

Sorption Studies of Rhodamine-B by *Glossocardia linearifolia* Stem

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Abstract: The present research work deals with utilization of *Glossocardia linearifolia* stem carbon as an adsorbent for the removal of RhB dyes from the aqueous solutions. The effect of contact time, initial dye concentration, dose of sorbent, chloride ions and pH were considered. Adsorption isotherm data were tested with using Langmuir and Freundlich modes and the adsorption follows both models. The kinetic studies made with pseudo second order, Elovich model and intra- particle diffusion model. Thermodynamic parameters such as ΔH^0 , ΔS^0 and ΔG^0 were evaluated which indicated that the adsorption was spontaneous and endothermic nature.

Keywords: Isotherm, Kinetics, AGLS, Rhodamine –B, Thermodynamics

1. Introduction

A large quantity of highly coloured wastewater effluent is discharged by the textile industries into the nearby assisted lands or river without showing any treatment due to the reason that the conventional treatment was very expensive. At the same time, low cost technologies don't allow a wishful color removal and this lead to certain disadvantages. This shows that the removal of color from effluents is one of the major environmental problems. Coagulation, electro coagulation, flotation, chemical oxidation, filtration, ozonation, membrane separation, ion-exchange, aerobic and anaerobic microbial degradation are said to be the possible method of color removal from the textile effluents. All of these methods having any one limitation and none is said to be successful in removing the color from waste water completely. The adsorption process has been found to be an effective method for the treatment of dye containing wastewater [1, 2].

2. Material and Methods

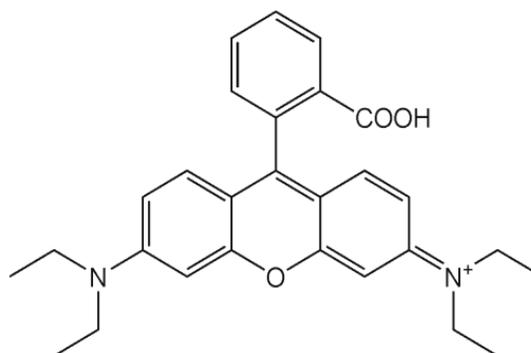
2.1 Adsorbent

The *Glossocardia linearifolia* stem obtained from agricultural area was activated at 600°C in a muffle furnace for 5 hrs, then it was taken out ground well to fine powder and stored in a vacuum desiccators.

2.2 Adsorbate

The stock solution of RhB was prepared by dissolving 1 g of dye in 1000 ml of distilled water. The experimental solutions say (50 to 250 mg/L) from stock solution were prepared by diluting to desired concentrations in accurate proportion. The

structural formula of RhB and characteristics (Table .1) are given in below.



Structure of Rhodamine- B

Table 1: Characteristics of Rhodamine-B dye

Colour Index No.	45170
Formula	C ₂₈ H ₃₁ N ₂ O ₃ Cl
Formula Weight	479.02
O _{max} (nm)	554
H(dm ³ mol ⁻¹ cm ⁻¹)	60000.00

2.3 Batch adsorption experiments

Batch adsorption experiments were carried out in a mechanical shaker at a constant speed of 150 rpm at 30°C using 250 glass-stopper flask containing 25mg AGLS with 50 ml of dyes solution at different concentration with various initial pH values. The samples were withdrawn from the agitating flask at specific time intervals. The adsorbent were separated from the solution by centrifugation (REMI Make) at 1500 rpm for 50 minutes. The supernatant solution was analyzed to

determine the residual dye concentration using UV-Visible spectrophotometer at $\lambda_{max} = 553.8 \text{ nm}$.

