



## Adsorption of Basic Dye (Rhodamine B) by a Low Cost Activated Carbon from Agricultural Solid Waste: *Leucaena leucocephala* Seed Shell Waste

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### ABSTRACT

The adsorption of Rhodamine B (Basic dye) on *Leucaena leucocephala* seed shell waste carbon was investigated to assess the possible use of this adsorbent for the processing of dyeing industry wastewater. The influence of various factors such as initial dye concentration, agitation time and temperature on the adsorption capacity has been studied. The percentage removal of dye is observed to decrease with the increase in initial dye concentration. With increase in temperature the adsorption of dye also increases, indicating endothermic nature of the reaction. Adsorption isothermal data could be interpreted by the Langmuir and Freundlich equations. Kinetic data have been studied using Elovich and Pseudo-second order equations for understanding the reaction mechanism.

### INTRODUCTION

Discharge of organic pollutants like dyeing industry wastewater into water bodies contaminates the environment. Because of their high water solubility and colour, dyes impart bad taste and odour problems to drinking water supplies even at the parts per million levels. Before discharging dyeing industry wastewater into the natural water streams it needs to be treated. Adsorption can be effective for the treatment for the dyes at the intermediate concentrations. The adsorption process can be pictured as one in which molecules of adsorbate are held on the solid surface of adsorbent by chemical and physical bonding. Activated carbon (granular and powdered form) is the most widely used adsorbent for this process (Dimitrova 2002, Hylander & Siman 2001, Szogi et al. 1997, Cheung et al. 2001). It has good capacity for the adsorption of many organic molecules. In spite of this it suffers from few disadvantages. Activated carbon is quite expensive and its regeneration produces additional effluent and results in considerable loss (10-15%) of the adsorbent. This has led many workers to search for cheaper substitutes. Crab shell (Ann et al. 2001), peanut hull pellets (Brown et al. 2000), Petiolar felt-seath of palm (Iqbal et al. 2002), corn starch (Kweon et al. 2001), soyabean hull and sugar beat fibre (Jambulingam et al. 2005), rice husk (Low & Lee 1997), spent grain (Low et al. 2000), de-oiled soya (Gupta et al. 2005), *Ipomoea carnea* stem (Karthikeyan et al. 2007), *Leucaena leucocephala* shell waste (Karthikeyan et al. 2001), turmeric waste (Karthikeyan et al. 2008), Pomegranate peel (Jambulingam et al. 2007) and sawdust (Marshall & Johns 1996) are some new adsorbents, which have been tried with varying success.

Moreover, the affinity of carbon surface towards solute molecules must be enhanced in order to increase the extent of solute adsorption. From a physical interaction perspective, it is important to

have a good compatibility between the size distributions of activated carbon pores and solution. Comparison of size information available for commercial activated carbon pores and solute molecules in natural waters suggest that some fractions of solute will be able to access finer carbon pores (Namasivayam & Yamuna 1999). Therefore, they will be prevented from fully employing the large surface area (and pore volume) available for adsorption. In the present investigation, the adsorption of Rhodamine B (Basic dye) on to activated carbon prepared from *Leucaena leucocephala* seed shell waste by carbonization with sulphuric acid has been achieved. The kinetic and equilibrium adsorption data obtained were utilized to characterize the sample prepared.

## MATERIALS AND METHODS

**Preparation of adsorbent:** *Leucaena leucocephala* seed shell waste was collected from local area of Erode district, Tamilnadu, India. It was dried, charred with excess quantity of concentrated sulphuric acid keeping at 120°C for 10 hours. Then the resultant carbon was washed with excess quantity of distilled water and dried at 110°C for 1 hour (Murugan & Subramaniam 2003) and the material obtained was soaked in 5% sodium bicarbonate solution and allowed to stand overnight to remove any residual acid. The material was thoroughly washed with hot distilled water until washings were nearly of neutral effect. To eliminate surface groups and thermal activation, the carbonized material was treated at 800°C during 60 min in a furnace under N<sub>2</sub> flow (100cm<sup>3</sup> min<sup>-1</sup>). The resulting carbon was ground in a mill, washed with pure distilled water, and finally dried at 120°C. The dried powder was sieved in the size range from 125-250µm.

