



Research Article

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## Equilibrium Isotherm, Kinetic and Thermodynamic studies of Rhodamine B Adsorption using *Thespesia populnea* Bark

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### ABSTRACT

The adsorption of Rhodamine B from aqueous solution by *Thespesia Populnea* Bark (TPC) as activated carbon are studied through Langmuir Freundlich, effect of pH and kinetic models, the experimental data's are fitted to the Langmuir and Freundlich isotherm. Gibbs free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) are calculated for thermodynamic parameters. The effect of temperature variation study proved that the Rhodamine B dye absorption was endothermic and spontaneous.

**Key words:** Rhodamine B, Adsorption Isotherm, Activated Carbon, Thermodynamic Parameters, Equilibrium and Kinetics.

### Abbreviation

*Thespesia Populnea* Bark Carbon (TPC)  
Adsorption efficiency ( $Q_m$ )  
Adsorption energy ( $b$ )  
Adsorption capacity ( $K_f$ )

### INTRODUCTION

Dye contaminated waste water originates from various industries such as lather, textile, printing food and paper industry. Can provoke serious environmental impact in the neighboring water bodies because of the presence of toxic dyes. Dyes and pigments, if not properly treated, can also have detrimental effects on human health. Therefore these coloured contaminants must be removed from waste water from industries.

Adsorption is very important process due to its technological, environmental and biological importance. Furthermore the practical applications of adsorption process in industry and environmental protection are important. Adsorption is a method for separation of mixtures that based on the change in concentration of components at the interface. The development of adsorption at surface science is considered as physical science that representing an interdisciplinary area between chemistry, physics, biology and engineering. The practical applications of adsorption can be at separation and purification of liquid and gas mixtures, bulk chemicals, drying gases and liquids before loading them into industrial systems, removal of impurities from liquid and gas media, recovery of chemicals from industrial and vent gases and water purification. Activated carbon is the most widespread uses of for liquid-phase adsorption in water treatment and has increased throughout the world[1,2] Adsorption is a suitable technique for the removal dye from waste water and aqueous solutions. In this study, the effect of some operational parameters such as initial dye concentration, effect of pH, adsorbent dose and temperature on the adsorptive capacity of the TPC. The equilibrium, kinetic and thermodynamic data of the adsorption process were then studied to understand the adsorption mechanism of Rhodamine B molecules on TPC. The objective of the study is find out the ability of TPC in absorbing dyes from their aqueous solution. Data obtained can be use as a basic consideration in treating waste water contaminated by dyes.

## EXPERIMENTAL SECTION

### Adsorption Experiments

#### Batch equilibrium method

The experiments were done in a batch process at 30, 40, 50 and 60°C. the known weight of activated carbon was added to 50 ml of the dye solutions with an initial concentration of 10mg/L to 50 mg/L, which is produced from 1000 mg/ L of Rhodamine B stock solution. The structure of Rhodamine B is given in the following Figure 1. The contents were carefully shaken using a mechanical shaker with a speed of 120 rpm. The residual solution was then filtered at preset time intervals and the concentration of the filtrate has been measured. The effect of variable parameters like initial concentration, adsorbent dose, contact time, initial pH, chloride ion, and temperature were studied thoroughly and reported in the results and discussion part. The physical properties of the prepared activated carbon were studied by standard procedures. The zero point charge and the surface functional groups of the activated carbon were studied by the following methods.

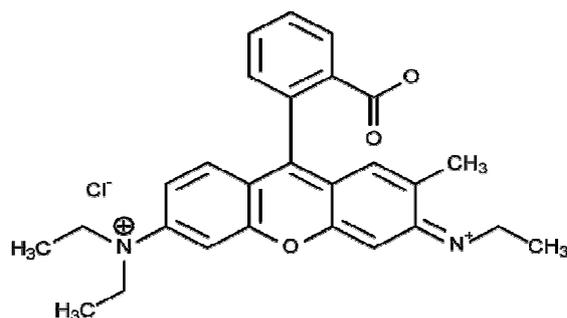


Fig (1) Structure of Rhodamine B

#### Drift method

The zero point charge of the carbon ( $pH_{zpc}$ ) was measured using the pH drift method[3]. The pH of the solution was adjusted by using 0.01M. sodium hydroxide or hydrochloric acid. Nitrogen was bubbled through the solution at 25°C to remove the dissolved carbon dioxide. 25 mg of the activated carbon was added to 50 ml of the solution. After stabilization, the final pH was recorded. The graphs of final pH versus initial pH were used to determine the zero point charge of the activated carbon.