Dyes amount adsorbed at time t , q_t (mg/g) and equilibrium adsorption q_e (mg/g) was calculated from the mass balance principle

$$q_t = (C_i - C_t)V/W \dots\dots\dots(1)$$

Where q_t is the amount of dye adsorbed (mg/g) and C_t (mg/L) is the liquid phase concentration of dye at time t , C_0 is the initial concentration of dye solution (mg/L), V is the volume of the solution (L), W (g) is the mass of dry adsorbents when t is equal to contact time of equilibrium $C_t = C_e$ $q_t = q_e$ then equation (1) becomes

$$q_e = (C_i - C_e) V/W \dots\dots\dots(2)$$

The amount of dye adsorbed was calculated from the equation (2). The dye removal percentage determined from the equation (3)

$$R\% = (C_i - C_t) \times 100 / C_i \dots\dots\dots(3)$$

3. Results and Discussion

3.1 Effect of contact time and initial concentrations

The influence of dyes concentration and contact time on the adsorption uptake of RhB with different initial concentration (50 to 250 mg/L), was mixed with 25 mg of AGLS. The Figure 1 reveals that, the dyes uptake was rapid for first 50 minutes. After 50 minutes it was constant with increase in contact time. Based on the results 50 minutes was taken as the contact time to the adsorption process., The equilibrium adsorption capacity (q_e) of RhB dyes on to AGLS increased from 90.856 mg/g to 228.241 mg/g. This result indicates that the initial concentration strongly affects the adsorption capacity.

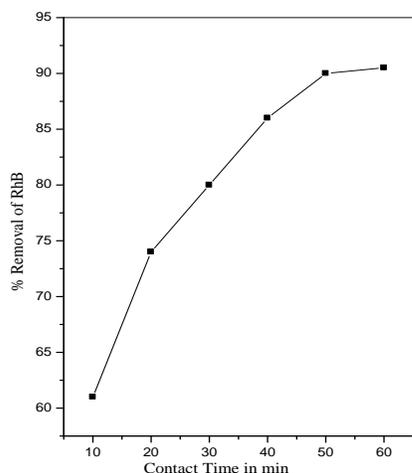


Fig:1- Effect of Contact time on the removal of RhB onto POP [RhB]=50mg/L; Adsorbent dose 25mg/50ml; Temperatur 30°C

3.2 Effect of adsorbent dosage

The effect of adsorbent dose was analyzed for the removal of dyes from the aqueous solution. The experiments were

investigated by adsorbent dose varied from 10 to 250 mg agitating with 50 ml of different concentration of dye solution. The Figure 2 shows the adsorption of RhB dyes increases rapidly with increase the amount of *Glossocardia linearifolia* stem carbon due to greater availability of the adsorbent surface area at higher concentration. The significant change in RhB dyes was observed when dosage was increased from 10 to 250 mg and the further addition of the sorbent beyond this did not show big change in the sorption process. This is due to overlapping of adsorption sites as a result of overcrowding of AGLS particles [3].

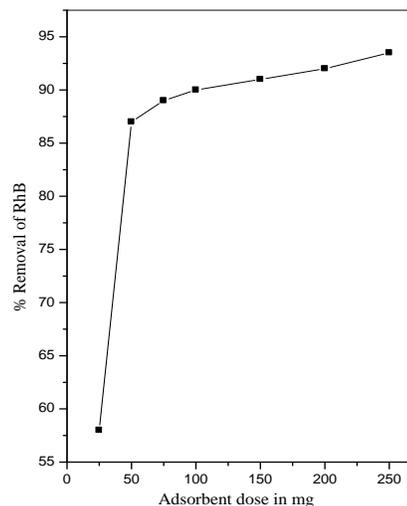


Fig:2- Effect of Adsorbent dose on the removal of RhB onto POP [RhB]=50mg/L; Contact time 50min; Temperature 30°C

3.3 Effect of pH

The pH value of the solution was an important controlling parameter in the adsorption process. The effect of pH on RhB dye adsorption onto *Glossocardia linearifolia* stem carbon was analysed over the pH range of 3.0- 10.0 and the results are shown in Figure. 3. RhB dye adsorption was found to increase with increase in the initial solution pH up to 6.5. When $\text{pH} > 6.5$ removal of RhB dye was decreased. This may be due to the occupation of sites by anionic species which retards the approach of such ions further towards the adsorbent surface. The experimental results showed that the optimum pH range for the adsorption RhB dye is 2.0 to 6.5.