The batch adsorption studies were performed at 30°C. 100mg of adsorbent was mixed with known initial concentration (20, 40, 60 mg/L respectively) of Rhodamine B solution and agitated, the adsorbent and the adsorbate were separated by filtration and the filtrate was analysed for residual Rhodamine B concentration spectrophotometrically (using Elico make Bio-UV Spectrophotometer, Model BL-192).

**Characterization of adsorbent:** The N<sub>2</sub> adsorption-desorption isotherms of activated carbon were measured at 77K using a gas sorption analyser (Nova 1000, Quanta Chrome Corporation) in order to determine the surface areas and total pore volume. The surface areas were calculated using the BET equation. In addition, the t-plot method was applied to calculate the micropore volumes and external surface areas (meso porous surface area). The total pore volumes were estimated to be the liquid volume of adsorbate (N<sub>2</sub>) at a relative pressure of 0.99. All the surface areas were calculated from the nitrogen adsorption isotherms by assuming the area of a nitrogen molecule to be 0.162nm<sup>2</sup>.

The electronic structure of carbon samples was examined using FT-IR 1725 × (Perkin-Elmer) spectrometer. The measurements were carried out over the range of 4000-400cm<sup>-1</sup>. Carbon samples (0.33 wt %) were stirred with dry KBr (Merk, spectroscopy grade) and then pressed to form appropriate tablets. The surface morphologies of carbon samples were observed with SEM (HITACHI S3000N).

**Adsorbate:** A stock solution of 100 mg/L of Rhodamine B was prepared by dissolving 1 g of dye in 100mL of double distilled water and used for further studies by diluting as concentrations required. The properties of dye Rhodamine B is presented in Table 1.

Table 1: Properties of Rhodamine B.

Parameters	Value
Suggested Name	Rhodamine B
C.I Number	45170
C.I. Name	Basic violet
Class	Rhodamine
Ionization	Basic
Empirical formula	C <sub>28</sub> H <sub>31</sub> N <sub>2</sub> O <sub>3</sub> Cl
Formula weight	479.029

**Isotherm models:** The study of the Langmuir isotherm is essential in assessing the adsorption efficiency of the adsorbent. This study is also useful in optimizing conditions for effective adsorption. In this respect, the Langmuir isotherm is important, though the restrictions and the limitations of this model have been well recognized (Langmuir 1918).

The Langmuir and the rearranged Langmuir equations are given below.

$$\frac{1}{q_e} = \frac{1}{Q_o b} \cdot \frac{1}{C_e} + \frac{1}{Q_o} \tag{1}$$

$$\frac{C_e}{q_e} = \frac{C_e}{Q_o} + \frac{1}{Q_o b}$$

Where,

$q_e$  = the amount of dye removed at equilibrium, mg/g

$C_e$  = the equilibrium concentration of dye, mg/L

$Q_o$  = the Langmuir constant related to the adsorption capacity, mg/g

$b$  = the Langmuir constant related to the energy of adsorption, L/mg

The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless parameter,  $R_L$ , which is defined by  $R_L = 1/1 + bC_o$ , where  $C_o$  is the initial dye concentration (mg/L) and  $b$  is the Langmuir constant (L/mg). The parameter  $R_L$  indicates the nature of the isotherm as

$R_L$	Type of isotherm
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

The present research works aims at to determining how well the Langmuir model can be applied to the chosen adsorbate-adsorbent system. In addition, it finds out the influence of the temperature of the working solution, particle size of the adsorbent and pH of the working solution, on both the Langmuir constants.

**Freundlich model:** At equilibrium conditions, the adsorbed amount,  $q_e$  can also be predicted by using the Freundlich equation.

$$q_e = k_f C_e^{1/n} \tag{2}$$

Where,

$q_e$  = dye concentration in solid at equilibrium, mg/g

$C_e$  = dye concentration in solution at equilibrium, mg/L

$k_f$  = measure of adsorption capacity

$n$  = adsorption intensity

A logarithmic form of the above equation is:

$$\log q_e = \log k_f + (1/n) \log C_e \tag{3}$$

The values of  $n$  and  $k_f$  were determined from the plot  $\log C_e$  vs  $\log q_e$  for different carbon dosage. Where,  $k_f$  is the indication of the adsorbent capacity and  $1/n$  is a measure of surface heterogeneity, ranging between 0 and 1, becoming more heterogeneous as its value gets closer to zero.