## RESULTS AND DISCUSSION

### Characteristics of the adsorbent

Characteristics of the adsorbent studied from standard procedures drift method, and titration studies are given in table in Table1.

Table 1-Characteristics of the Adsorbent

Properties	TPC
Particle size(mm)	0.041
Density (g/cc)	0.3243
Moisture content (%)	0.32550
Loss in ignition (%)	0.273
pH of aqueous solution	6.5

Table 2 – Equilibrium parameters for the adsorption of Dye onto activated carbon

[RDB]	$C_e$ (mg/L)				$Q_e$ (mg/g)				Dye removed (%)			
	Temperature ° C											
	30	40	50	60	30	40	50	60	30	40	50	60
10	0.941	0.640	0.450	0.301	18.11	18.71	19.09	19.39	90.58	93.59	95.49	96.98
20	2.754	2.516	2.309	2.115	34.49	34.96	35.38	35.76	86.22	87.41	88.45	89.42
30	5.241	5.001	4.801	4.601	49.51	49.99	50.39	50.79	82.52	83.32	83.99	84.66
40	8.581	8.014	7.517	7.018	62.83	63.97	64.96	65.96	78.54	79.96	81.20	82.45
50	12.40	11.516	10.61	9.795	75.18	76.96	78.76	80.41	75.18	76.96	78.76	80.41

### Effect of Carbon Dosage and Initial Concentration

The absorption of the Rhodamine B dye on carbon has been studied by varying the carbon dose (10-50 mg/ 50 ml) for 100 mg / litre of dye concentration. As shown in Fig.(3), the percentage of adsorption increased with the increase in the carbon concentration. This was attributed to increased carbon surface area and the availability of more

adsorption sites[4]. Hence all studies were carried out with 0.025mg of adsorbent / 50 ml of the changing adsorbate solutions of 10, 20, 30, 40 and 50. As a result, the amount of MG dye adsorbed per gram reduced with increase in the dosage of TPC is shown in Fig. (3). This reveals that the direct and equilibrium capacities of MG are functions of the TPC activated carbon dosage. The equilibrium values obtained from the studies are tabulated in Table.2.

#### Effect of contact time

It is found that the effect of contact time on the amount of dye adsorbed was investigated at 100 mg/L concentration of the dye as shown in Fig.4. It is observed that the percentage removal of dye increases rapidly with an rise in contact time initially, and thereafter, beyond a contact time of about 50 min, no noticeable change in the percentage removal is observed the percentage removals after 50 min were 85%.Therefore, the optimum contact time is considered to be 50 min. this is also the equilibrium time of the batch adsorption experiments, since beyond a contact time of 50 min, adsorption is not changed. The rapid the removal of dye is observed at the beginning of the contact time due to the percentage of large number of binding sites available for adsorption[5].

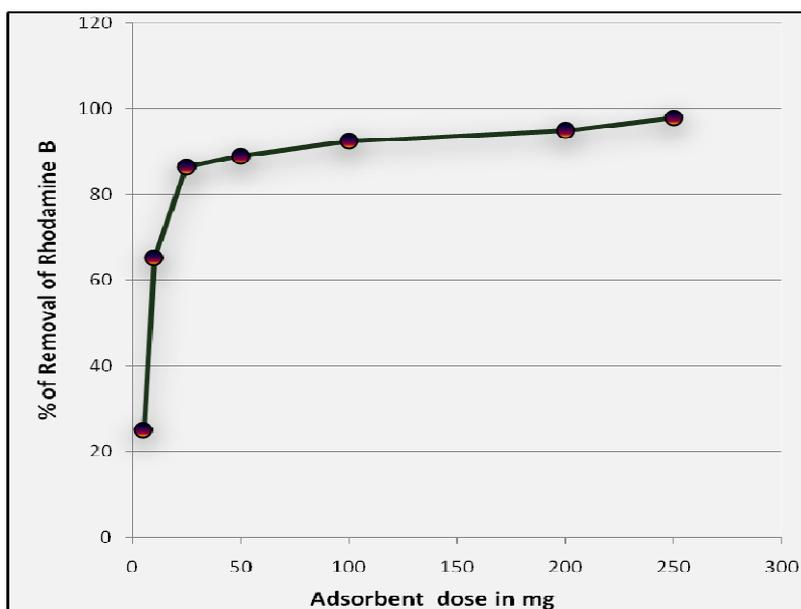


Fig. 3- Effect of adsorbent dose on the adsorption of Rhodamine B onto TPC  
[Rhodamine B]= 100mg/L: contact time = 60min: pH=6.5

