

## Kinetic and Thermodynamic Studies on the Adsorption Behaviour of Rhodamine-B Dye onto Carbonized Powder of Polyalthia Longifolia Seeds (Ashoka)

Musale S. S.<sup>1\*</sup>, Kashalkar R. V.<sup>2</sup>

<sup>1</sup>Mewar University, Gangrar, Chittorgarh, Rajasthan 312901, India

<sup>2</sup>Head of Chemistry Department (Retd), S.P. College Pune, India

**Abstract** : Removal of Rhodamine-B from aqueous media was achieved onto carbonized powder of polyalthia longifolia seeds as a new low cost adsorbent. The adsorption of basic Rhodamine-B occurred by studying the effect of adsorbent amount, dye concentration, contact time, pH and temperature. Adsorption Study of removal of Rhodamine-B from aqueous solution at 610 nm wavelength has been investigated through a batch study. Solutions of dye having concentrations 10, 20, 30 & 40 mg/lit were used. Maximum removal of dye was found to be 93% for 10 mg/lit solution, in 120 min with 6.5 pH, 250 mg/50 ml as dose and 60°C temperature. The adsorption followed pseudo-2<sup>nd</sup> order kinetics. Both intra-particle and film diffusion governed the adsorption process. Thermodynamic parameters, such as standard Gibbs free energy ( $\Delta G^0$ ), standard enthalpy ( $\Delta H^0$ ) and standard entropy ( $\Delta S^0$ ) were calculated. All results found concluded that carbonized powder of polyalthia longifolia seeds could be effectively employed as effective new low cost adsorbent for the removal textile dyes from aqueous solutions.

**Keywords** : Rhodamine-B, Polyalthia Longifolia, Lagergren 1<sup>st</sup> order, Pseudo 2<sup>nd</sup> order, Kinetic and Thermodynamic, Clean & Cheap, Biosorbent.

### Introduction:

Synthetic dyes are one of the most important hazardous species found in textile industry produces in wastewater. There are more than 100,000 commercially available dyes with over a tone of dye stuffs produced annually<sup>25</sup>. Dye houses, paper printers and textile dyers which uses dyes for different purposes, releases waste water in to nearby land or rivers without any treatment because the conventional treatment methods are not cost effective<sup>26</sup>. Its presence in water bodies reduces light penetration, precluding the photosynthesis of aqueous flora.

Numerous methods have been designed to remove dyes from waste water, and such methods can be divided into physical, chemical and biological methods. Among these, the adsorption technique using low cost adsorbents derived from various natural, agricultural and industrial wastes are effective in removing various dyes from waste waters. Adsorption is, however, more superior among all these methods because of its low cost, simple design, easy operation and the possibility of adsorbent recycling<sup>33</sup>. Various low cost adsorbents were prepared from waste agricultural materials such as coconut husk, date stone<sup>27</sup>, jujuba seed<sup>28</sup>, garlic peel<sup>29</sup>, olive waste cake<sup>30</sup>, apple wastes<sup>31</sup>, periwinkle shell<sup>32</sup> etc. The present study undertaken to evaluate the efficiency of a carbon adsorbent prepared from seeds of polyalthia longifolia for the removal of dye in aqueous solution.

## Materials and Methods:

To study the adsorption of dye all chemicals used were of analytical grade. Digital colorimeter (Make: Equiptronics) Model EQ-650-A and Digital pH Meter (Make: Equiptronics) Model EQ-610 were used.

### 1. Preparation of Carbonized Powder of Polyalthia Longifolia Seeds (CPPL)

Seeds of polyalthia Longifolia were collected from the local areas Hadapsar Pune district, India. The seeds were washed with water and dried at 110 to 120° C in the oven. Then they are crushed into small pieces then carbonized in the muffle furnace at temperature 600°C in presence of inert medium of nitrogen gas for 6-7 hrs. Carbonized material was grinded into fine powder with the help of mortar and pestle. Then it was passed through a 63 mesh sieve to get particles of uniform size and stored in air tight container.

### 2. Preparation of dye solutions

Rhodamine-B stock solution was prepared by dissolving 1000 mg of dye in 1 lit of distilled water, and lower concentrations were obtained by dilution of the stock solution. Rhodamine-B solutions of different concentrations. (10 to 40 mg/L) were prepared by using the stock solution. The pH of solution adjusted using 0.1 N HCl or NaOH solutions.