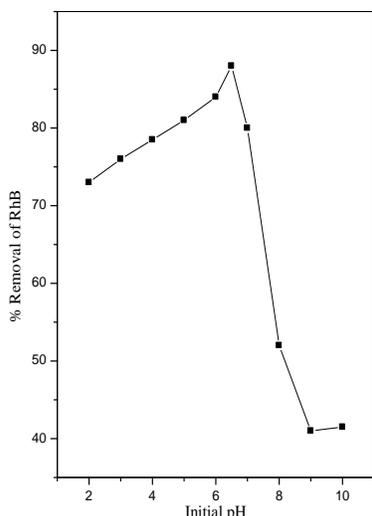


Fig.3- Effect of Initial pH on the removal of RhB Dye onto POP
 [RhB]=50mg/L; Contact time=50min; Adsorbent dose=25mg/50ml;Temp=30°C

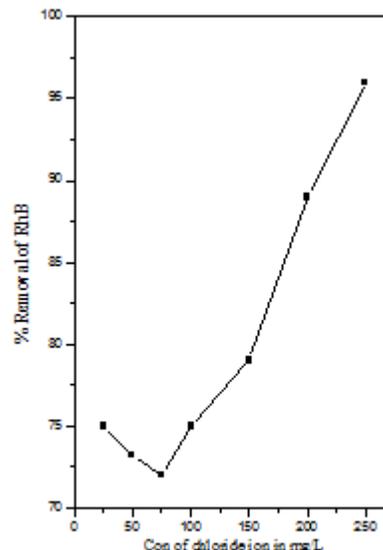


Fig.4- Effect of the other ions on the adsorption of RhB onto POP
 [RhB]=50mg/L; Contact time=50 min; Temp 30°C; Adsorbent dose=25mg/50ml

3.4 Effect of ionic strength

The Figure 4 shows the effect of sodium chloride on the adsorption of Rhodamine-B on AGLS was studied by the addition of NaCl. The low concentrate NaCl solution had little influence on the adsorption capacity. When the concentration of NaCl increases, the ionic strength is raised. At higher ionic strength, the adsorption of Rhodamine-B will be high owing to the partial neutralization of the positive charge on the AGLS surface and a consequent compression of the electrical double layer by the Cl⁻ anion. The chloride ion also enhances adsorption of Rhodamine -B ion by pairing their charges, and hence reducing the repulsion between the RhB molecules adsorbed on the surface. This initiates AGLS to adsorb more positive Rhodamine-B ions [4, 5, 6,7]

3.5 Adsorption isotherms

The distribution of dyes between the liquid phase and solid phase can be described by several isotherms. Langmuir and Freundlich isotherm equations have been used in this study.

3.5.1. Langmuir isotherm

The Langmuir model assumes that the uptake of dye occurs on the homogeneous surface by monolayer adsorption without any interaction between adsorbed dyes. The Langmuir isotherm [8] has been represented as

$$C_e / q_e = (1 / Q_0 b) + (C_e / Q_0) \text{----- (4)}$$

Where q_e (mg/g) is the amount of dye adsorbed onto per unit mass Langmuir isotherm model confirms the homogeneous nature of Glossocardia linearifolia stem carbon. The results also enhance confirm the formation monolayer coverage of RhB dye molecule at surface of AGLS. Similar results were reported by adsorption of cango red dye on activated carbon from coir pith[9 10]. C_e (mg/L) is the equilibrium concentration of the dye ions, Q_0 (mg/g) and b (mg/L) are Langmuir constants related to the adsorption and energy of adsorption respectively. The plot of C_e/q_e against C_e gives straight line .The constant Q_0 and b can be calculated from the slope and intercept and their values are given in Table .2. This indicates that the adsorption of RhB on to Glossocardia linearifolia stem carbon follows the Langmuir isotherm. The essential feature of the Langmuir isotherm can be explained in terms of a dimensionless equilibrium parameter which is defined by following equation [11, 12]

