Removal of Hazardous Rhodamine B Dye by Using Chemically Activated Low Cost Adsorbent: Pine Cone Charcoal

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Abstract

Various severe environmental problems have been caused by the effluents coming from dye industries, as it contain a mixture of chemicals and dyestuff, which are very toxic to living organisms. The present work has been designed with an aim to use inexpensive and efficient technique for the removal of dyes. The present investigation revealed a potential use of Pine cone charcoal (PCC), pretreated with H_2SO_4 for the removal of hazardous Rhodamine B dye from aqueous solution. The adsorbent has been characterized with the help of FT-IR and SEM analysis. The adsorption studies have been carried out at different temperatures, adsorbent dose, dye concentrations and pH. The experimental data has been analyzed by Langmuir, Freundlich and Temkin adsorption isotherms and data fitted well for all these models. Thermodynamic parameters, i.e. change in free energy, enthalpy and entropy have also been evaluated. The negative value of free energy indicates the spontaneous nature and the positive value of enthalpy suggest the endothermic nature of the process. The adsorption of Rhodamine B follows Pseudo-second-order kinetics and intra-particle-diffusion model.

Keywords: Adsorption, kinetics, Pine cone charcoal, Rhodamine B.

Introduction

Water, the main elixir of life, is being contaminated with various toxic pollutants in a gradual way. Many industries, especially the textile industry consume a major share of fresh water for processing, washing and dyeing of products and afterwards, this wastewater containing toxic dyes has been discharged directly into water system [1-2]. Most of the synthetic dyes are non-biodegradable and even carcinogenic in nature, and leads to various health hazards to humans and aquatic living organism [3-4]. So the water pollution resulted from untreated dye effluent, is a major environmental issue because of toxicity and possible accumulation of effluents in the environment [5-6].

Rhodamine B is a basic cationic dye, widely used in textile, cotton, paper and food industry [7]. Rhodamine B dye, is aristocratically known to cause many health related problems including, irritation, redness and pain in eyes and respiratory problems [8]. If it is swallowed, can cause irritation in the gastrointestinal track and if inhaled, cause coughing, sore throat and chest pain (9). Thus the dye must be properly treated before discharging in any water source.

A number of physical and chemical methods such as; photochemical degradation [10], electrochemical degradation [11], coagulation and flocculation [12], membrane separation [13], activated carbon adsorption [14], oxidation or ozonation, [15] etc. have been used for the treatment of dye wastewater. Literature study reveals that these methods are highly expensive, having disposal problems, etc. [16-17]. Among all theses, adsorption is most promising decolourization technique for wastewater treatment [18]. Activated carbon has been widely used as an adsorbent due to its large surface area and high adsorption capacity but its use is limited because of its high cost [19]. Therefore the low cost adsorbents from agriculture waste have attracted considerable attention for the removal of dye from wastewater. In the present work Pine cone charcoal has been prepared and used for the removal of Rhodamine B dye from aqueous solution.

Materials and Methods

Equipments:

Mechanical shaker, i.e., REMI motor has been used to stirrer the solution containing adsorbate-adsorbent solution. Accurate weighing of materials has been performed by using analytical weighing balance. The solution has been centrifuged with the help of centrifuge device using Centrifuge Remi Equipment, Bombay (India). The pH of aqueous solution has been recorded with the help of digital pH meter ELICO PRIVATE LIMITED, Hyderabad (India). pH meter has been calibrated with 4.0 and 9.2 buffer solutions. The concentration of dye in solution has been determined by using Shimadzu- 1800, UV-Visible Spectrophotometer. FTIR (Fourier Transform Infrared) spectra have been obtained on FTIR spectrometer (Perkin – Elmer spectrophotometer-RXI).

Preparation of dye solution:

Rhodamine-B, [9-(2-carboxyphenyl)-6-diethylamino-3-xanthenylidene]-diethylammonium chloride dye has been purchased from S.D. Fine Chemicals, Mumbai, India. Stock solution of 500 mg/L of dye has been prepared by dissolving 0.5 g of dye in 1000 mL of deionised water. Other desirable experimental concentrations have been prepared by diluting the stock solution.

