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Removal of Rhodamine B Dye from Water Samples using Modified Chitosan

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Abstract—*Rhodamine B has been found to be one of the toxic dyes found in water obtained from industry effluents. This study deals with the removal of this dye using modified chitosan by treating with sulphuric acid, by the process of adsorption. Chitosan is a linear polysaccharide obtained from deacetylation of Chitin which is known for its biocompatibility and biodegradability. The sorption of Rhodamine B was done by batch method and detected using UV-visible spectrophotometer at 555 nm. Various parameters like pH, mass of adsorbate, concentration of adsorbent and time of contact were optimized. It was observed that under the optimized conditions the percentage efficiency for the removal of Rhodamine B was very good. Adsorption studies were carried out using Langmuir and Freundlich isotherms and kinetics studies were done along with thermodynamic parameters. This technique can be used for the removal of Rhodamine B from water obtained from industries.*

Keywords: *Chitosan, adsorption, Rhodamine B, spectrophotometry*

1. INTRODUCTION

Industrial wastewaters discharges coloured materials into stream and rivers which is widely used in textile, paper, plastic, food and cosmetic industries. Dyes cause several problems since they are generally stable to light and oxidation and hence they cannot be treated by conventional methods of aerobic digestion.[1] Physiochemical processes are generally used to treat dyes laden wastewater. These processes include flocculation, electro floatation, precipitation, electrokinetic coagulation, ion exchange, membrane filtration, electrochemical destruction etc. All these processes are costly and cannot be used by small industries to treat wide range of dye containing waste water[2]. The adsorption process is the best technique for the removal of dyes from wastewater especially if the adsorbent is inexpensive and readily available.

Activated carbon is the most widely used adsorbent due to its large surface area, microporous structure, and the high cost. This has led to search of cheaper adsorbent. Investigators have studied the feasibility of using low cost substances [3], such as waste apricot[4], coconut shell[5], diary sludge[6], bamboo grass treated with concentrated sulphuric acid[7], peat[8] as adsorbents for the removal of dyes and metals from wastewater.

The purpose of present work is to study the mechanism of adsorption of Rhodamine B on modified chitosan. The kinetic, equilibrium and thermodynamic parameters are studied to describe the rate and mechanism of adsorption to determine the factor controlling the rate of adsorption and to find out the possibility of using these biomaterials as low cost adsorbents for the removal of dye Rhodamine B. The effect of solution concentration, adsorbent dose, contact time, pH and temperature has been evaluated.

2. MATERIALS AND METHODS

2.1 Dye solution preparation

Accurately weighed quantity of dye was dissolve in double distilled water to prepare the stock solution (10mg/l).

2.2 Adsorbent

Accurately weighed chitosan powder was taken in a round bottom flask. To it, 100 ml of v/v sulfuric acid solution was added and stirred using a magnetic stirrer for 1 hour at room temperature. The reaction mixture was filtered and the residue was washed with distilled water. The washing was tested for complete removal of sulfate ions to give a solid residue of SSC. The residue was dried at 60°C in a hot air oven for 1 hour.

2.3 Estimation of optimum pH

The pH was varied from 2-10 by using 0.5 M HNO_3 and 0.1M NaOH. The absorbance was noted using U.V- Visible spectrophotometer at 555nm. Then fixed amount of dosage (0.1g) was added in each flask. Flasks were then kept in shaker for 30 min. at room temperature. Absorbance was noted at 555nm using UV spectrophotometer.

2.4 Estimation of optimum adsorbent dosage

50ml of Rhodamine B solution of 10mg/l concentration were taken in 5 different flasks. Then different amount of adsorbent (0.1g, 0.2g, 0.5g, 1.0g, 2.0g) were added in each flask and kept in a shaker for about 30 minutes at 25°C. Absorbance was noted at 555nm using UV spectrophotometer.

2.5 Estimation of optimum contact time

50ml of Rhodamine B solution of 10mg/l concentration were taken in 6 different flasks. The fixed amount of dosage (0.1g) was added in each flask. Flasks were kept in a shaker for 15 min, 30min, 60min, 90min, 120min, and 180min at 25°C. Absorbance was noted at 555nm using UV spectrophotometer.

2.6 Estimation of optimum dye concentration

50ml of Rhodamine B solution of different concentrations (0.1, 0.25, 0.5, and 0.75) of dye solution were taken in 5 flasks. The fixed amount of adsorbent (0.1g) was added in each flask. Flasks were then kept in shaker for about 30minutes at 25°C. Absorbance was noted at 555nm using UV spectrophotometer.

