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Research Article

SORPTION STUDIES OF RHODAMINE-B BY PLASTER OF PARIS

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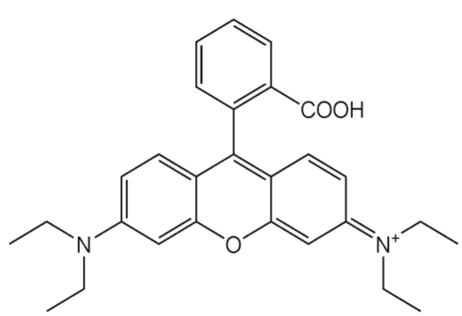
ABSTRACT
The present research work deals with utilization of plaster of paris as an adsorbent for the removal of RhB dyes from the aqueous solutions. The effect of contact time, initial dye concentration, dose of sorbent, chloride ions and pH were considered. Adsorption isotherm data were tested with 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 follows spontaneous and endothermic nature.

***Key Words**: Isotherm, Kinetics, Plaster of pairs (POP), Rhodamine –B, Thermodynamics*

INTRODUCTION
A large quantity of highly coloured wastewater effluent is discharged in a large quantity by the textile industries into the nearly 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 is shows that the removal of color from effluents is one of the major environmental problems. The adsorption process has been found to be an effective method for the treatment of dye containing wastewater 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 (Ozacar and Sengil, 2004; and Lorenc- Grabowska and Gryglewicz, 2007).

MATERIALS AND METHODS
Absorbent
The Plaster of Paris obtained from commercial shop was activated at 400^0C in a muffle furnace for 5 hrs, then it was taken out ground well to fine powder and stored in a vacuum desiccators.



Structure of Rhodamine- B

Adsorbate

The stock solution of RhB was prepared by dissolving 1 g of dye in 1000 ml of distilled water. The experimental solution say (50 to 250 mg/L) from stock solution by diluting to desired concentrations in accurate proportion. The structural formula of RhB and characteristics are given in Table 1.

Table 1: Characteristics Of Rhodamine-B Dye

Colour Index No.	45170
Formula	$C_{28}H_{31}N_2O_3Cl$
Formula Weight	479.02
O_{max} (nm)	554
H (dm^3 mol^{-1} cm^{-1})	60000.00

Batch Adsorption Experiments

Batch adsorption experiments were carried out in a mechanical shaker at a constant speed of 150 rpm at 30^0C using with 250 glass- stopper flask contain 25mg pop with 50 ml of dyes solution at different concentration with various initial pH values the samples were withdrawn from the shaker during agitating flask at present time introvals.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 λmax = 553.8.

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

$$q_t = (C_i - C_t)V/W \quad \text{……………………..(1)}$$

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

$$q_e = (C_i - C_e) V/W \quad \text{…………………………..(2)}$$

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

$$R\% = (C_i - C_t) \times 100/ C_i \quad \text{……………………(3)}$$

RESULTS AND DISCUSION

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 pop. 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) RhB dyes on to pop increased from 90.856 mg/g to 228.241 mg/g. This result indicates that the initial concentration strongly affects the adsorption capacity.

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 plaster of paris due to greater availability of the adsorbent surface area at higher concentration of 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 big change in the sorption process. This is due to overlapping of adsorption sites as a result of overcrowding of POP particles (Kumar and Kiruthika, 2009).

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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 plaster of paris 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 an increase in the initial solution pH .When pH > 6.5 decrease the removal of RhB dye may be due to the occupation sites by anionic species which retards the approach of such ions further towards the adsorbent surface. The experimental results the optimum pH range for the adsorption RhB dye is 2.0 to 6.5.