**Kinetic models:** In order to investigate the mechanism of sorption and potential controlling steps such as mass transport, several kinetic models were tested including the Elovich model and the pseudo second order kinetic model for a batch contact time process, where the rate of sorption of dye on to the given adsorbent is proportional to the amount of dye sorbed from the solution phase.

**Elovich model:** The Elovich or Roginsky-Zeldovich equation is generally expressed as follows:

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \quad \dots(4)$$

Where,

$q_t$  = the amount of dye adsorbed mg/g, at time t

$\alpha$  = the initial dye sorption rate, mg/g, min

$\beta$  = the desorption constant, g/mg during any one experiment

To simplify the Elovich equation, Chien & Clayton (1980) assumed  $\alpha\beta t \gg 1$ , and on applying the boundary conditions  $q_t = 0$  at  $t = 0$  and  $q_t = q_t$  at  $t = t$ , equation becomes (Parks 1986):

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad \dots(5)$$

This constant can be obtained from the slope and intercept of linear plot of  $q_t$  versus  $\ln t$ . The equation will be used to test the applicability of the Elovich equation to the kinetics of chosen adsorbent-adsorbate system.

**Pseudo second order model:** To describe dye adsorption the modified pseudo second order kinetic equation is expressed as (Ho & Mcay 2000):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad \dots(6)$$

Where,

$q_e$  = The amount of dye adsorbed at equilibrium, mg/g

$q_t$  = The amount of dye adsorbed at time t, mg/g

$K_2$  = The rate constant for pseudo first orders adsorption, g/mg.min.

$$t/q_t = \frac{t}{k_2 q_e^2} + \frac{1}{q_e} t \quad \dots(7)$$

In the limit  $q_t/t \rightarrow 0$ , the initial sorption rate, h, is given by  $k_2 q_e^2$ , mg/g min.

Plot of  $t/q_t$  versus t of the above equation should give a linear relationship with a slop of  $1/q_e$  and an intercept of  $1/k_2 q_e^2$ .

A relatively high value of the coefficient of determination ( $R^2$ ) was used as criteria for the best fit (Chien & Clayton 1980). The regression coefficient ( $R^2$ ) and standard error of estimate were calculated as follows:

$$R^2 = \frac{\Sigma q^2 - \Sigma(q - q')^2}{\Sigma q^2}$$

Where, q and q' are the measured and calculated amounts of dye adsorbed on chosen adsorbent

respectively.

**Adsorption thermodynamics:** Any chemical system tends to attain a state of equilibrium from one of non-equilibrium. The thermodynamic parameters, which characterize the equilibrium of a system are the Gibbs free energy change  $\Delta G$ , the enthalpy change  $\Delta H$  and the entropy change  $\Delta S$ . These parameters were determined using the following relations (Sumanjit & Prasad 2001, Stephen Inbaraj & Sulochana 2002).

$$K_c = C_{Ae} / C_e$$

$$\Delta G = -RT \ln K_c$$

$$\log K_c = \Delta S / 2.303 R - \Delta H / 2.303 RT \quad \dots(8)$$

Where,  $K_c$  is the equilibrium constant,  $C_{Ae}$  is the solid phase concentration at equilibrium,  $C_e$  is the residual concentration at equilibrium. R is the gas constant (J/mole) and T is the temperature in Kelvin.

## RESULTS AND DISCUSSION

**Surface characters of activated carbon:** The morphological study by SEM of the above adsorbent shown in the Fig. 1 revealed that it is highly porous in nature (Yoshida et al. 1993). From the SEM results, it was found that there are holes and cave type openings on the surface of the specimen that would definitely have increased the surface that are available for the adsorption (Ibrahim et al. 1999). The FT-IR spectrum of the activated *Leucaena leucocephala* seed shell waste carbon shown in Fig. 2 revealed that the carbon contains four classes of surface oxides: carboxyl, lactones, phenols and carbonyls.