Preparation of Adsorbent:

Pine cones have been collected from Punjabi university campus, Patiala, India. The collected cones have been thoroughly washed with deionised water to remove the dust particles and other water soluble materials. Then kept in the oven at 80^0C for three days. The dried material has been burnt in a container for at least three hours and then allowed to cool at room temperature. The ash of pine cones has been obtained. After that washed with deionised water till the colour of washing becomes clear and kept in the oven. The finely dried carbonized pine cones material have been mixed with 2N H_2SO_4 and kept overnight. The resulting chemically activated charcoal again washed with deionised water continuously in order to remove residual acid. Finally the washed material has been kept in the oven at 80^0C for 24 hours for the removal of moisture. The dried charcoal was crushed into fine powder, sieved in uniform size particle and kept in air tight bottles for further uses.

Experimental procedure:

Batch adsorption studies have been used to optimize the dye adsorption by using PCC. The selected parameters for the adsorption process are; adsorbent dose (1.0-2.5 g), dye concentration (50-125 mg/L) and contact time (10, 20, 30, 45, 60, 90, and 120 minutes). In order to investigate the effect of these experimental factors, the batch adsorption experiments have been carried out by agitating 100 mL solution of fixed initial dye concentration with definite amount of adsorbent dose at mechanical shaker at constant speed. 5 mL solution has been withdrawn at prefixed time intervals, filtered and centrifuged. The concentration of dye after equilibrium adsorption has been measured with UV Visible spectrophotometer at the maximum wavelength of dye.

The amount of dye adsorbed per gram of the adsorbent has been evaluated by using the given formula:

$$q_e = \frac{c_0 - c_e}{w} \times V$$

C_o = Initial Concentration of dye, C_t = Liquid phase concentrations of dye at any time (in mg/L), V = Volume of dye taken for adsorption in mL, W = Weight of adsorbent dose, in gram.
The removal percentage of Rhodamine B dye has been calculated by following equation:

Percentage removal (%) = $= \frac{c_0 - c_e}{w} \times 100\%$

Result and Discussion

Batch adsorption studies:

Batch adsorption studies with respect to influence of adsorbent dosage, contact time, initial dye concentration, pH and temperature has been carried out.

Effect of adsorbent dose:

The effect of adsorbent dose has been studied with 75 mg/L of dye solution with varying amount of adsorbent dose ranging from 1.0 to 2.5 g at room temperature (308 K). Fig. 1(a) indicates that there is a significant increase in percentage removal of dye on increasing the adsorbent dose. Increased dye removal is attributed to increased surface area and availability of more adsorption sites. But on the other hand adsorption capacity decreases with increase of adsorbent dosage. The decrease in adsorption capacity is ascribed to the fact that the concentration of solute in solution is low as compared to the concentration of solute on the surface, which leads to desorption of solute. As a result some of the adsorption sites remained unsaturated during the adsorption process [20].

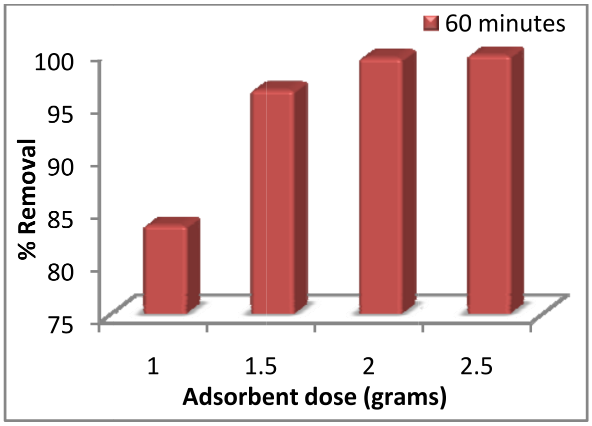


Fig. 1(a). Effect of adsorbent dose on percentage removal of dye.

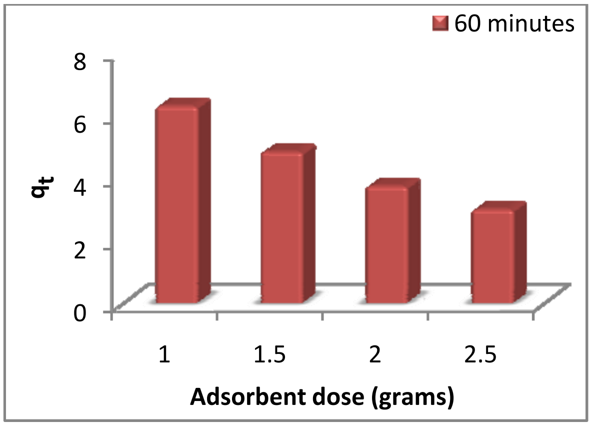


Fig. 1(b). Effect of adsorbent dose on adsorption capacity of dye.