Table 2: Equilibrium parameters for adsorption of RhB dye onto AGLS

C_0	Ce (Mg / L)				Qe (Mg / g)				R (%)			
	30° C	40° C	50° C	60° C	30° C	40° C	50° C	60° C	30° C	40° C	50° C	60° C
50	4.5720	4.1824	3.8496	3.6432	90.856	91.6352	92.3008	92.7136	90.856	91.6352	92.3008	92.7136
100	16.4696	14.8200	12.5976	11.0048	167.0608	170.36	174.8048	177.9904	83.5304	85.1800	87.4024	88.9952
150	35.8792	32.2032	28.6728	25.5552	228.2416	235.5936	242.6544	248.8896	76.0805	78.5312	80.8848	82.9632
200	70.0368	65.3768	58.6728	55.6192	259.9264	269.2464	342.6544	288.7616	64.9816	67.3116	85.6636	72.1904
250	113.5560	107.6576	60.4792	96.3480	272.888	284.6848	379.0416	307.304	54.5776	56.9369	75.8083	61.4608

$$R_L = 1/1+bC_0 \text{ ----- (5)}$$

where b (L/mg) is the Langmuir constants related to the energy of adsorption and C₀ is the initial dye concentration (mg/L). The values of R_L indicate the types of isotherm process and are given as below

R _L values	Adsorption
R _L > 1	Un favourable
R _L =1	Linear
0 < R _L <1	Favourable
R _L =0	Irreversible

3.5.2. Freundlich isotherm model

The Freundlich isotherm is an empirical equation. It is based on multilayer adsorption on heterogeneous surface [13]. The linear form of Freundlich equation is given as

$$\log q_e = \log k_f + 1/n \log C_e \text{ -----(6)}$$

where q_e is the amount of dye adsorbed per unit gram of adsorbent (mg/L), C_e is the equilibrium concentration in solution after adsorption(mg/L), K_f (mg/g(L/mg)) is the Freundlich constant related to binding energy and n (g/L) is the heterogeneity factor. The values of K_f and n were obtained from the intercepts (logk_f) and slope (1/n) of the plot of log q_e vs log C_e. Values of K_f and n are given the Table .3. The values of 1/n is less than unity, it is indicating the favorable adsorption [14]. The plot of logq_e versus log C_e gives a straight line with slope 1/n which indicates that the adsorption of RhB on to AGLS follows the Freundlich isotherm mode.

Table 3: Langmuir and freundlich isotherm parameters for adsorption of RhB on to AGLS

Temperature °C	Langmuir Parameter		Freundlich Parameter	
	Q ₀	b	K _f	n
30°	301.3624	0.0857	5.842156	2.8586
40°	314.1805	0.0901	5.9434510	2.8154
50°	499.2253	0.0485	5.27933	1.8840
60°	338.244	0.1042	6.17865	2.7442

3.6 Thermodynamics Parameters

Thermodynamic parameters like ΔH⁰, ΔS⁰ and ΔG⁰ can be determined at different temperature namely 303, 313, 323 and 333 K by using the following relations

$$K_0 = C_d / C_e \text{ ----- (7)}$$

$$\Delta G^0 = -RT \ln K_0 \text{ ----- (8)}$$

$$\log K_0 = \Delta S^0 / 2.303R - \Delta H^0 / 2.303RT \text{ ----- (9)}$$

Where K₀ is the equilibrium constant, C_{ad} is the solid phase concentration at equilibrium (mg/L), C_e is the equilibrium concentration of the dye solution (mg/L), R is the gas constant and T is the absolute solution temperature in Kelvin. The ΔH⁰ and ΔS⁰ values for dye sorption can be determined from the slope and intercept of the linear plot of logK₀ Vs 1/T .The values are presented in Table 4. The positive values of ΔH⁰

