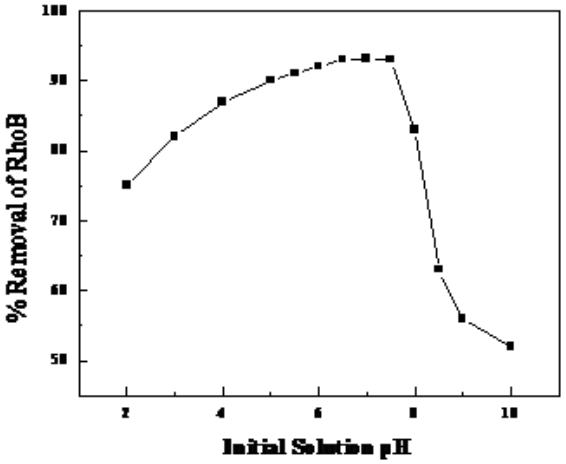

Figure 3. Effect of initial pH for the adsorption of Rhodamine B dye
[RhoB]=50 mg/L; Temp=30°C; Adsorbent dose=25mg/50ml; Contact time=60 minute.

Effect of temperature

The effect of temperature was carried out at four different temperatures such as 30°C, 40°C, 50°C and 60°C in a thermostatic water bath shaker for 60 minutes. Samples were withdrawn at suitable time interval, filtered and the filtrate was analyzed for the remaining dye concentration. Temperature has significant effects on the adsorption capacity, thermodynamic parameter and kinetic process depends on the structure and surface functional groups of an adsorbent.

ADSORPTION ISOTHERMS

The adsorption isotherms shows how the adsorbate molecules are distributed between the adsorbent and solution. The Freundlich and Langmuir isotherm were used to measure the adsorption capacity of the PJBC absorbent for the removal of RhoB dyes.

Langmuir isotherm

The Langmuir [10] isotherm equation can be described by

$$C_e/q_e = \frac{1}{Q_m b} + \frac{C_e}{Q_m} \qquad (4)$$

Where C_e (mg/L) is the equilibrium concentration of the adsorbate, q_e (mg/g) is the amount of adsorbate per unit mass of adsorbent, Q_m and b are Langmuir constants related to adsorption capacity and rate of adsorption respectively. Q_m is the amount of adsorbate at complete monolayer coverage (mg/g) which gives the maximum adsorption capacity of the adsorbent and b (L/mg) is the langmuir isotherm constant that relates to the energy of adsorption (or rate of adsorption). The linear plot of specific adsorption capacity c_e/q_e against the equilibrium concentration (C_e) (figure not given) shows that the adsorption obeys the langmuir model. The Langmuir constant Q_m and b were determined from the slope and intercept of the plot. The equilibrium parameter R_L [11] is used to find out the feasibility of the Langmuir isotherm

$$R_L = \frac{1}{1 + bC_0} \qquad (5)$$

Where C_o (mg/L) is the initial concentration of adsorbate and b (L/mg) is langmuir isotherm constant. The R_L value between $0 < R_L < 1$ is favorable for adsorption.

Freundlich isotherm

The linear form of Freundlich isotherm [12] is represented by the equation

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \qquad (6)$$

Where q_e is the amount of dyes adsorbed per unit weight of the adsorbent, (mg/L), K_f is [mg/g (mg/L) $^{-1/n}$] measure of adsorption capacity and 1/n is the adsorption Intensity. In general if K_f value increases then adsorption capacity for a given adsorbate increases. The magnitude of the exponent 1/n gives an indication of the favorability of adsorption. The value of $n > 1$ represents favorable adsorption condition [13] (or) the values of 1/n are lies in the range of 1 to 10 confirms the favorable condition for adsorption. Freundlich and Langmuir models were used to fit the experimental data and their values were given in the Table 1. The R_L values at different temperature were calculated and given in Table. 2.

Table 1. Adsorption isotherms parameter for the adsorption of RhoB dye

Temp. (^oC)	Langmuir Parameters		Freundlich Parameters	
	Q_m	b	K_f	n
30	433.52	0.0753	58.3042	2.1722
40	443.33	0.0928	62.8876	2.3501
50	612.66	0.0638	54.8782	1.6583
60	472.14	0.0920	61.7108	2.1672

Table 2. Equilibrium parameter (R_L) for the adsorption of RhoB dye

(C_0) mg	Temperature			
	30^{o}C	40^{o}C	50^{o}C	60^{o}C
50	0.2098	0.1772	0.2387	0.1785
100	0.1172	0.0972	0.1355	0.0980
150	0.0813	0.0670	0.0946	0.0675
200	0.0622	0.0511	0.0727	0.0515
250	0.0504	0.0413	0.0590	0.0416

From the table 1 and 2, It was clear that, their Langmuir adsorption capacity (Q_m) non linearly increases with increase in temperature and adsorption intensity (b) also non linearly increases with increase in temperature. These Q_m and b values clearly shows that monolayer adsorption was disturbed by the increase in temperature. The R_L values lies in between 0 and 1 indicates favorable adsorption for all the initial concentration and temperature under investigation.