Effect of contact time and initial dye concentration:

The adsorption process is highly influenced by the variation in contact time and initial dye concentration. To study the effect of contact time, 100 mL dye solution of known concentration and pH has been added to 2.0 g of adsorbent. The mixture has been stirred at 450 rpm on mechanical shaker for different intervals of time (10, 20, 30, 45, 60, 90 and 120 minutes). It has been observed from Fig. 2(a) and 2(b) that percentage of dye removal and amount of the dye uptake has been increased with increase in contact time. Figure indicates that after 60 minutes, the amount of dye adsorbed on the adsorbent did not change significantly. Thus 60 minutes has been considered as equilibrium time for all the adsorption experiments.

The percentage dye removal has been found to be decreases with increase in initial dye concentration (as shown in Fig. 2(a)), due to lesser number of active sites at higher dye concentrations [21]. But on increasing the dye concentration, the amount of dye adsorbed per unit weight of the adsorbent increase because as the dye concentration increases, the driving forces of concentration gradient increases, which enhances the interaction between dye and adsorbent [22].

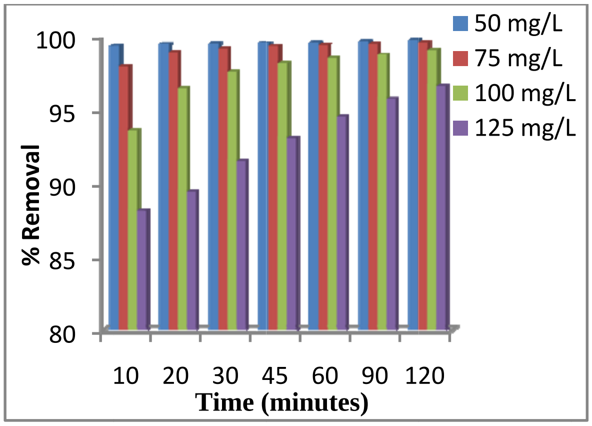


Fig. 2(a). Effect of initial dye concentration and contact time on percentage removal of dye.

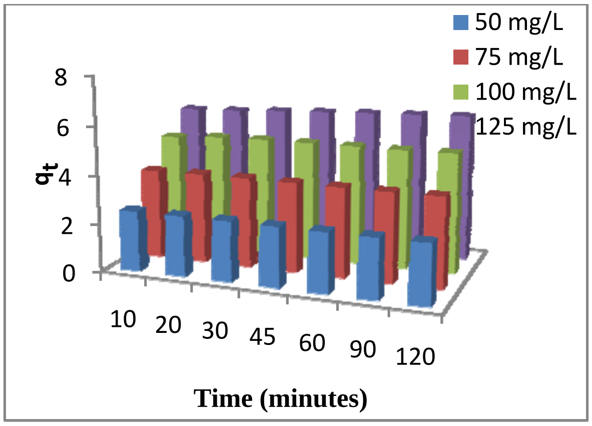


Fig. 2(b). Effect of initial dye concentration and contact time on adsorption capacity of dye.

Effect of pH:

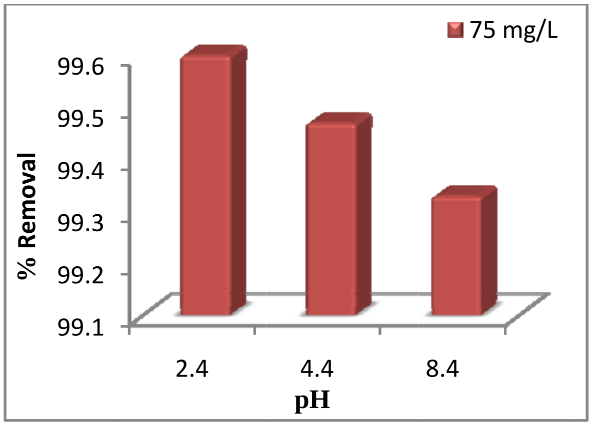
pH of the solution played an important role to control the adsorption of dye on adsorbent surface. The effect of pH on Rhodamine B adsorption has been studied by using 2.0 g of PCC and 75 mg/L dye solution at three different pH (2.4, 4.4 and 8.4) and the results have been shown Fig. 3. It has been found that maximum dye removal has been obtained at pH= 2.4 and minimum at pH= 8.4. At lower pH, the Rhodamine B ions are readily entered into the pore structure of PCC surface, which increase the percentage removal. But at higher pH value, the zwitterionic form of Rhodamine B in water may increase the aggregation of dye to form larger molecules (dimer), which are unable to enter into the pore and hence results in decrease of percentage removal [23].