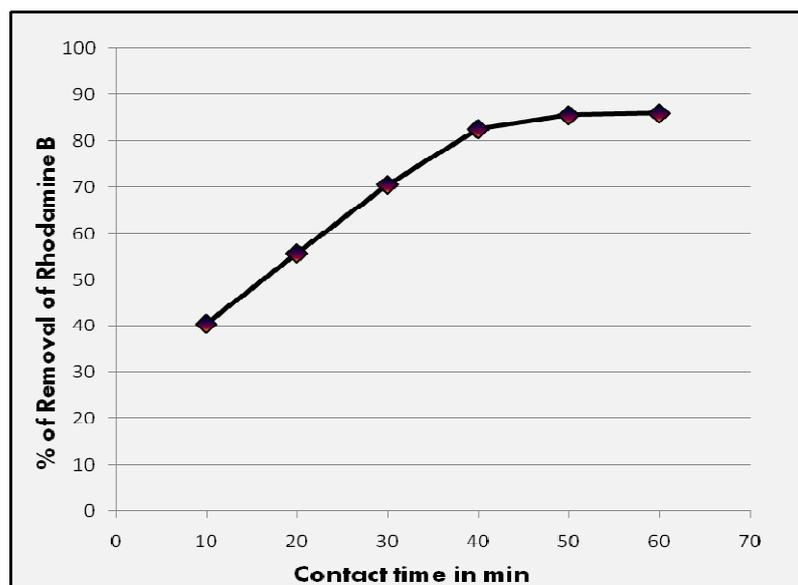


Fig. 4- Effect of Contact time on the adsorption of Rhodamine B onto TPC  
[Rhodamine B]= 100mg/L: Adsorbent dose = 25mg/ 50ml: pH=6.5

**Adsorption isotherms**

Adsorption isotherm describes how pollutants interact with adsorbent materials with relate to adsorption properties and equilibrium data. The experimental data indicated that the adsorption isotherms are well described by the Langmuir and Freundlich isotherm[6].

**Langmuir isotherm**

Langmuir sorption isotherm is well known of all isotherms describing sorption[7] and it has been applied in many sorption processes[8]. It is represented as:

$$C_{eq}/Q_{eq} = 1/Q_m b + C_{eq}/Q_m \quad (1)$$

Where  $C_{eq}$  is the equilibrium concentration of adsorbate in the solution (mg/L),  $Q_{eq}$  is the amount adsorbed at equilibrium (mg/g),  $Q_m$  and  $b$  are Langmuir constants related to adsorption efficiency and energy of adsorption, respectively. The linear plots of  $C_{eq}/Q_{eq}$  vs.  $C_{eq}$  suggest the applicability of the Langmuir isotherms Fig. (5). The values of  $Q_m$  and  $b$  were calculated from slope and intercepts of the plots, which are listed 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. The values can conclude that the maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on adsorbent surface with constant energy and no diffusion of adsorbate in plane of the adsorbent surface. To confirm the favourability of the adsorption process, the separation factor ( $R_L$ ) was determined and given in Table 3. The values were established to be between 0 and 1 and confirm that the ongoing adsorption process is favourable[9].

**Freundlich isotherm**

The Freundlich equation was employed for the adsorption of Rhodamine B dye on the adsorbent. The logarithmic form of Freundlich equation is represented as given in the following equation.

$$\log Q_e = \log K_f + 1/n \log C_e \quad (2)$$

Where  $Q_e$  is the amount of Rhodamine B dye adsorbed (mg/g),  $C_e$  is the equilibrium concentration of dye in solution (mg/L), and  $K_f$  and  $n$  are constants which integrate the factors affecting the adsorption capacity and intensity of adsorption, respectively. Linear plots of  $\log Q_{eq}$  versus  $\log C_{eq}$  shows that the adsorption of Rhodamine B obeys the Freundlich adsorption isotherm, which is given in Figure 6. The  $K_f$  and  $n$  values are given in Table 3 indicate that the increase of negative charges on the adsorbent surface makes electrostatic force like Vanderwaal's between the carbon surface and dye ion. The molecular weight and size 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 indication of the bond energies between dye and adsorbent, and the possibility of slight chemisorptions rather than physisorption[10, 11]. However, the multilayer adsorption of Rhodamine B dye through the percolation process may be possible. The values of  $n$  are less than one, indicating the physisorption is much more favourable.