The assignment of the specific wave number to a given functional group was not possible because the adsorption bands of various functional groups overlap and shift, depending on their molecular structure and environment.

Shift in absorption position may be caused by factors such as intramolecular and intermolecular hydrogen bonding, steric effect and degree of conjugation. For instance, within its given range, the position of C = O stretching band (common to carbonyls, carboxylic acids and lactones) is determined by many factors such as:

1. The physical state
2. Electronic and mass effects of neighbouring substituents
3. Conjugation
4. Hydrogen bonding
5. Ring strain

The FT-IR absorption bands of oxygen groups on the surface of activated carbon prepared using *Leucaena leucocephala* seed shell waste activated carbon are likely to be affected by some or all of the factors listed above.

The carbon exhibit a very intense/sharp H-bonded-OH stretching of carboxyl, phenol chelated and alcohols vibration from 3600-3000  $\text{cm}^{-1}$  and aliphatic "C-H" stretching absorption from 2750 to 3000  $\text{cm}^{-1}$ . The group of bands appeared in the region 1420 to 1460  $\text{cm}^{-1}$ . The broad band observed in the spectrum of "OH" derivatives between 900 to 1250  $\text{cm}^{-1}$  was assigned due to a characteristic absorption of "-C-OH" group.

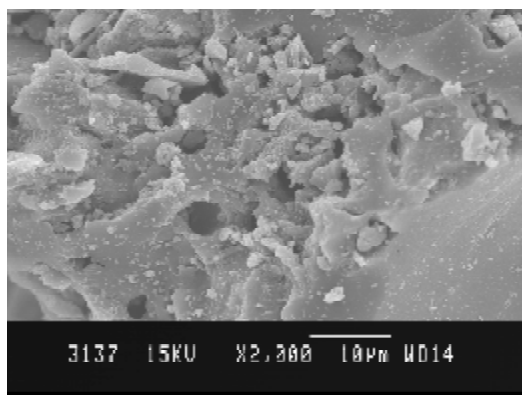


Fig. 1: SEM Image of activated *Leucaena leucocephala* seed shell waste carbon.

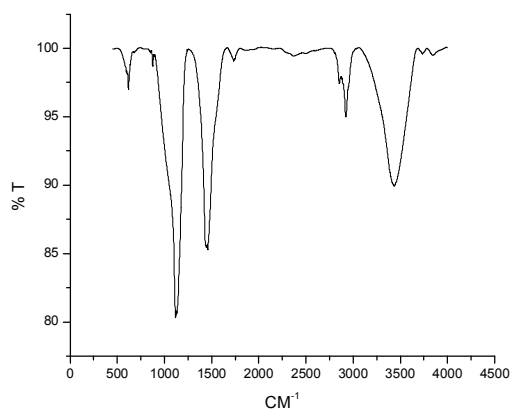


Fig. 2: FT-IR spectrum of *Leucaena leucocephala* seed shell waste activated carbon.

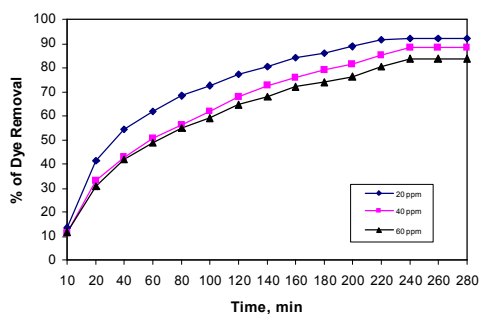


Fig. 3: Effect of agitation time on rhodamine B removal-initial dye concentration variation.

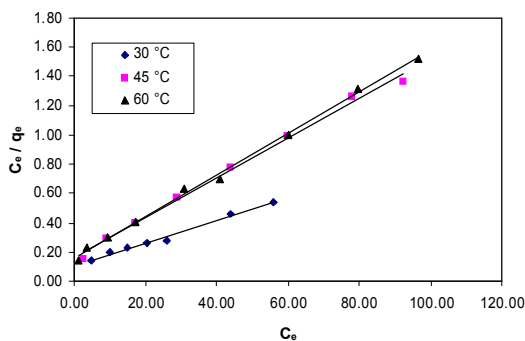


Fig. 4: Langmuir plot-temperature variation.