Effect of Temperature:

The variation of adsorption capacity and percentage removal of dye with varying temperature is another important parameter because temperature increases the rate of diffusion of the adsorbate molecules across the external boundary layer. The adsorption of Rhodamine B at three different temperatures (308. 313 and 318 K) has been shown in Fig. 4. The result indicates that percentage removal increases with increase in temperature, which confirms the endothermic nature of adsorption.

Desorption studies:

Desorption studies helps in elucidating the mechanism of adsorption process, recovery of adsorbent from dye-loaded solution and also for the regeneration of spent adsorbents, which in turn may reduce operational cost and protect the environment. In order to access the recyclability of PCC, the adsorbent collected after adsorption has been dried and divided into three parts. One part is dissolved in water, other in 1N acetic acid and the remaining in 1N hydrochloric acid for 24 hours and then washed gently with water to remove any desorbed dye.



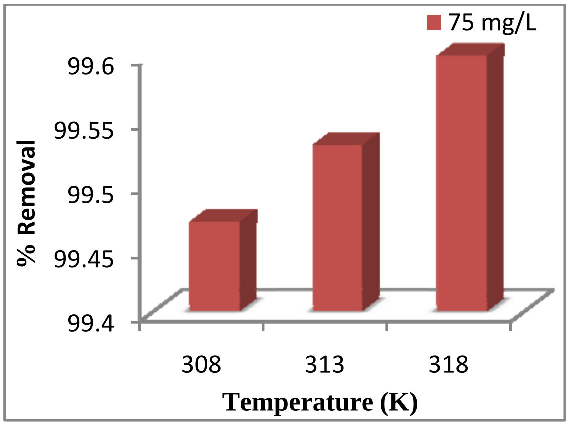


Fig. 3. Effect of pH on percentage removal of Rhodamine B dye.

Fig. 4. Effect of temperature on percentage removal of Rhodamine B dye.

To study the recycling efficiency, 100 mL solution of 75 mg/L dye has been agitated separately along with 2.0 g of recycled adsorbent for 60 minutes. The solutions have been subjected to UV-Visible spectrophotometer. The result indicates that 87% of dye has been removed by using the adsorbent, which is activated with hydrochloric acid. Thus the effect of various reagents used for desorption studies indicate that hydrochloric acid is a better reagent for regeneration of adsorbent.

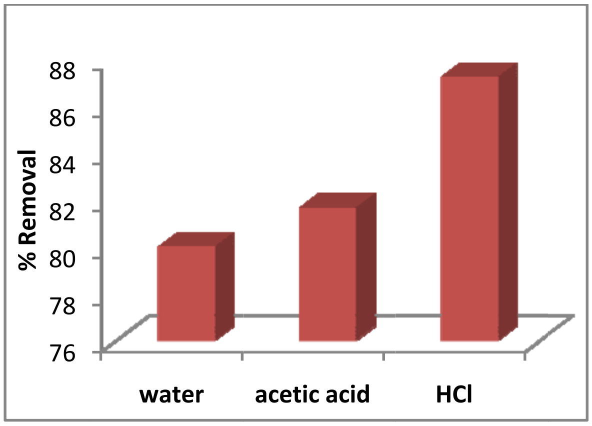


Fig. 5. Desorption studies by using various reagents.

Adsorption Isotherms:

Adsorption isotherms have been used to determine the adsorption capacity of adsorbents. In the present work Langmuir, Freundlich and Temkin adsorption isotherms have been selected to describe the relationship between the amount of dye adsorbed (q_e) and its equilibrium concentration (C_e).