confirm the endothermic adsorption of RhB on to AGLS. The more negative values of ΔG⁰ indicate the feasibility of dye adsorption and its process is spontaneous nature. The positive values of ΔS⁰ shows the increased randomness at the solid – solution interface. In desorption of dye the adsorbed water molecules, and which are displaced by the adsorbate species, gain more translational entropy than it is lost by the adsorbate molecules, thus allowing prevalence of randomness in the system [15,16].

Table 4: Dimensionless separation factor (RL) for adsorption of RhB on to AGLS

Initial Concentration (C ₀)	Temperature °C			
	30°C	40°C	50°C	60°C
50	0.1892	0.1816	0.2916	0.16097
100	0.1044	0.0998	0.1707	0.0875
150	0.0721	0.0688	0.12069	0.0601
200	0.0551	0.05255	0.0933	0.0457
250	0.0446	0.0424	0.0760	0.0369

3.7 Pseudo- second – order kinetic model

The linear form of the pseudo second order kinetic rate equation [17] is expressed as

$$t/q_t = 1/K_{2ad} q_e^2 + 1/q_e(t) \text{(10)}$$

Where k₂(g/mg min) is the second order rate constant, q_e is the amount of dye adsorbed on the per unit mass of adsorbent(mg/g) at equilibrium, q_t is the amount of dye adsorbed at time t, per unit mass of adsorbent(mg/g)

The values of k₂ and equilibrium capacity (q_e) can be calculated from the slope and intercepts of the curve plot of t/q_t versus 1/q_e. The second – order rate constant k₂, calculated h values and (γ) values are given in table. A plot of t/q_t versus 1/q_e gives a straight line. It reveals that the adsorption process follows pseudo- second- order kinetic model

Table 5: Thermodynamic parameters for the adsorption of RhB on to AGLS

C ₀	ΔG°				ΔH°	ΔS°
	30° C	40° C	50° C	60° C		
50	- 5784.398	- 6229.299	- 6670.417	- 7041.853	6.9963	42.2260
100	- 4090.317	- 4550.842	- 5201.707	- 5786.989	13.2972	57.2473
150	- 2914.899	- 3374.887	- 3873.834	- 4382.693	11.9331	48.9613
200	- 1557.41	- 1879.66	- 4800.531	- 2641.003	17.8549	64.7018
250	- 462.5602	- 726.7643	- 3067.287	- 1292.153	14.7502	50.7482

3.8 The Elovich equation

The Elovich model is a rate equation, for the heterogeneous absorbing surface is heterogeneous [18, 19] It is generally represented as

$$dq_t / dt = \alpha \exp (-\beta q_t) \text{ (11)}$$

where α is the initial adsorption (mg.g⁻¹.min⁻¹), β is the adsorption constant(g/mg) during any one experiment. To simplify the Elovich equation, it is assumed that α β t >> T and

by applying the boundary conditions $q_t = 0$ at $t=0$ and $q_t = q_t$ at $t=t$ equation (11) becomes

$$q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln(t) \dots\dots\dots(12)$$

A plot of $\ln q_t$ vs $\ln t$ should yield a linear trace with a slope of $(1/\beta)$ and an intercept of $(1/\beta) \ln(\alpha\beta)$. The plots are linear with good correlation coefficient and the results are tabulated in Table.6.