### 3. Batch adsorption studies

Batch experiment was carried out with different concentrations of dye solutions from 10 mg/l to 40 mg/l taken in a 250 ml clean flask. 250 mg of adsorbent dose was mixed with Rhodamine B dye solution and kept on magnetic stirrer with heater. Experimental parameters such as, adsorbent dosage 250 mg, contact time is 120 min, pH-3 to 6.5, initial concentration 10 mg/l to 40 mg/l and temperature 25-60°C were investigated by changing one parameter at a time, while other parameters are kept constant. After filtration, the dye solutions were analyzed by using colorimeter. The percentage of Rhodamine B dye removal was calculated by using the following equation.

$$\% \text{ Adsorption} = (X / C_0) * 100$$

Where,

X = Amount adsorbed

C<sub>0</sub> = Amount of Rhodamine-B present in 50 ml

Similarly adsorption capacity is calculated using equation.

$$\text{Adsorption capacity} = (X / m) * 1$$

Where,

m = Amount of adsorbent in 50 ml dye solution

## Results and Discussion

### 1. Effect of contact time

It is observed that initially the percentage removal of the dye increases rapidly and then increases in a slow and gradual manner till it reaches the equilibrium. This is because a large number of surface sites are available for adsorption at the initial stages and as the adsorption process continues the adsorption sites available decreases. There was no appreciable change in the adsorption percentage above 120 min. Hence all the experiments were conducted for a period of 120 min.

### 2. Effect of pH

Effect of pH on the adsorption capacity of adsorbent dose was studied in the pH range 3 to 6.5. The percentage of dye adsorption was determined by varying the pH of the solution, fixing the other parameters constant. The pH of the solution was adjusted by adding 0.1 N HCl or 0.1 N NaOH solution. When the pH increased and reached a maximum at pH 6 then pH of the medium was maintained at 6 for further studies.

### 3. Effect of Adsorbent dose

Effect of adsorbent dose on the removal of Rhodamine B dye from aqueous solution was investigated by varying adsorbent dose from 50 mg to 250 mg. keeping the other parameters constant. When the adsorbent dosage was increased the percentage of adsorption increased and reaches the maximum at an adsorbent dosage of 250 mg, further addition of the adsorbent dosage has no significant effect. The maximum dye uptake occurred at 250 mg dose, hence it was chosen as the optimized dose.

### 4. Effect of Initial concentrations and temperature

Effect of initial concentrations (10 to 40 mg/lit) and temperature (25 to 60°C) on adsorption were studied. During the experimentation work it was observed that as the concentration of Rhodamine-B solution increases %removal decreases (51.56 to 86.05%) to (43.59 to 61.54%) at 25°C, while at 60°C it changes from (65.12 to 93.02%) to (51.28 to 70.51%). As the concentration increases %adsorption decreases because less sites are available for adsorption, maximum dye uptake takes place at 250 mg/50 ml 10 mg/lit solution of Rhodamine-B.

### Lagergren Pseudo 1<sup>st</sup> Order Kinetic Model

The pseudo first order equation which was suggested by Lagergren is as:

$$Dq / dt = K_1 (q_e - q_t)$$

Where

$q_e$  : Amount adsorbed at equilibrium (mg/gm)

$q_t$  : Amount adsorbed at time t (mg/gm)

$K_1$  : Lagergren rate constant of pseudo 1<sup>st</sup> Order ( $\text{min}^{-1}$ )

After integrating the equation between the limits

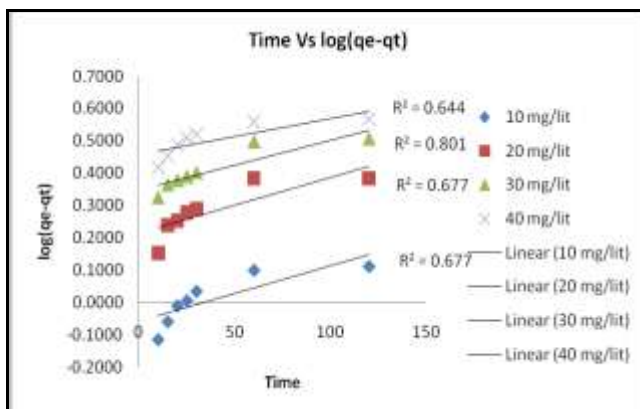
$t = 0$  to  $t = t$  and  $q = 0$  to  $q = q_e$

$$\log(q_e - q_t) = \log q_e - K_1 t / 2.3030 \quad (1)$$

linear plot of  $\log(q_e - q_t)$  vs. t are obtained and the lagergren rate constant,  $K_1$  are determined from the slope of plot.