**Table.3 Langmuir Isotherm, Freundlich Isotherm results and Dimensionless separation factor ( $R_L$ )**

[RDB]	Temperature C°	Langmuir Isotherm Results			Freundlich Isotherm Results			Dimensionless Separation Factor( $R_L$ )				
		Statistical parameters/constants			Statistical parameters/constants			[RDB] <sub>e</sub> ( mg/L)				
		$r^2$	$Q_m$	$b$	$r^2$	$K_f$	$n$	10	20	30	40	50
	30	0.9874	103.09	0.1945	0.9114	3.608	1.807	0.339	0.204	0.146	0.113	0.093
	40	0.9884	98.03	0.2557	0.9145	3.895	2.039	0.281	0.163	0.115	0.089	0.072
	50	0.9869	96.15	0.3125	0.9151	4.124	2.248	0.242	0.137	0.096	0.074	0.060
	60	0.9854	93.45	0.3846	0.9123	4.349	2.501	0.206	0.115	0.079	0.061	0.049

**Effect of temperature**

The effect of temperature was studied in the range of 30 to 60°C by keeping the rest parameters such as adsorbate concentration at 100mg/ L<sup>-1</sup>, the pH at 6.5 and the adsorbent concentration at 25 mg in 50 ml.

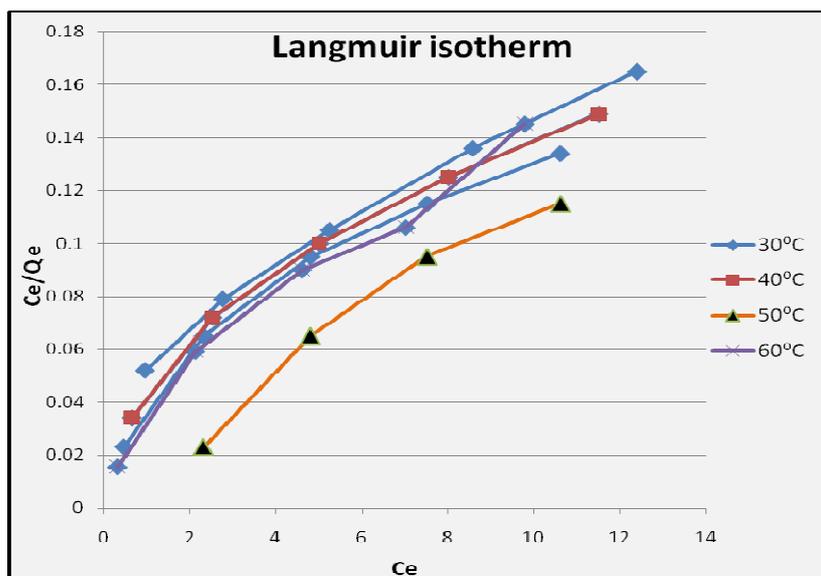


Fig. 5- Langmuir Isotherm for the adsorption of Rhodamine B onto TPC

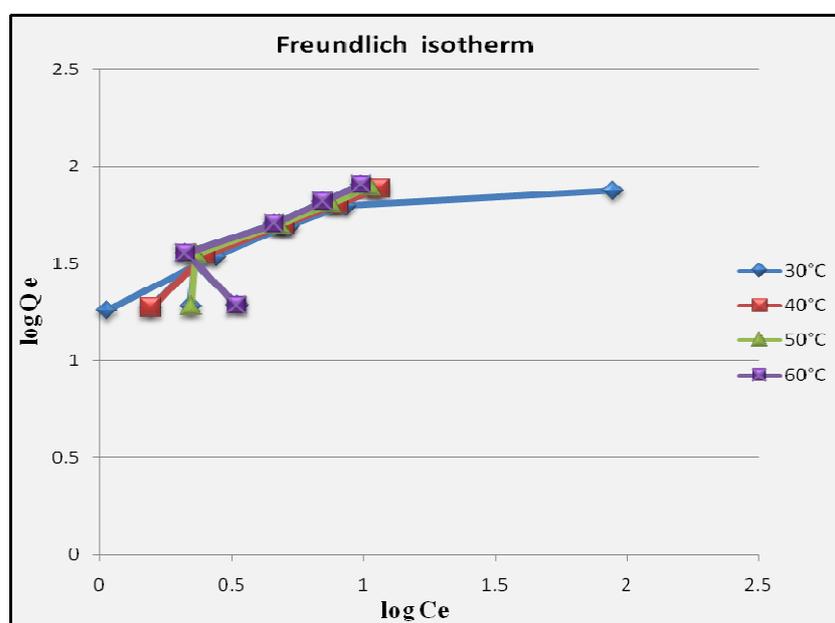


Fig 6- Freundlich Isotherm for the adsorption of Rhodamine B onto TPC

Adsorption capacity of the carbon increased with increase of the temperature in the system from 30°C to 60°C. Thermodynamic parameters such as change in free energy ( $\Delta G^\circ$ ) (kJ/mol), enthalpy ( $\Delta H^\circ$ ) (kJ/mol) and entropy ( $\Delta S^\circ$ ) (J/K/mol) were determined using the following equations

$$K_0 = C_{\text{solid}}/C_{\text{liquid}}$$

$$\Delta G^\circ = -RT \ln K_0$$

$$\log K_0 = \Delta S^\circ / (2.303R) - \Delta H^\circ / (2.303RT)$$

Where  $K_0$  is the equilibrium constant,  $C_{\text{solid}}$  is the solid phase concentration at equilibrium (mg/L),  $C_{\text{liquid}}$  is the liquid phase concentration at equilibrium (mg/L),  $T$  is the temperature in Kelvin, and  $R$  is the gas constant. The  $\Delta H^\circ$  and  $\Delta S^\circ$  values obtained from the slope and intercept of Van't Hoff plots has been given in Table 4. The values of  $\Delta H^\circ$  is the range of 1 to 93 kJ/mol shows the physisorption. It is found that from results that physisorption is highly favourable for the adsorption of Rhodamine B.