The Freundlich isotherm parameter indicates that the adsorption capacity non linearly increases with increase temperature and the n value indicates the adsorption is a favorable process. Multilayer adsorption is disturbed above 40^{o}C, but very small difference in energy of adsorption. From these adsorption parameter shows the Langmuir and freundlich adsorption is physical adsorption.

Thermodynamic treatment of the adsorption process

Thermodynamic parameters such as ΔG^0, ΔH^0, ΔS^0 were calculated using the following relation as shown in Table.3.

$$\Delta G^0 = -RT \ln K_0 \quad (7)$$

$$\ln K_0 = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (8)$$

Where $\Delta G^0$is the free energy change of adsorption (KJ/mol), T is the temperature in Kelvin and R is the universal gas constant (8.314 J $mol^{-1}K^{-1}$). ΔH^0 is the standard heat change of adsorption (KJ/mol) and ΔS^0 is standard entropy change (J/mol/K). The equilibrium constant (K_0) for the adsorption's reaction was determined from the slope of the plot of $\ln(q_e/c_e)$ against c_e at different temperature and extrapolating to zero c_e according to the method [14].The value of ΔH^0 and ΔS^0 can be obtained from the slope and intercept of plot of $\ln K_0$ against 1/T.

The thermodynamic study of the adsorption of RhoB using PJBC, all the free energy changes are negative, this indicates the adsorption is a spontaneous process. The free energy increases with increase in temperature, this is due to increase in the active site on the adsorbent. All the ΔH^0 values are negative, this explain adsorption is an exothermic process. All the ΔH^o values are below -17 KJ/mol. This indicates the adsorption is physical adsorption. All the ΔS^0 values are positive, this indicates that there is an increase in the randomness during the adsorption. From the thermodynamic aspect, the adsorption of RhoB using PJBC is physical adsorption.

Table 3. Thermodynamic parameter for the adsorption of RhoB dye

(C_0) mg	ΔG^0 (KJ/mol)				ΔH^0 (KJ/mol)	ΔS^0 (J/mol/K)
	30^{o}C	40^{o}C	50^{o}C	60^{o}C		
50	-6.48	-7.61	-7.61	-7.64	-3.81	34.97
100	-5.66	-6.52	-6.52	-7.93	-16.87	74.23
150	-4.79	-4.93	-4.93	-5.99	-8.13	42.32
200	-3.46	-3.81	-3.81	-4.53	-15.01	61.57
250	-2.51	-2.92	-2.94	-3.80	-15.45	59.62

Adsorption Kinetics

The kinetics of RhoB dye adsorption using PJBC were analyzed using pseudo second order and intraparticle diffusion models.

Pseudo second order

Pseudo second order adsorption kinetic rate equation [15, 16] is

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{1}{q_e} t \qquad (9)$$

Where k_2 is the rate constant of pseudo second order adsorption (g $mg^{-1}min^{-1}$). The q_t (mg/g) and q_e(mg/g) were the amount of adsorption at time "t" and equilibrium. The plot of (t/q_t) against (t) should give a linear relationship from which q_e and k_2 can be determined from the slope and intercept.

Intraparticle diffusion model

The intraparticle diffusion theory proposed by [17] is

$$q_t = k_{id} t^{1/2} + C \qquad (10)$$

Where k_{id} is the intraparticle diffusion rate constant (mg $g^{-1}min^{-1/2}$) and C is constant. If the rate limiting step is intraparticle diffusion, the q_t of adsorbed dye (mg/g) depending on the square root of the contact time ($t^{1/2}$) should yield a straight line passing through the origin. The slope of the plot of q_t against $t^{1/2}$ will give the value of the intraparticle diffusion rate constant (k_{id}) and correlation coefficient (R^2). The conformity of the experimental data were analyzed by using the correlation coefficients (R^2) value. A relatively high R^2 value indicates that the model successfully describes the kinetics of RhoB adsorption.

The adsorption kinetics such as pseudo second order and intraparticle diffusion model were used to fit the experimental data using linear regression analysis method. The parameters of those models were summarized in Table.4. From the kinetic data, the pseudo second order correlation coefficient (R^2) value were almost close to 1. The q_e values calculated from the pseudo second order model were very close to the experimentally calculated q_e value. So the adsorption of RhoB using PJBC follows pseudo second order kinetic model.

In the intraparticle diffusion model correlation coefficient (R^2) values were also almost close to 1 and also give the intercept value. This intercept value indicates that the lines were not passing through origin, therefore some other adsorption process affect the intraparticle diffusion. This was due to the surface adsorption or boundary layer adsorption. Almost all the correlation coefficient (R^2) value were greater than 0.9900. So the intraparticle diffusion takes place along with the boundary layer effect.