**Table 1: Lagergren Pseudo 1st Order Parameters**

	10 mg/lit	20 mg/lit	30 mg/lit	40 mg/lit
<b>m</b>	0.001	0.001	0.001	0.001
<b>c</b>	-0.059	0.213	0.346	0.457
<b>q<sub>e</sub></b>	-1.0423	1.633	2.2181	2.8641
<b>K<sub>1</sub></b>	0.0023	0.0023	0.0023	0.0023
<b>R<sup>2</sup></b>	0.677	0.677	0.80	0.644



**Figure 1. Lagergren 1<sup>st</sup> Order**

The plot of  $\log(q_e - q_t)$  vs  $t$  indicates that they are not linear and the correlation coefficient,  $R^2$  Value is also very small. This clearly reveals that the pseudo first order model of Lagergren is not applicable to Rhodamine-B and CPPL adsorption system.

### Pseudo 2<sup>nd</sup> Order Kinetic Model

Pseudo 2<sup>nd</sup> order kinetic equation was developed by Ho and McKay which is given as:

$$dq/dt = k_2 (q_e - q)^2$$

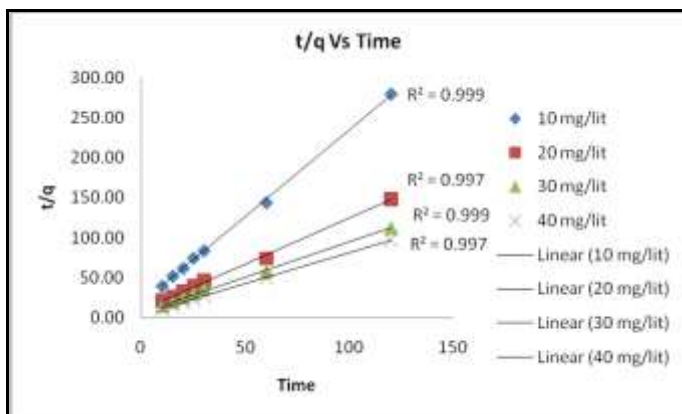
after integrating the equation between the limits  $t = 0$  to  $t = t$  and  $q = 0$  to  $q = q_e$  gives

$$t/a = (1/k_2 q_e^2) + (1/q_e) * t \quad (2)$$

Comparative value of  $m$ ,  $c$ ,  $q_e$  and  $k_2$  for different concentration solution is as:

**Table 2: Pseudo 2nd Order Kinetic parameters**

	10 mg/lit	20 mg/lit	30 mg/lit	40 mg/lit
<b>m</b>	2.159	1.146	0.873	0.778
<b>c</b>	18.14	9.771	7.157	3.784
<b>q<sub>e</sub></b>	0.4632	0.8726	1.1455	1.2853
<b>k<sub>2</sub></b>	0.2569	0.1344	0.1064	0.1599
<b>R<sup>2</sup></b>	0.99	0.99	0.99	0.99



**Figure 2. Pseudo 2nd Order**

After plot of  $t/q$  vs  $t$  it is observed that the nature of line is straight line which gives  $k_2$  and  $q_e$  from the intercept and slope. So it follows pseudo 2<sup>nd</sup> order kinetic model.

### Internal Diffusion Method (Weber and Moris)

The relation between amount adsorbed and the reaction time can be expressed as:

$$q = K_w t^{1/2} + C \quad (3)$$

Where

$K_w$ : Intra particle diffusion rate constant (mg/gm/min)

$C$ : Intercept (mg/gm)

$q$ : Amount adsorbed (mg)

In this model, due to porous nature of adsorbent, pore diffusion is expanded to be surface sorption. Therefore the rate constant of intraparticle transport,  $K_w$  was evaluated from the slopes of linear portion of the plots of  $q$  Vs  $t^{1/2}$ . The line is straight line but it does not pass through origin means it does not follow intraparticle diffusion.