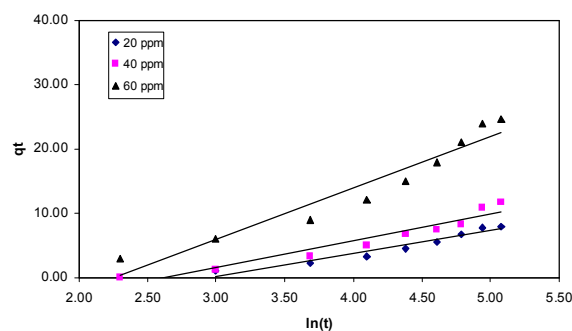


Fig. 5: Freundlich plot-temperature variation.

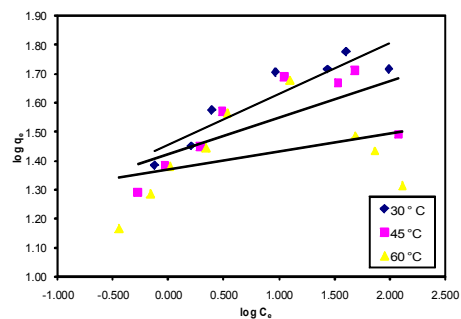


Fig. 6: Elovich plot of rhodamine B removal-initial dye concentration variation.

**Effect of agitation time:** The uptake of Rhodamine B from water by activated *Leucaena leucocephala* seed shell waste carbon increases up to 93.4% when the agitation time was varied from 10 to 160 minutes and attains equilibrium in 240 minutes at 30°C and at pH 7.0, when the initial concentration of the Rhodamine B solution used was 20 mg/L and the adsorbent dosage 100mg. The increase in

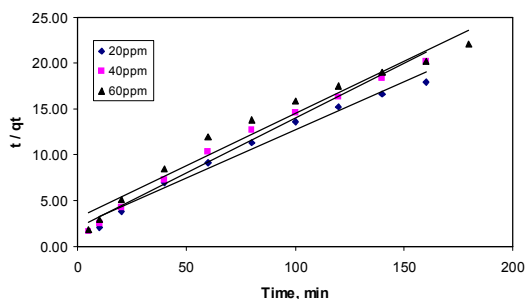


Fig. 7: Pseudo second order plot for rhodamine B removal-initial dye concentration variation.

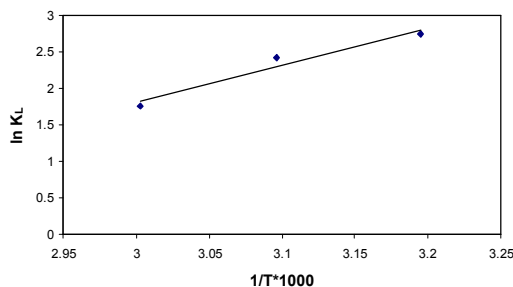


Fig. 8: A plot of temperature Vs  $\ln K_L$ .

adsorption of Rhodamine B with increase in agitation time may be attributed to the increased intra particle diffusion occurring at long shaking time (Fig. 3). A similar result was observed by Rao & Bhole (2001) in the removal of chromium using fly ash and bagasse.

**Effect of initial concentration of Rhodamine B solution:** The initial concentration of Rhodamine B solution was varied (20, 40 and 60mg/L) and batch adsorption experiments were carried out with 100mg of the adsorbent at 30°C and at pH ≈ 7.0. An increased removal of Rhodamine B from 75 to 93.4% was observed with 100 mg of the adsorbent in agitation time of 240 minutes when the initial concentration of the Rhodamine B solution varied from 20, 40, 60, mg/L. The higher uptake of Rhodamine B at low concentration may be attributed to the availability of more active centres on the surface of the adsorbent for lesser number of adsorbate species. Rhodamine B adsorption curves are single, smooth and continuous (Fig. 3) suggesting the possible monolayer coverage of dye molecules on the surface of the adsorbent. Mise & Rajamanya also reported a similar result in the removal of Rhodamine B using activated carbon (Shashikant et al. 2003).