3.9 The intra- particle diffusion model

The intra- particle diffusion model from Weber and Morris [20] following equation

$$q_t = k_{ipd} \cdot t^{1/2} + C_i \dots\dots\dots(12)$$

Where K_{ipd} is the intra – particle diffusion rate constant (mg/g min), q_t is the amount of dye adsorbed on to adsorbent at time t (mg/g), C_i is the intercept which gives an idea about the thickness of the boundary layer. The plot of q_t against $t^{1/2}$ gives multi-linearity, it shows two linear portions. The first part of the curve is attributed to boundary layer diffusion while the final liner part shows intra- particle diffusion. Since the line does not pass through the origin, it is clear that intra-particle diffusion is involved in the adsorption process but it is not involved in the rate limiting steps. The diffusion parameters are presented in Table 6.

Table 6: The kinetic parameters for adsorption of RhB dye on to AGLS

Co	Temp °C	PSEUDO SECOND ORDER				ELOVICH MODEL			INTRAPARTICLE DIFFUSION		
		q_e	K_{2ad}	γ	h	α	β	γ	K_{IPD}	γ	C_i
50	30	100.8416	0.00128	0.9922	13.1031	116.813	0.06918	0.9962	1.6297	0.9981	0.1813
	40	100.9679	0.00136	0.9921	13.8596	155.5612	0.07242	0.9972	1.6513	0.9985	0.1707
	50	101.0214	0.00144	0.9918	14.7907	211.4376	0.0758	0.9943	1.6717	0.9975	0.1609
	60	101.6164	0.001429	0.9915	14.7512	198.9897	0.07455	0.9933	1.6702	0.9988	0.1630
100	30	185.7339	0.00067	0.9914	23.3008	188.3596	0.036776	0.9937	1.5828	0.9976	0.1866
	40	188.8360	0.000679	0.9913	24.2185	222.6997	0.0371	0.9939	1.6020	0.9989	0.1801
	50	192.4480	0.00072	0.9919	26.7034	298.5088	0.0400	0.9938	1.6311	0.9977	0.1707
	60	196.1968	0.00071	0.9927	27.4316	296.7924	0.0370	0.9948	1.6381	0.9991	0.1719
150	30	257.8151	0.00042	0.9929	28.2159	168.2467	0.0246	0.9961	1.5069	0.9992	0.2061
	40	263.6841	0.00044	0.9930	31.2017	218.3458	0.0250	0.9964	1.5407	0.9995	0.1951
	50	270.8011	0.00046	0.9933	34.1309	270.5353	0.0251	0.9969	1.5695	0.9984	0.1874
	60	275.2979	0.000383	0.9935	29.0319	335.5586	0.0268	0.9970	1.5857	0.9978	0.1724
200	30	303.5679	0.00028	0.9945	25.9927	96.3851	0.0183	0.9966	1.3586	0.9917	0.2506
	40	311.11633	0.00029	0.9949	28.4424	119.392	0.01862	0.9965	1.3980	0.9901	0.2367
	50	319.9139	0.00030	0.9953	31.0343	144.0399	0.01864	0.9977	1.4320	0.9906	0.2266
	60	327.5337	0.00033	0.9959	35.4715	193.6464	0.01900	0.9915	1.4755	0.9907	0.2120
250	30	332.9001	0.00019	0.9962	22.0311	60.2233	0.0150	0.9918	1.1910	0.9909	0.3016
	40	344.2053	0.0002	0.9967	23.6782	67.5429	0.0148	0.9937	1.2245	0.9912	0.2927
	50	359.2018	0.00018	0.9974	24.2962	69.2362	0.01418	0.9968	1.2392	0.9914	0.2937
	60	364.5738	0.00021	0.9975	27.9942	88.5406	0.0145	0.9992	1.2937	0.9915	0.2730

4. Conclusion

The experimental results show that the Glossocardia linearifolia stem carbon for the adsorption of RhB dye was effective. The adsorption of RhB dye adsorption was increased with increase in the dosage of sorbent and decreasing with increasing initial concentration. The adsorption data's were well fit in both Freundlich and Langmuir model and was well described by pseudo- second–order kinetics model. A series of experiments were conducted by batch system and it was observed that more than 90% of dye removal was archived by using 25 mg of Glossocardia linearifolia stem carbon.

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