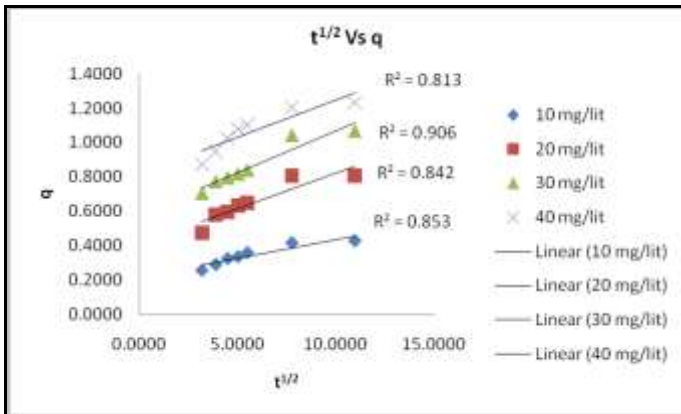


Figure 3. Internal Diffusion Method

Table 3: Internal Diffusion parameters

	10 mg/lit	20 mg/lit	30 mg/lit	40 mg/lit
<b>c</b>	0.218	0.408	0.578	0.813
<b>K<sub>w</sub></b>	0.021	0.041	0.049	0.043

**Thermodynamic Parameters**

Thermodynamic parameters, standard free energy ( $\Delta G^\circ$ ), change in Standard enthalpy ( $\Delta H^\circ$ ) and change in Standard entropy ( $\Delta S^\circ$ ) for the adsorption of Rhodamine B onto the adsorbent were calculated using the following equations. The negative value of  $\Delta G^\circ$  indicates that the adsorption process is spontaneous and highly favourable. The positive value of  $\Delta S^\circ$  indicates the increased randomness at the solid solution interface. The positive value of  $\Delta H^\circ$  indicates that the adsorption process is endothermic and physical in nature.

Thermodynamic parameters are evaluated using equation  $\Delta G = -2.303 RT \log Kc$

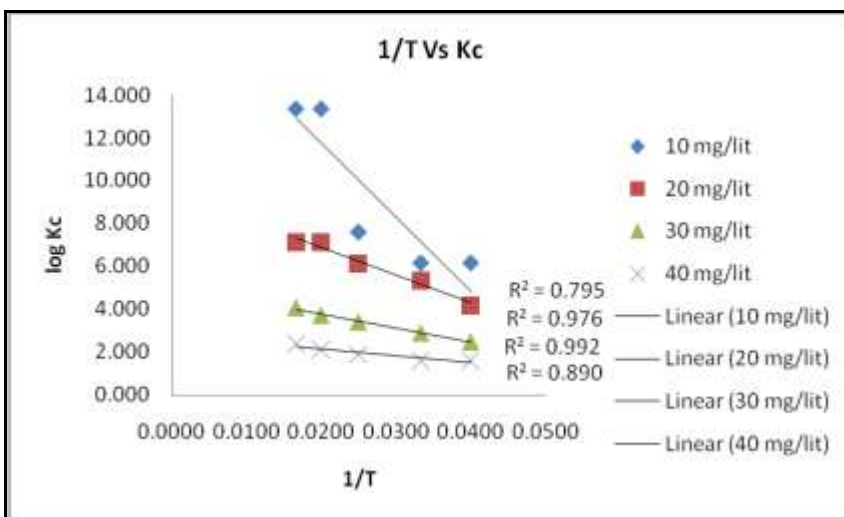


Figure 4. Study of thermodynamic parameters

**Table 4: Thermodynamic Parameters for different concentration solutions of Rhodamine-B solution**

		10 mg/lit	20 mg/lit	30 mg/lit	40 mg/lit	
25°C	Kc	6.1666	4.1818	2.4736	1.6	
	ΔG	-4507.9	-3545.4	-2244.36	-1164.68	Spontaneous
30°C	Kc	6.1666	5.3333	2.8823	1.6	
	ΔG	-4583.5	-4217.7	-2667.26	-1184.22	Spontaneous
40°C	Kc	7.6	6.125	3.4	1.88	
	ΔG	-5278.7	-4717.17	-3185.18	-1655.3	Spontaneous
50°C	Kc	13.33	7.14	3.7142	2.12	
	ΔG	-6957.2	-5280.79	-3524.41	-2018.2	Spontaneous
60°C	Kc	13.33	7.14	4.07	2.39	
	ΔG	-7172.6	-5444.29	-3891.48	-2414.18	Spontaneous
	ΔH	6596.19	2487.2	1272.3	643.3	Endothermic behaviour
	ΔS	356.51	181.7	97.7	54.12	Favourable

### Conclusions:

The equilibrium and thermodynamic studies related to the uptake of Rhodamine B dye by adsorbent from aqueous solution was studied. The adsorption was found to highly dependent on various parameters like adsorbent dosage, contact time, pH, initial concentration, and temperature. The adsorption data was fitted the best in Langmuir adsorption model. The result of this study indicates that this adsorbent can be successfully utilized for the removal on Rhodamine B from aqueous solution.

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