Langmuir Adsorption Isotherm:

Langmuir adsorption isotherm has been used for the estimation of maximum adsorption capacity corresponds to a complete monolayer coverage on adsorbent surface, i.e., it is restricted to monolayer adsorption. The linearised Langmuir isotherm is expressed by the following equation [24]:

$$\frac{c_e}{q_e} = \frac{c_e}{q_m} + \frac{1}{q_m - b_L}$$

Where, C_e is the concentration of dye in the solution at equilibrium (mg/ L), q_e is the amount of dye adsorbed at equilibrium (mg/g), q_m is the monolayer adsorption capacity of adsorbent (mg/g) and b_L is the

Langmuir adsorption constant (L/mg*)*. The linear plot of specific adsorption capacity C_e/q_e against the equilibrium concentration C_e suggests the applicability of Langmuir isotherm. The q_m and b_L have been determined from the slope and intercept of plot and has been given in Table 2.

The adsorption process favourbility has been confirmed by calculating the dimensionless equilibrium parameter (R_L) which is expressed as: $R_L = \frac{1}{(1 + b_L.c_0)}$

The adsorption process is said to be favourable if R_L value falls between 0 and 1, i.e., ($0<R_L<1$), linear when $R_L=1$, irreversible when $R_L = 0$ and unfavourable when $R_L > 1$.

A comparison of adsorbent capacity of PCC with other adsorbents (Table 1) shows that PCC has a greater adsorption capacity than others.

Table 1: Comparison of adsorption capacities of different waste adsorbents for removal of Rhodamine B dye:

Waste Materials	Adsorption capacity (mg/g)	References
Akash kinari coal	1.183	[25]
Mango leaf powder	2.67	[23]
Exhausted coffee ground powder	5.255	[26]
Paper industry waste sludge	6.711	Present study

Freundlich Adsorption Isotherm:

Freundlich adsorption isotherm is an empirical equation that involves heterogeneous adsorption. Freundlich isotherm relates the concentration of a solute on the surface of an adsorbent to the concentration of solute in the liquid. It is described by the equation given below [27]:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$

K_f is Freundlich constant, which indicates the extent of adsorption and represents the amount of dye adsorbed on adsorbent for unit equilibrium concentration and 1/n is heterogeneity factor, which is related to the capacity and intensity of the adsorption. The linear plot between log q_e verses log C_e (Fig. 6(b)) has been employed to evaluate the intercept log K_f and the slope 1/n respectively (listed in Table-2).

Temkin Adsorption Isotherm:

Temkin adsorption isotherm can be expressed by the equation as follow [28]:

$$q_e = B\ln K_T + B\ln C_e$$

where, B is constant related to heat of adsorption and K_T is Temkin isotherm constant. A straight line plot of q_e verses $\ln C_e$ (Fig. 6(c)) enables the determination of the isotherm constants and their values are given in Table 2.

Adsorption Kinetics:

In order to examine the controlling mechanism of the adsorption processes such as mass transfer and chemical reactions, kinetic studies have been proposed. The kinetics of Rhodamine B dye onto PCC has been studied by using Pseudo-First-order, Pseudo-Second-order and Intra-particle-diffusion model with all initial dye concentrations.

Pseudo-First-order kinetic model:

The integrated linear form of Lagergren's first order equation is as follow [29]:

$$\log(q_e - q_c) = \log q_e - \frac{K_1}{2.303}t$$

K_1 is the Pseudo-first order rate constant (min^{-1}). The plot between $log\ (q_e - q_t)$ verses time t should be a straight line , so the data is subjected to this equation and it has been found that it does not fit to straight line.

Table 2. Parameters of Langmuir, Freundlich and Temkin adsorption isotherm for the uptake of Rhodamine B on to PCC.

Temperature (K)	Langmuir Constants				Freundlich Constants			Temkin Constants		
	q_m (mg/g)	b_L (L/mg)	R^2	R_L	n	K_f	R^2	B	K_T	R^2
308	6.173	3.375	0.999	0.0039	4.367	4.121	0.889	0.934	4.305	0.953
313	6.329	4.270	0.998	0.0031	4.310	4.498	0.973	0.938	1.012	0.998
318	6.494	6.160	0.996	0.0022	5.556	4.592	0.931	0.954	2.884	0.980