Effect of Ionic Strength

The effect of sodium chloride on the adsorption of Rhodamine-B on POP 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 POP 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 POP to adsorbs more positive Rhodamine-B ions (Arivoli *et al.,* 2007; Arivoli *et al.,* 2007; Guo *et al.,* 2005; and Sreedhar and Anirudhan, 1999)

Adsorption Isotherms

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

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 (Langmuir, 1918) has been represented as

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

Where q_e (mg/g) is the amount of dye adsorbed onto per unit mass Langmuir isotherm model confirm the homogeneous nature of plaster of paris. The results also enhance the formation monolayer coverage of RhB dye molecule at surface of POP, similar results reported by adsorption of cango red dye on activated carbon from coir pith (9 10) by the adsorption direct dyes of adsorbent to form complete monolayer on the sorbent surface, Ce (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 Ce/qe against Ce gives straight line .The constant Q_0 and b can be calculated from the slope and intercept and their values are given in Table .3. This indicates that the adsorption of RhB on to plaster of paris 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 (Weber and Chakravorti, 1974; and McKay *et al.*, 1982).

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

Where b (L/mg) is the Langmuir constants related to the energy of adsorption and C_0 is the initial dye concentration (mg/L).The values of R_L indicate the types of isotherm process and 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

Table 2: Equilibrium parameters for adsorption of rhb dye onto pop

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	28.6728	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

Table 3: Langmuir and Freundlich Isotherm Parameter for Adsorption of Rhb On To Pop

TEMPERATURE	LANGUMUIR PARAMETER		FRUENDLICH PARAMETER	
^{0}C	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

Table 4: Dimensionless Seperation Factor (Rl)

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

Table 5: Thermodynamic Parameter for the Adsorption of Rhb On To Pop

Co	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

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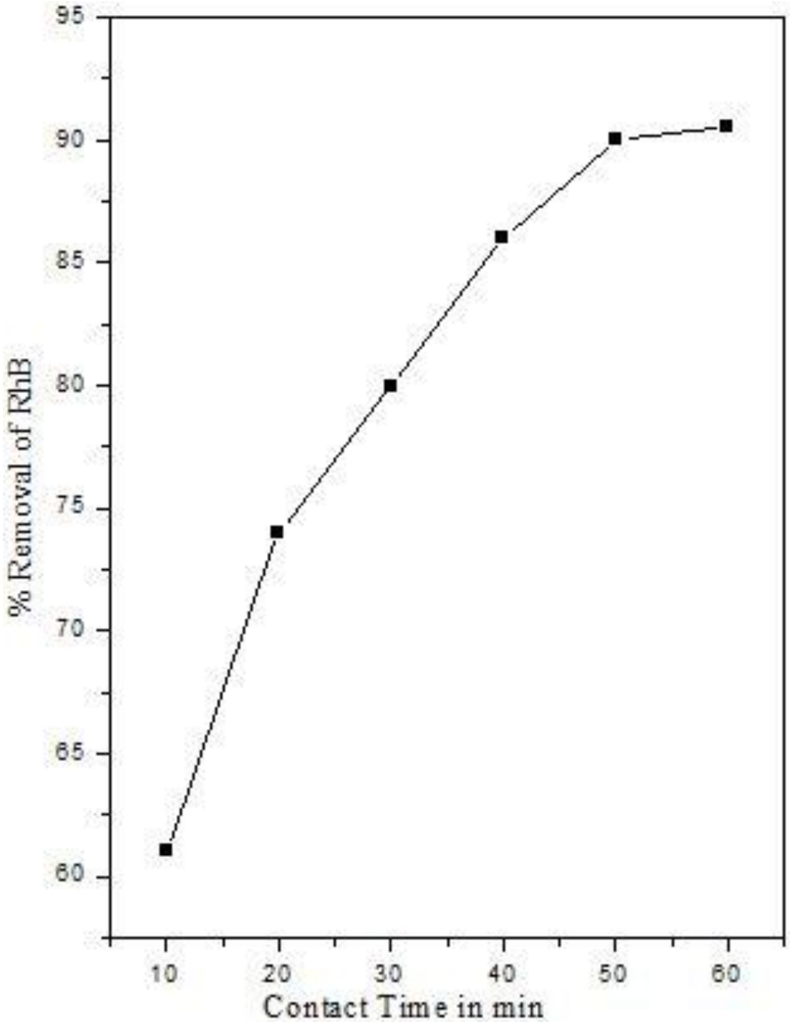