**Isothermal modelling:** The Langmuir adsorption isotherm obtained in 240 minutes of agitation time is shown in the Fig. 4. The values of  $R_L < 1$ , obtained in this study indicates the applicability of Langmuir adsorption isotherm.

Fig. 5 shows that the values of adsorption intensity  $1/n > 1$  reveal that the applicability of Freundlich adsorption is not good when compared to Langmuir adsorption isotherm. The values of  $k_f$  are given in Table 3. The study of temperature effects on the Freundlich parameter reveals decreasing trend in the adsorption capacity with increase in temperature. These data are useful for practical design purposes.

**Kinetic modelling: Elovich model:** The results of the sorption of Rhodamine B on to *Leucaena leucocephala* seed shell waste carbon have been represented in the form of Elovich Equation (Fig. 6) at various initial dye concentrations viz. 20, 40 and 60 mg/L. From the plot, a linear relationship between the amount of Rhodamine B adsorbed,  $q_t$  and  $\ln(t)$  was established.

Table 5 shows the kinetic constants obtained from the Elovich equation. It can be seen from the data that the values of  $\alpha$  and  $\beta$  varied as a function of initial Rhodamine B

Table 2: Values of energy of activation  $E_a$ , entropy of activation  $\Delta S^\ddagger$  and pre-exponential constant  $D_0$  for the present study.

S.No.	Parameter	Value
1.	$D_i, \text{cm}^2\text{s}^{-1}$	
	30°C	$1.3876 \times 10^{-11}$
	45°C	$1.2728 \times 10^{-11}$
	60°C	$1.0341 \times 10^{-11}$
2.	$E_a, \text{KJmol}^{-1}$	-9.5735
3.	$\Delta S^\ddagger, \text{JK}^{-1}\text{mol}^{-1}$	-185.02
4.	$D_0, \text{cm}^2\text{s}^{-1}$	$9.3325 \times 10^{-12}$

concentration. Thus, on increasing the initial concentration of Rhodamine B from 20 mg/L to 60 mg/L, the value of  $\alpha$  increased from 16.86 to 79.14 mg/(g.min) and the  $\beta$  value decreased from 0.319 to 0.105 g/mg. Although the Elovich equation does not provide any mechanistic evidence, it has proved suitable for highly heterogeneous systems of the adsorption of Rhodamine B on to *Leucaena leucocephala* seed shell waste carbon.

**Pseudo second order model:** The same data are shown as pseudo second order equations in Fig. 6 at various initial dye concentrations (20, 40, 60 mg/L). These plots show that the data fit has good correlation coefficients ( $> 0.991$ ) when pseudo second order equation was employed. It was possible to ascertain from them whether the rate determining process is a chemical reaction. As the initial dye concentration increases from 20mg/L to 60 mg/L, the equilibrium sorption capacity  $q_e$ , increased from 13.53 mg/g to 49.48 mg/g. Rhodamine B sorbed at any contact time increases.

The corresponding linear plots of the values of  $q_e$ ,  $k_2$  and  $h$  against  $C_0$  were regressed to obtain the expressions for these values in terms of the initial Rhodamine B concentration,  $C_0$ , with high correlation coefficients ( $> 0.992$ ). Hence, it was further considered that  $q_e$ ,  $k_2$  and  $h$  could be expressed as functions of  $C_0$  as follows:

$$q_e = \frac{C_0}{1.010C_0 - 20.85} \quad \dots(9)$$

$$k_2 = \frac{C_0}{109.4C_0 - 1.616 \times 10^4} \quad \dots(10)$$

$$h = \frac{C_0}{0.6113C_0 - 11.19} \quad \dots(11)$$

Substituting the values of  $q_e$ ,  $k_2$  and  $h$  from equations (9) and (11) into equations (7), the rate law for a pseudo-second order reaction and the relationship of  $q_t$ ,  $C_0$  and  $t$  can be represented as:

$$q_t = \frac{C_0 t}{(0.6113C_0 - 11.19) + (1.010C_0 - 20.85)t} \quad \dots(12)$$

Equation (12) represents the generalized productive model for Rhodamine B adsorption at any contact time and initial concentration within the specified concentration range. It indicates that the amount of Rhodamine B at any contact time increased with increasing the initial dye concentration. This is obvious for higher initial concentration values, as a more efficient utilization of the sportive capacities of the sorbent would be expected due to greater sorption driving force. This equation can then be used to derive the amount of Rhodamine B sorbed at any given initial dye concentration and reaction time.