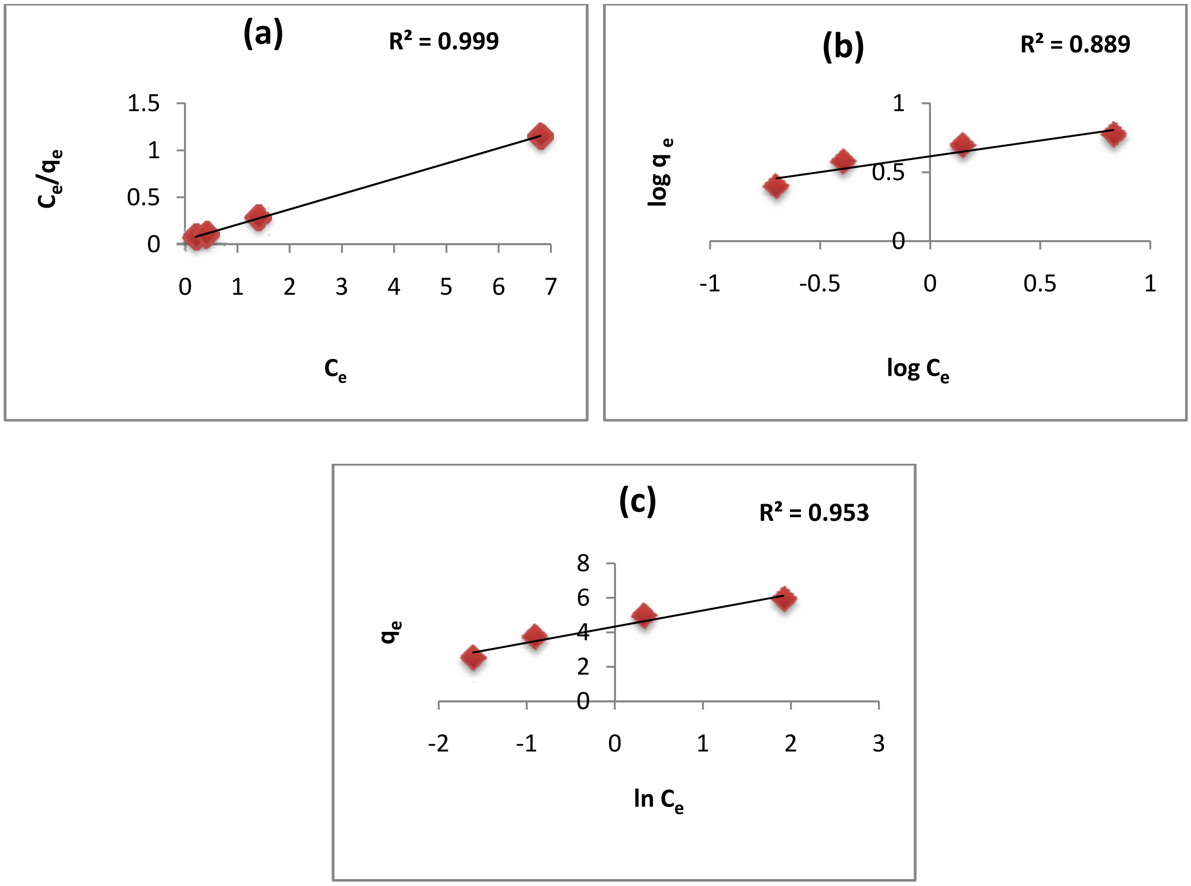


Fig.6(a). Langmuir isotherm plot for Rhodamine B adsorption. **(b).** Freundlich isotherm plot for Rhodamine B adsorption **(c).** Temkin isotherm plot for Rhodamine B adsorption.

Pseudo-Second-order kinetic model:

Since the data do not fit to pseudo-first order kinetic model thus it is subjected to pseudo-second order kinetic model in order to determine the kinetics of adsorption process. The Pseudo-second–order adsorption kinetic rate equation is expressed as [30]: $\frac{t}{q_t} = \frac{1}{K_2 q_e^{2}} + \frac{1}{q_e} t$

Where, K_2 (g.mg-1.min-1) is the rate constant of Pseudo-second-order adsorption. It is evident from Fig. 7(a) that adsorption of Rhodamine B dye has been well described by Pseudo-second-order kinetic model because the plot of t/q_t verses t gives a linear relationship. The value of q_e and K_2 has been determined from the slope and intercept respectively and listed in Table 3.