Figure 1: Effect of Contact time on the removal of RHB on to POP (RHB)=50mg/L; Adsorbent dose 25 mg/50ml; Temperature 30^{0}C

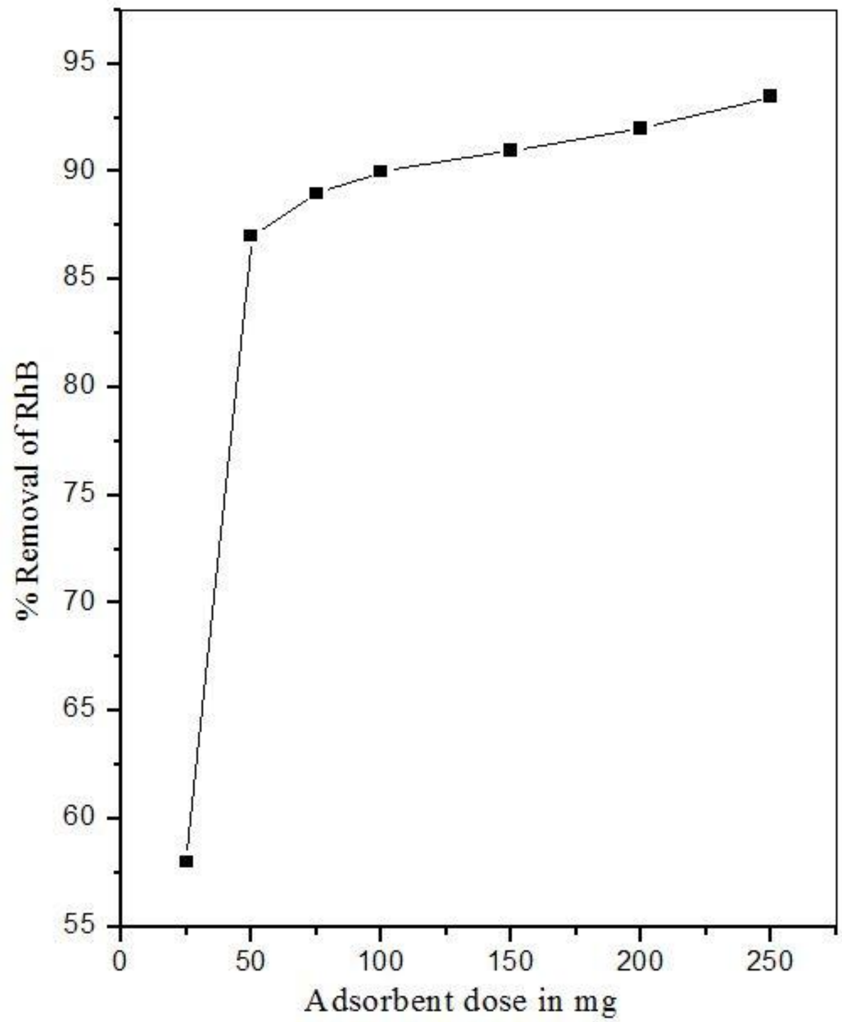

Figure 2: Effect of Adsorbent dose on the removal if RHB on to POP (RhB) = 50mg/L; Contact Time = 50 min; Temperature 30^{0}C