Table 4. Adsorption Kinetic parameters for the adsorption of RhoB dye

C_0 mg	Temp (°C)	Pseudo second order			Intraparticle diffusion	
		q_e	$K_2 \times 10^{-3}$	R^2	K_{id}	R^2
50	30	95.51	2.75	0.9981	3.8196	0.8085
	40	98.95	3.56	0.9994	2.6180	0.9968
	50	97.49	4.32	0.9990	2.0710	0.9588
	60	100.59	2.68	0.9989	3.9662	0.7819
100	30	192.01	1.36	0.9998	6.8361	0.9650
	40	193.46	1.60	0.9984	5.3788	0.9830
	50	195.03	1.72	0.9987	5.0687	0.9824
	60	197.56	1.67	0.9990	5.3814	0.9986
150	30	273.69	1.05	0.9981	8.1088	0.9920
	40	272.42	1.26	0.9995	7.4371	0.9942
	50	279.73	1.05	0.9983	8.0941	0.9876
	60	281.13	1.13	0.9987	8.0941	0.9938
200	30	336.42	0.76	0.9976	10.8212	0.9878
	40	343.39	0.73	0.9980	11.5235	0.9976
	50	343.68	0.88	0.9980	9.5606	0.9777
	60	350.12	0.86	0.9982	9.8786	0.9894
250	30	390.70	0.51	0.9927	14.2744	0.8667
	40	396.79	0.68	0.9982	12.4403	0.9964
	50	408.38	0.65	0.9983	13.0622	0.9951
	60	420.89	0.61	0.9979	13.6199	0.9919

CONCLUSIONS

The results of this study shows that the Prosopis Juliflora Bark Carbon can be used for the removal of the dyes Rhodamine B from aqueous solution. The equilibrium data were fitted to the Langmuir and Freundlich models. The thermodynamic

studies indicates that adsorption process is exothermic and physical adsorption. The kinetics of the adsorption process was the best fit with pseudo second order kinetic and intraparticle diffusion model. This adsorption studies shows that Prosopis Juliflora Bark Carbon can be used as an efficient adsorbent for the removal of Rhodamine B dyes from aqueous solution.

REFERENCES

1. Ngah WSW, Ariff NFM, Hanafiah MAKM; Preparation, characterization and environmental application of crosslinked chitosan coated bentonite for tartrazine adsorption from aqueous solutions Water Air Soil and Pollu., 2010; 206: 225- 236.
2. Namasivayam C, Radhika R, Suba S; Uptake of dyes by a promising locally available agricultural solid waste: coir pith. Waste Managet., 2001; 21: 381–387.
3. Chen KC, Wu JY, Huang CC, Liang YM, Hwang SCJ; Decolorization of azo dye using PVA-immobilized microorganisms. J. Biotechnol., 2003; 101: 241–252.
4. Mall ID, Srivastava VC, Agarwal NK; Removal of Orange-G and methyl violet dyes by adsorption onto bagasse fly ash kinetic study and equilibrium isotherm analyses. Dyes Pigments, 2006; 69: 210–223.
5. Hamdaoui O; Batch study of liquid-phase adsorption of methylene blue using cedar sawdust and crushed brick. J. Hazard. Mater. 2006; 135: 264–273.
6. Faria PCC, Orfao JJM, Pereira MFR; Adsorption of anionic and cationic dyes on activated carbons with different surface chemistries. Water Res., 2004; 38: 2043–2052.
7. Nakagawa K, Namba A, Mukai SR, Tamon H, Ariyadejwanich P, Tanthapanichakoon W; Adsorption of phenol and reactive dye from aqueous solution on activated carbons derived from solid wastes, Water Res., 2004; 38: 1791–1798.
8. Sumanjit, Tejinder pal singh walia, Ishu kansal; Removal of Rhodamine-B by Adsorption on Walnut Shell Charcoal. J. Surface Sci. Technol., 2008; 24 (3-4): 179-193.
9. Hameed BH; Removal of cationic dye from aqueous solution using jackfruit peel as non-conventional low-cost adsorbent. J. Hazard. Mater. 2009; 162: 344-350.
10. Langmuir I; The adsorption of gases on plane surfaces of glass mica, and platinum. J. Am. Chem. Soc., 1918; 57: 1361-1403.
11. McKay C, Blair HS, Gardner JR; Adsorption of dyes on chitin.I. Equilibrium Studies. J. Appl. Polymer Sci., 1982; 27: 3043-3057.
12. Freundlich H;Per dye adsorption in losungen (adsorption in solution), Z. Phys. Chem., 1906; 57: 384-470.
13. Hameed BH;A novel agricultural waste adsorbent for the removal of cationic dye from aqueous solution, J. Hazard. Mater. 2009; 162: 305-311.
14. Khan AA, Singh RP;Adsorption thermodynamics of carbofuran on Sn (IV) arsenosilicate in H^+, Na^+ and Ca^{2+} forms. Colloids and Surfaces, 1987; 24: 33-42.
15. Ho YS, McKay G;The kinetic of sorption of divalent metal ions onto sphagnum moss peat, Water Res., 2000; 34: 735-742.
16. Ho YS, McKay G; Sorption of dye from aqueous solution by peat. Chem. Eng. J., 1998; 70: 115-124.
17. Weber WJ, Morris JC; Kinetics of adsorption on carbon from solutions. J.Sanitary Eng. Div., 1964; 90: 79-107.