The positive values of  $\Delta H^\circ$  indicate the endothermic nature of adsorption which governs the possibility of physical adsorption[6,10 and 11]. Because in the case of physical adsorption, while increasing the temperature of the system, the extent of dye adsorption increases, there is no possibility of chemisorption.

The negative values of  $\Delta G^\circ$  (Table4) indicate that the adsorption is highly favourable and spontaneous. The positive values of  $\Delta S^\circ$  (Table4) show the increased disorder and randomness at the solid solution interface of malachite green with TPC adsorbent.

Table 4 – Equilibrium constant and thermodynamic parameters for the adsorption of Rhodamine B onto activated carbon

[RDB]	$\Delta H^\circ$	$\Delta S^\circ$	$K_d$				$\Delta G^\circ$			
			Temperature							
			30°	40°	50°	60°	30°	40°	50°	60°
10	33.47	129.2	9.621	14.62	21.19	32.16	-5703.2	-6980.3	-8200.9	-9609.5
20	8.373	42.87	6.260	6.948	7.661	8.453	-4620.9	-5044.5	-5467.9	-5909.7
30	4.330	27.20	4.723	4.998	5.248	5.520	-3911.1	-4187.4	-4452.0	-4729.7
40	6.944	33.69	3.661	3.990	4.320	4.699	-3269.3	-3601.5	-3929.9	-4284.0
50	8.502	37.24	3.030	3.341	3.708	4.104	-2792.9	-3139.5	-3519.6	-3909.5

### Effect of pH

The pH level of the aqueous solution is an important variable for the adsorption of dyes on the adsorbent. The solution of pH has been controlled by the addition of HCl or NaOH. The influences of pH on the adsorption of Rhodamine B onto modified activated carbon are shown in Figure 7.

The uptake of Rhodamine B dye has been minimum at pH 3 and maximum at pH 6.5. However, when the pH of the solution increased (more than pH 7), the uptake of Rhodamine B ions also increased; It appears that a change in pH of the solution results in the formation of different ionic species, and a different carbon surface charge. When the pH value is lower than 6.5, the Rhodamine B dyes are able to enter into the pore structure. As the pH value increased to above 7, the zwitter ions form of Rhodamine B in water may raise the aggregation of Rhodamine B to form a bigger molecular form (dimer) and become unable to enter into the pore structure of the carbon surface.