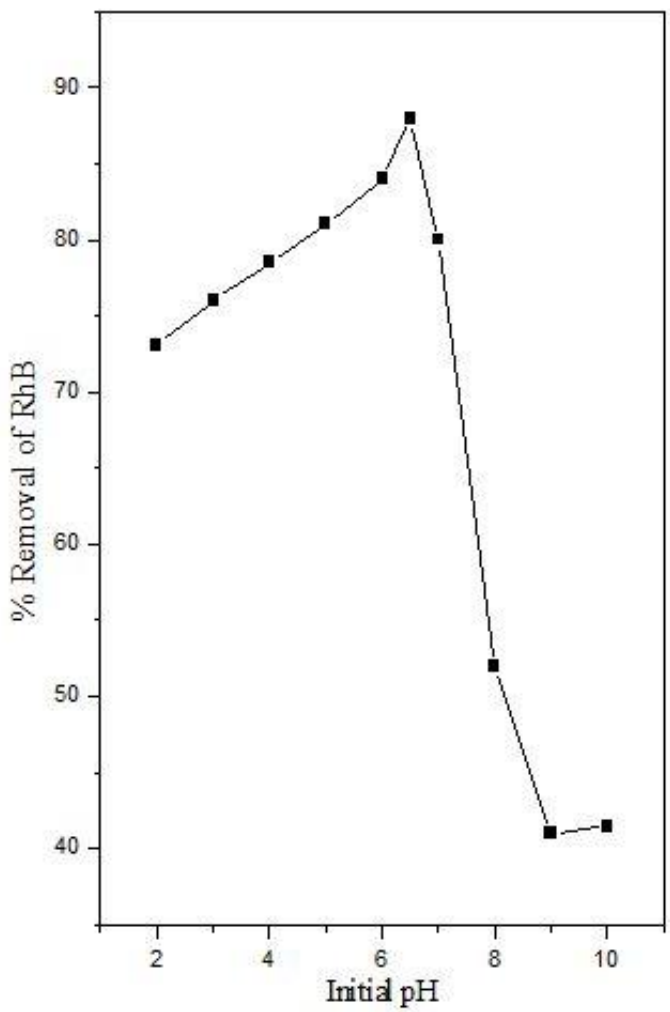

Figure 3: Effect of Initial pH removal of RHB on to POP (RhB) = 50mg/L; Contact Time= 50 min; Adsorbent dose=25mg/50ml; Temperature 30^0C

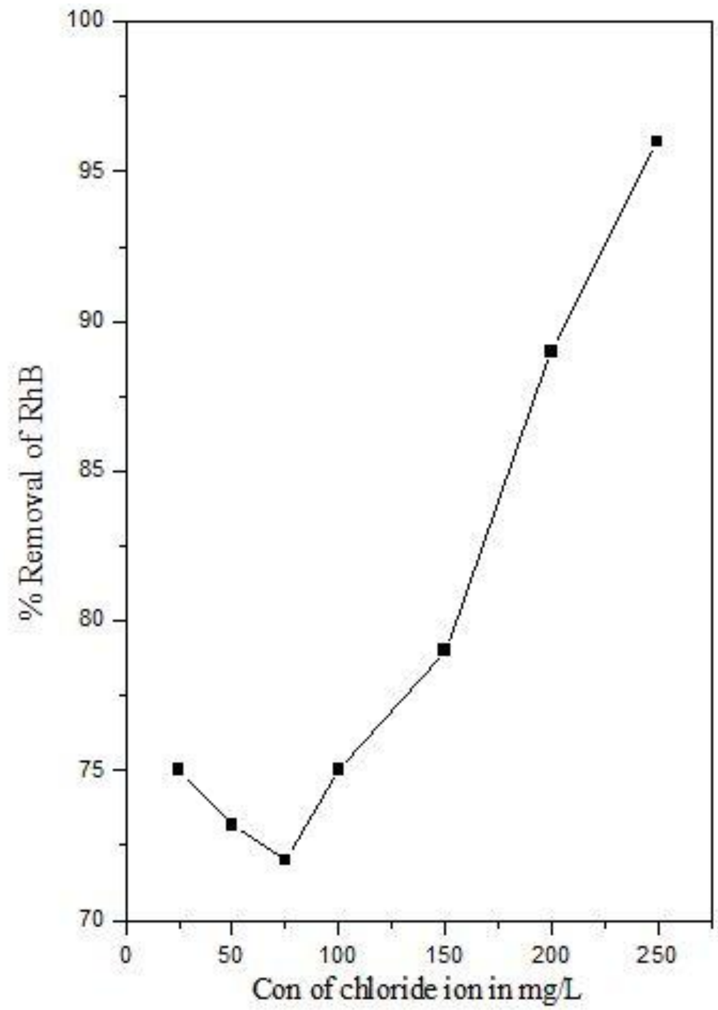

Figure 4: Effect of other ions on the adsorption of RHB on to POP (RhB) = 50mg/L; Contact Time= 50 min; Adsorbent dose=25mg/50ml; Temperature 30^0C