Intra-Particle-diffusion model:

The Intra-particle-diffusion equation can be written as [31]: $q_t = K_{ipd} t^{1/2} + C$

Where, q_t is the amount of dye adsorbed onto the adsorbent at time t (mg/g), K_{ipd} is the intra-particle diffusion rate constant (mg g^{-1} min^{-1}) and C is the constant (mg/g). A linear plot of q_t verses $t_{1/2}$ indicates that the uptake was controlled by intra-particle diffusion (Fig 7(b)). The intra-particle diffusion rate constant K_{ipd} and C are calculated from the slope and intercept of the plot (shown in Table 3).

Table 3. Pseudo-second-order and Intra-particle-diffusion values for Rhodamine B adsorption on PCC.

C_0 (mg/L)	**Pseudo-second-order calculated**			**Intra-particle diffusion parameters**		
	K_2 (g $mg^{-1}min^{-1}$)	**q_e (mg/g)**	**R^2**	**K_{ipd} (mg $g^{-1}min^{-1}$)**	**C (mg/g)**	**R^2**
50	5.000	2.500	1.000	0.001	2.482	0.958
75	1.616	3.745	1.000	0.006	3.674	0.704
100	0.315	5.000	1.000	0.030	4.668	0.745
125	0.090	6.135	0.999	0.071	5.309	0.964

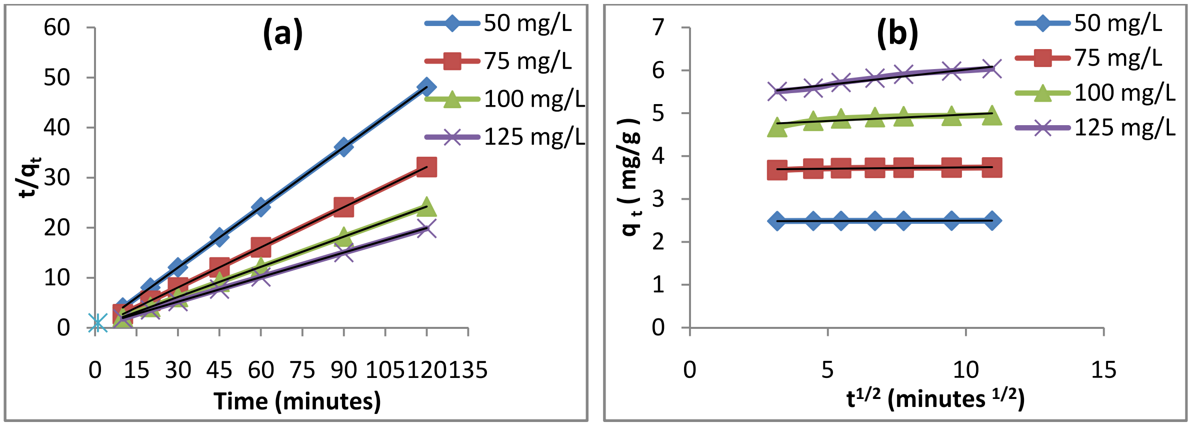


Fig. 7(a) Pseudo-second-order kinetics for Rhodamine B adsorption. **(b).** Intra-particle-diffusion values for Rhodamine B adsorption on PCC.

Adsorption Thermodynamics:

Thermodynamic parameters including change in enthalpy (*ΔH*), entropy (*ΔS*) and Gibbs free energy (*ΔG*) has been obtained from the experimental data and can be used to predict the spontaneity of adsorption process. In the present study, the effect of temperature on adsorption has been carried out at three different temperatures (308, 313 and 318 K) for all initial dye concentrations. Change in free energy can be determined by using rate equation as given below:

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

Where, *T* is temperature in Kelvin, *R* is the universal gas constant (8.314 J mol/k)

The change in enthalpy and entropy has been obtained from the slope and intercept of linear plot of $\ln K_0$ verses $1/T$ (Van't Hoffs equation) in linear expression given below:

$$\ln K_o = \Delta S/R - \Delta H/RT$$

The values of thermodynamic parameters calculated by using above equation are listed in Table 3. The change in free energy (*ΔG*) is negative for Rhodamine B adsorption at all temperatures, indicates the spontaneous nature of process. The positive values of ΔH show the endothermic nature of adsorption and it governs the possibility of physical adsorption. Similarly a positive value of ΔS suggests the increased randomness at the solid/ liquid interface during the adsorption process.