The mathematical treatment as suggested by Boyd et al. (1947) was used to identify whether the ongoing process is particle diffusion or film diffusion. These mathematical models also helped in

Table 3: Some selected properties of activated *Leucaena leucocephala* seed shell waste carbon.

S. No	Properties	Value
1	BET Surface area, m <sup>2</sup> /g	499.23
2	S <sub>EXT</sub> , m <sup>2</sup> /g	328.06
3	V <sub>micro</sub> , cm <sup>3</sup> /g	138.77
4	S <sub>micro</sub> , m <sup>2</sup> /g	0.04
5	V <sub>tot</sub> , cm <sup>3</sup> /g	96.58
6	Porosity, $\zeta$ p	49.08
7	Bulk density, g/cm <sup>3</sup>	0.19
8	Moisture content, %	29.09
9	Iodine Number	299.23



Table 4: Parameters of Langmuir and Freundlich adsorption isotherms for the adsorption of Rhodamine B.

Temperature, °C	Langmuir Isotherm		Freundlich Isotherm		
	b	Q <sub>0</sub>	1/n	n	k <sub>f</sub>
30	0.2013	105.26	0.3889	2.571	26.06
45	0.3257	113.64	0.3308	3.023	34.99
60	0.4682	123.46	0.3008	3.324	44.93

Table 5: Kinetic model values for the adsorption of Rhodamine B.

Concentration, ppm	Elovich Values			Pseudo second order values			
	α	β	r <sup>2</sup>	q <sub>e</sub>	K <sub>2</sub> × 10 <sup>3</sup>	h	R <sup>2</sup>
30	16.86	0.319	0.920	13.53	0.1520	0.278	0.902
40	41.40	0.159	0.912	28.49	0.0048	0.395	0.899
60	79.14	0.105	0.854	49.48	0.0019	0.480	0.862

determining the mechanism of the undergoing process. An established fact is that when a solid chemical substance adsorbs over the porous adsorbent, three types of diffusion processes take place in following three consecutive steps:

- i. Transport of the ingoing adsorbate ions to external surface of the adsorbent (film diffusion).
- ii. Transport of the adsorbate ions within the pores of the adsorbent except for a small amount of adsorption, which occurs on the external surface (particle diffusion).
- iii. Adsorption of the ingoing adsorbate ions on the interior surface of the adsorbent.

The third step is very fast and can not be considered as a rate-determining step, while for the adsorption carrying out via remaining two steps, the following three possibilities exist.

Case 1: External transport > internal transport, where rate is governed by particle diffusion.

Case 2: External transport < internal transport, where the rate is governed by film diffusion.

Case 3: External transport near to the internal transport, which accounts for the transport of the adsorbate ions to the boundary and may not be possible within a significant rate, which later on gives rise to the formation of a liquid film surrounded by the adsorbent particles with a proper concentration gradient.

To investigate the actual process involved in the present adsorption, the quantitative treatment of the sorption dynamics was as described by the following equation:

$$F = 1 - \frac{6}{\pi^2} \sum_{N=1}^{\infty} \frac{1}{n^2} \exp\left[-\frac{Dit\pi^2 n^2}{r^2}\right] \quad \dots(13)$$

$$F = 1 - \frac{6}{\pi^2} \sum_{N=1}^{\infty} \frac{1}{n^2} \exp[-n^2 \beta_i] \quad \dots(14)$$

Where F is the fractional attainment of equilibrium at time t and is obtained by using following equation, and n is the adsorption intensity of the adsorbate.

$$F = \frac{q_t}{q_e}$$

Where,  $q_t$  and  $q_e$  are the amounts adsorbed at time  $t$  and at equilibrium respectively.