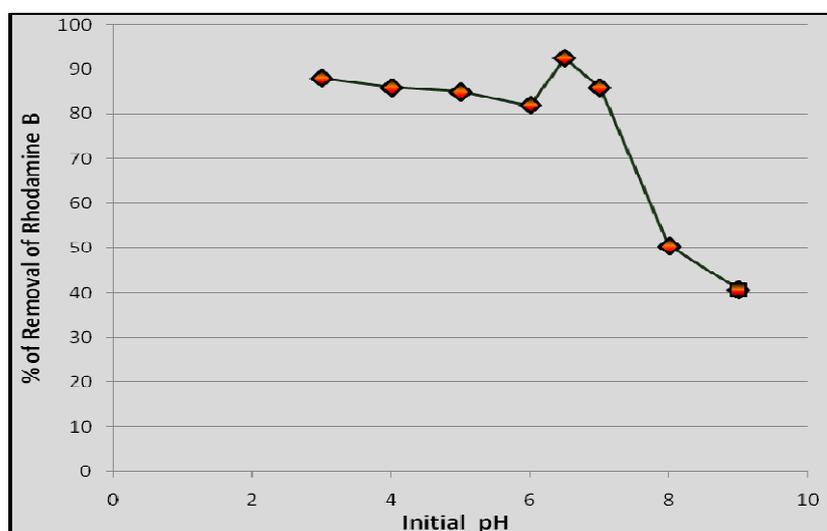


Fig. 7- Effect of pH on the adsorption of Rhodamine B onto TPC

[MG]= 100mg/L: adsorbent dose  
= 25 mg / 50ml: contact time = 60min

The greater aggregation of the zwitter ionic form is due to the attractive electrostatic interaction between the ionic groups of the monomer. When the pH value is more than 9, the existence of TPC surface creates a competition between ionic dyes and decreases the aggregation of Rhodamine B. It also causes an increase in the adsorption of Rhodamine B ions on the carbon surface. The effect of the charge on the carbon surface, and the electrostatic force of attraction and repulsion between the carbon surface and the malachite green ions, cannot explain the outcome[11, 12].

### Effect of the Ionic Strength

The effect of sodium chloride on the adsorption of Rhodamine B on TPC is shown in Figure 8. The low concentrate NaCl solution had little influence on the adsorption capacity. When the concentration of NaCl increases, the ionic strength also increases. At higher ionic strength, the adsorption of Rhodamine B will be increased to the partial neutralization of the positive charge on the carbon surface and a consequent compression of the electrical double layer by the Cl<sup>-</sup> anion. The chloride ion also enhances adsorption of Rhodamine B dye ion by pairing their charges, and hence reducing the repulsion between the Rhodamine B dyes adsorbed on the surface. This initiates carbon to adsorb more positive Rhodamine B dye ions [13].

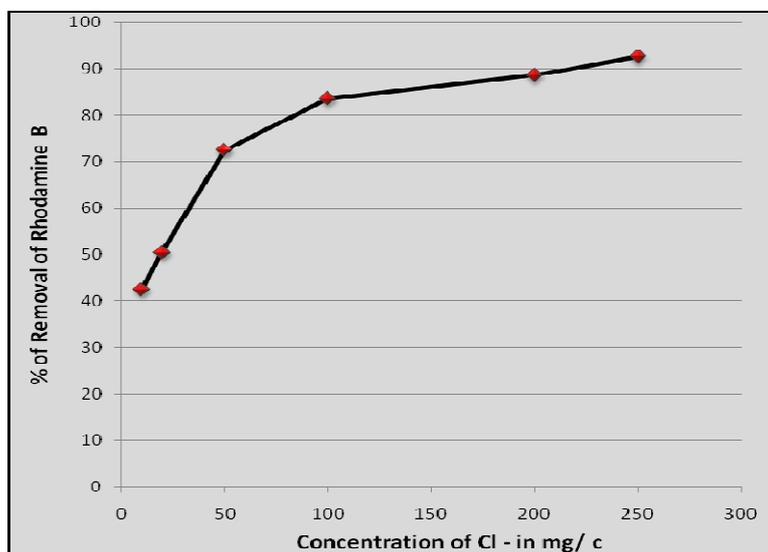
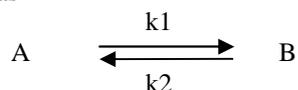