Table 4. Thermodynamic parameters for the adsorption of Rhodamine B onto PCC

C_o (mg/L)	$-\Delta G$ (KJ/mol)			ΔH (KJ/mol)	ΔS (KJ mol^{-1}K^{-1})
	308K	**313K**	**318K**		
50	14.1287	16.1669	18.2606	104.72	0.3860
75	13.3884	13.9553	14.5875	21.74	0.1140
100	10.8948	11.4779	13.0998	51.89	0.2034
125	7.3116	8.6159	10.3999	80.88	0.2860

Sem and FT-IR Analysis:

The surface morphology of PCC has been identified by using Scanning Electron Microscopy, i.e., SEM analysis. SEM images show a view from the external side of adsorbent before and after adsorption and have been shown in Fig. 8 (a) and 8 (b). The SEM micrograph 8 (a) shows that the adsorbent surface is irregular, rough and highly porous, indicating the possibility of its good adsorption properties. Fig. 8 (b) shows the surfaces of adsorbent after adsorption, it is clearly seen that the caves, pores and surfaces of adsorbent has been covered by dye and consequently the surface has become smooth, which shows that adsorption takes place.

The FT-IR spectra for two materials, i.e., unloaded and loaded adsorbent has been obtained by using FT-IR analysis. The unloaded PCC shows adsorption bands at 474.45 cm^{-1}, 797.18 cm^{-1}, 1149.66 cm^{-1}, 1618.66 cm^{-1}, 3441.80 cm^{-1} and 3606.44 cm^{-1} respectively. After adsorption, there is slight shifting of peaks and no new peak has been observed. However the two peaks at 3441.80 cm^{-1} and 3606.44 cm^{-1} become broad and converted to a single peak at 3443.21 cm^{-1} in loaded adsorbent spectra. Since no new peak has been observed, which indicates that no chemical bond is formed between adsorbate and adsorbent after adsorption, i.e., FT-IR data supports that adsorption of dye on adsorbent is due to physical forces.

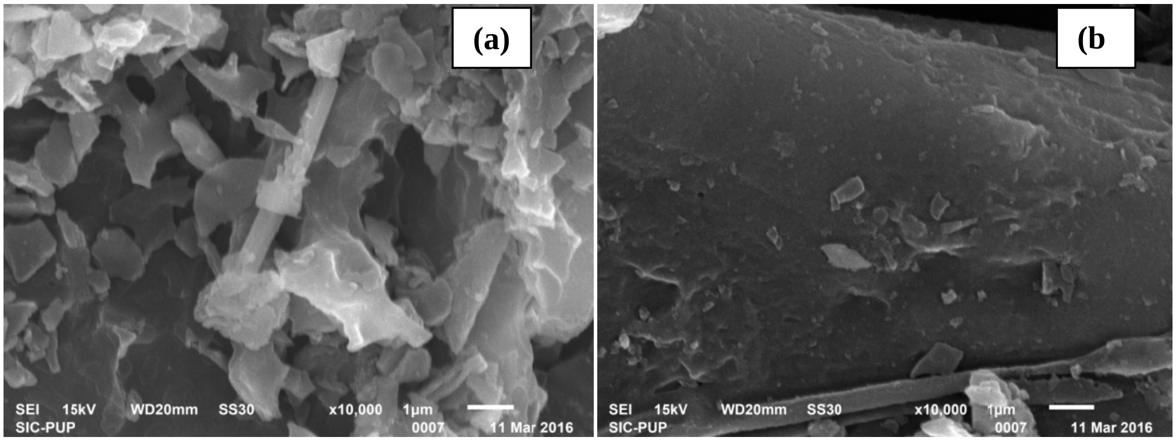


Fig. 8 (a) SEM image of PCC before adsorption. **(b).** SEM image of PCC after adsorption.

Conclusion:

The present work has shown the effectiveness of PCC for the removal of Rhodamine B dye from aqueous solution. The equilibrium, kinetics and thermodynamics of dye removal has been determined. The removal efficiency has been controlled by solution pH, adsorbent dose, dye concentration and temperature. The adsorption data has been correlated best with Langmuir isotherm model. The kinetics data agreed well with pseudo-second-order and Intra-particle diffusion rate equations. The negative values of ΔG indicated adsorption process is spontaneous. Thus it can be concluded that PCC can be used as highly effective and potential adsorbent for the removal of hazardous dyes.

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