On the basis of  $F$  values, corresponding values of  $B_t$  were obtained from Reichenberg's table (Reichenberg 1953) and the linearity test was carried out by plotting  $B_t$  with respect to time for both the solutions at different time intervals and at 30, 45 and 60°C. The linearity test of  $B_t$  versus time plot drawn for different concentrations is employed to distinguish between film diffusion and particle diffusion. From the slope of the straight line obtained from time versus  $B_t$  graph, the  $B$  value (time constant) were calculated. The values of effective diffusion coefficient ( $D_i$ ) were calculated at different temperatures using the following Equation.

$$B = \pi^2 D_i / r^2$$

Here, 'r' is the radius of the adsorbent particle. The  $D_i$  values are given in the Table 2.

The plot of  $1/T$  versus  $\log D_i$  was found linear with negative slope indicating the increase in the mobility of ions. This is due to the fact that with the rise in temperature the mobility of ions increases, which consequently decreases the retarding force acting on the diffusing ions.

The values of energy of activation  $E_a$ , entropy of activation  $\Delta S^\#$  and pre-exponential constant  $D_o$  were calculated using following equations.

$$D_i = D_o \exp [-E_a/RT] \quad \dots(15)$$

$$D_o = (2.72 d^2 kT/h) \cdot \exp [\Delta S^\#/R] \quad \dots(16)$$

where  $d$  is the average distance between the successive exchange sites and is taken as  $5A^\circ$ .  $R$ ,  $h$  and  $k$  are the Gas, Plank, and Boltzmann constants, respectively. The values of  $E_a$ ,  $D_i$ ,  $D_o$ ,  $\Delta S^\#$  and other parameters are given in Table 2. The negative values of  $\Delta S^\#$  reflect that no significant change occurs in the internal structure of chosen adsorbent during the adsorption process.

**Thermodynamic parameters:**  $\Delta H$  and  $\Delta S$  were obtained from the slope and intercept of Vent Hoff plot ( $1/T$  vs  $\log K_c$ ) as given in Fig. 8. Batch adsorption studies were carried out with Rhodamine B solution at  $pH \approx 7.0$  by varying the temperature (303 K, 318 K and 333 K). The initial concentration of Rhodamine B solution used was maintained to be 20 mg/L with 100 mg of the adsorbent. The free energy changes  $\Delta G$  (vary with temperature from -1918.88 to -4054.40 (KJ/mole) at 30 to 60 °C. The negative  $\Delta G$  value suggests the adsorption of Rhodamine B is spontaneous. Such negative values in all the temperatures under study suggest that the adsorption is more spontaneous. The enthalpy change  $\Delta H$  for adsorption of a standard adsorption process shows +ve values suggesting that the adsorption is an endothermic process (Shashikant et al. 2003). Enthalpy change,  $\Delta S$  was found to be 3.2550 J/K/mole, which suggests the randomness in the adsorption of Rhodamine B (Gupta et al. 1999) on the chosen adsorbent. Further investigations on a more detailed analysis of the presentation of carbons by different methods and their applications to the removal of heavy metals and pesticides are in progress.

## CONCLUSION

In the present study adsorption of Rhodamine B on activated *Leucaena leucocephala* seed shell waste carbon has been investigated. The data obtained through this work support that the *Leucaena leucocephala* carbon is an effective low cost adsorbent for the removal of Rhodamine B from

aqueous solution. The adsorption of Rhodamine B is dependent on the initial concentration and agitation time. Equilibrium of Rhodamine B adsorption reaches at 240 min. The values of  $R_L < 1$ , obtained in this study indicates the applicability of Langmuir adsorption isotherm. The study of temperature effects on the Freundlich parameters reveals that decreasing trend in the adsorption capacity with increase in temperature. These data are useful for practical design purposes.

The Elovich and pseudo-second order equations provided a best fit description for the sorption of Rhodamine B onto *Leucaena leucocephala* seed shell waste carbon, but the pseudo-second order equation had better correlation coefficient value than Elovich equation. Therefore, pseudo-second order was considered the most appropriate due to high correlation coefficient when compared to Elovich equation. The adsorption of Rhodamine B onto activated *Leucaena leucocephala* seed shell waste carbon is an endothermic reaction based on enthalpy change values.

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