Fig. 8- Effect of other ions on the removal of Rhodamine B dyes

[MG]= 100mg/L: adsorbent dose  
= 25 mg / 50ml: contact time = 60min

### Adsorption Kinetics

There are essentially three steps in the adsorption process by porous adsorbents [14]. 1. solute transfer from the bulk solution to the external surface of the sorbent through liquid boundary layer (film resistance); 2. solute transfer from the sorbent surface the intraparticle active sites (internal particle resistance); and 3. interaction of the solute with available sites on both the external and internal surface of the adsorbent (reaction resistance). One or more of the above mentioned steps may control the rate at which the solute is adsorbed on to the adsorbent. In this study, the kinetic of the dye removal were carried out to understand behavior of the chosen carbon. The adsorption of the Rhodamine B dye from an aqueous solution follows reversible first order kinetics, when a single species is considered on a heterogeneous surface. The heterogeneous equilibrium between the dye solution and the activated carbon have been expressed as



Where  $k_1$  is the forward rate constant and  $k_2$  is the backward rate constant.  $A$  represents the dye remaining in the aqueous solution and  $B$  represents the dyes adsorbed on the surface of the activated carbon. The equilibrium constant ( $K_0$ ) is the ratio of the concentration adsorbate in adsorbent in aqueous solution ( $K_0 = k_1/k_2$ ).

The kinetic study of the adsorption process, the following kinetic equation proposed by Natarajan and Khalaf, as cited in literature, were employed.

$$\log C_0/C_t = (K_{ad}/2.303)t$$

Where  $C_0$  and  $C_t$  are the concentration of the dye (in mg/L) at the time of zero and time  $t$  respectively. The rate constants ( $K_{ad}$ ) for the adsorption processes are 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 evaluated in literature is given by the following equation

$$K_{ad} = k_1 + k_2 = k_1 + (k_1/K_0) = k_1 [1 + 1/K_0]$$

The overall rate constant  $k_{ad}$  for the adsorption of dye at different temperatures is calculated from the slopes of the linear Natarajan-Khalaf plots. The rate constant values are given in Table 5 show that the rate constant ( $k_{ad}$ ) increases with increase in temperature, suggesting that the adsorption process is endothermic in nature. The rate constants for the forward and reverse processes collected in Table 5 shows that the forward rate constant is much higher than the reverse rate constant at all initial concentrations and temperatures, suggesting that the rate of adsorption is clearly dominant[15].

**Table 5- Rate constants for the adsorption of Rhodamine B dyes ( $k_{ad}$ ,  $\text{min}^{-1}$ ) and the constants for forward ( $k_1$ ,  $\text{min}^{-1}$ ) and reverse ( $k_2$ ,  $\text{min}^{-1}$ ) process.**

[RDB]	Temperature (C)											
	$k_{ad}$				$k_1$	$k_2$	$k_1$	$k_2$	$k_1$	$k_2$	$k_1$	$k_2$
	30°	40°	50°	60°	30°	40°	50°	60°	30°	40°	50°	60°
10	0.032	0.040	0.043	0.059	0.029	0.003	0.037	0.002	0.041	0.001	0.057	0.001
20	0.024	0.026	0.028	0.032	0.021	0.003	0.022	0.003	0.024	0.003	0.029	0.003
30	0.020	0.018	0.022	0.022	0.016	0.003	0.015	0.003	0.018	0.003	0.019	0.003
40	0.017	0.016	0.019	0.046	0.013	0.003	0.013	0.003	0.015	0.003	0.037	0.007
50	0.015	0.016	0.017	0.020	0.011	0.003	0.012	0.003	0.014	0.003	0.016	0.004

### Desorption Studies

Desorption studies assist to illuminate the nature of adsorption and recycling of the spent adsorbent. The effect of various reagents used for desorption studies indicate that hydrochloric acid is a better reagent for desorption. Desorption of Rhodamine B dye by dilute mineral acid indicates that the dyes were adsorbed onto the activated carbon through physisorption[16].

### CONCLUSION

TPC has been effectively employed for produced high quality activated carbon The experimental results were analyzed using the Langmuir, Freundlich isotherm. The low as well as high pH value paves the way to the optimum amount of adsorption of The maximum removal of Rhodamine B was obtained at pH 6.5, with a removal level of 92.84% by using TPC as activated carbon. The adsorption of Rhodamine B is increased with increasing ionic strength and temperature. The dimensionless separation factor ( $R_L$ ) showed that the activated carbon could be used for the removal of Rhodamine B dye from aqueous solution. The values of  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$  show that the carbon used has considerable potential to remove Rhodamine B dye from aqueous solution.

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