Table 6: The Kinetic Parameter for Adsorption of Rhb Dye On To Pop

Co	Temp	PSEUDO SECOND ORDER				ELOVICH MODEL			INTRAPARTICLE DIFFUSION		
	°C	q_e	K_{2ad}	γ	h	α	β	γ	K_{IPD}	γ	Ci
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

Freundlich Isotherm Model

The Freundlich isotherm is an empirical equation. It is based on multilayer adsorption on heterogeneous surface (Frendlich, 1906) 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 at per unit gram of adsorbent (mg/L), Ce 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 ($\log k_f$) 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 indicate favorable adsorption (Samnata *et al.*, 2000). 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 POP follows the Freundlich isotherm mode.

Thermodynamics Parameters

Thermodynamic parameters like ΔH^0, ΔS^0 and ΔG^0 can be determined at different temperature namely 303, 313, 323 and 333 K by using the following relations

$$K0 = Cad / Ce \text{ ------------------------ (7)}$$

$$\Delta G0 = -RT\ln K_0 \text{ ------------------------ (8)}$$

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

Where K_0 is the equilibrium constant, Cad is the solid phase concentration at equilibrium (mg/L), Ce is the equilibrium concentration of the dye solution (mg/L), R is the gas constant T is the absolute solution temperature in Kelvin. The ΔH^0 and ΔS^0 values for dye sorption can be determined from the slope and intercept of the linear plot of logK_0 vs 1/T .The values are presented in Table 4. The positive values of ΔH^0 confirm the endothermic adsorption of RhB on to POP. The more negative values of ΔG^0 indicate the feasibility of dye process is spontaneous nature. The positive values of ΔS^0shows the increased randomness at the solid – solution interface. In desorption of dye the adsorbed water molecules, 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 (Inbaraj *et al.*, 2002; and Namasivayam and Yamuna, 1995).

Pseudo- Second – Order Kinetic Model

The linear form of the pseudo second order kinetic rate equation (Ho and McKay, 2000) is expressed as

$$T/qt = 1/K_{2ad}\, qe^2 + 1/q_e (t) \text{ ……………… (10)}$$

Where k_2 (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 k_2 and equilibrium capacity (q_e) can be calculated from the slope and intercepts of the curve plot of t/qt versus 1/qe. The second – order rate constant $k_{2,}$ calculated h values and (γ) values are given in table 6. A plot of t/qt versus 1/q_e gives a straight line. It reveals that the adsorption process follows pseudo- second- order kinetics model

The Elovich Equation

The Elovich model is a rate equation, for the absorbing surface is heterogeneous (Chien and Clayton, 1980; and Spark, 1986) It is generally represented as

$$Dqt / d_t = \alpha \exp(-\beta q_t) \text{ …………… (11)}$$

Where α is the initial adsorption (mg.g^{-1}min^{-1}),β is the adsorption constant(g/mg) during any one experiment. To simply the Elovich equation, assumed $\alpha\beta t >> T$ and by applying the boundary conditions q_t= 0 at t=0 and q_t =q_t at t=t equation (11) becomes

$$q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln(t) \text{ ……………………(12)}$$

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

The Intra- Particle Diffusion Model

The intra- particle diffusion model from Weber and Morris (Weber and Morris, 1964) following equation

$$Qt = k_{ipd} .t^{1/2} + Ci \text{ ------------------------ } (12)$$

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 given an idea about the thickness of the boundary layer. The plot of qt against t $^{1/2}$ gives a multi-linearity,. it is shows two linear portion the first part curve attributed to boundary layer diffusion while the final liner part shows intra- particle diffusion. Where the line does not pass through the origin indicating that intra-particle involved in the adsorption process but it is not involved in the rate limiting steps the diffusion parameters present in Table 6.

CONCLUSION

The experimental results show that the plaster of paris for the adsorption of RhB dye was effective. The maximum adsorption of RhB dye adsorption was increased with increase in the dosage of sorbent and decreasing increasing with 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 Plaster of Paris.

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