2.7 Estimation of optimum Temperature:

50ml of Rhodamine B solution of 10mg/l concentration were taken in 3 different flasks and kept in shaker for about 30 minutes at different temperature (25°C, 35°C, and 45°C). Absorbance was noted at 555nm using UV spectrophotometer

2.8 Batch Adsorption studies:

The optimization of all parameters and the further studies were done by batch equilibrium method. They were carried out by adding known volume of prepared Rhodamine B solution into a number of flasks containing a known amount of adsorbent. The percentage removal efficiency was calculated by

Removal efficiency (%) = (ci−cf/ci) ∗100

Where,Ci is the initial concentration(mg/l) and c_f is the final concentration (mg/l)

3. RESULTS AND DISCUSSION

3.1 Effect of pH

The efficiency of adsorption is dependent on the pH of solution since variation in pH leads to the variation in the surface properties of the adsorbent and the degree of ionization. In this study, the maximum dye removal of 26.79% was obtained at pH 8 with modified chitosan for Rhodamine B. Hence it can be concluded that the basic range of dye is favourable with modified chitosan.

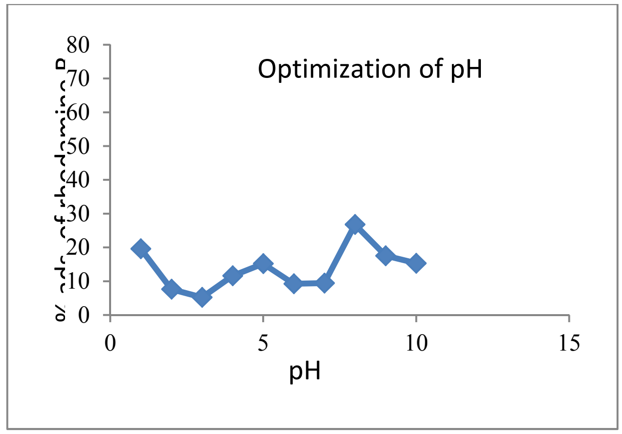

Fig. 1: Effect of pH on adsorption of rhodamine B with modified chitosan

3.2 Effect of adsorbent dosage

Removal of colour of dye directly depends on the mass of adsorbent. It was observed that the percentage removal of dye increases with the increase in adsorbent dosage. It is due to the fact that increase in adsorbent dose provides increase in pores available for adsorption and surface area also gets increased. In this study, the maximum dye removal of 48.60% was obtained with 2g of modified chitosan.

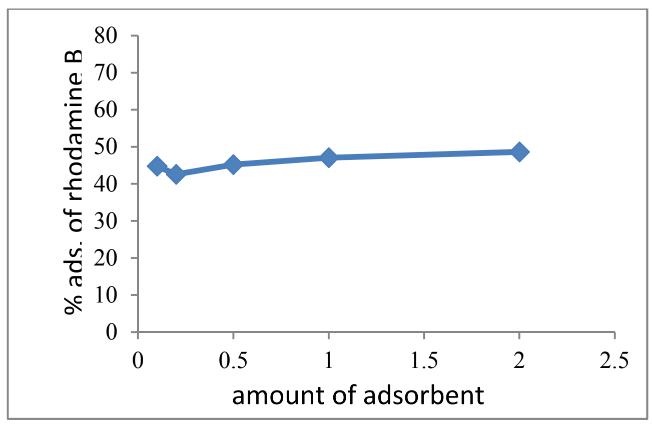

Fig. 2: Effect of adsorbent dosage on adsorption of rhodamine B with modified chitosan

3.3 Effect of contact time

It was observed that as contact time increases the %removal also showed an increase but not to a very large extent. In this study, the maximum dye removal of 49.1% was obtained at 180 minute

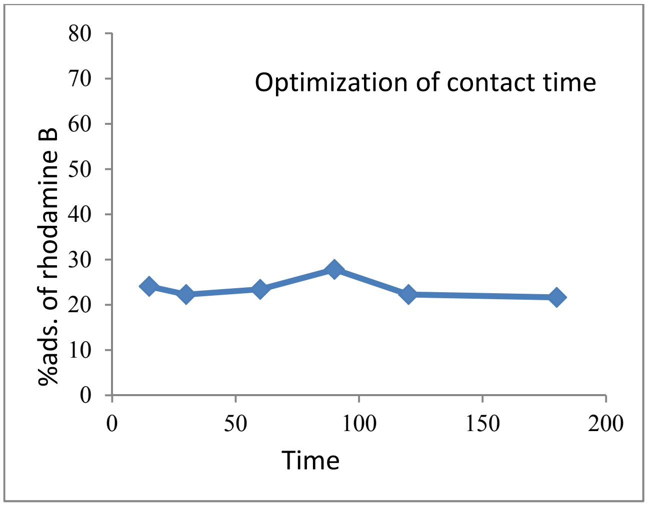

Fig. 3: Effect of contact time on adsorption of rhodamine B with modified chitosan

3.4 Effect of concentration of dye

It was observed that the percentage removal of dye decreases with the increase in concentration of dye. This is due to availability of active sites on adsorbent. The sorption becomes less efficient with increase in concentration of adsorbate. In this study, the maximum dye removal of 37.31% was obtained at 0. 5mg/l.

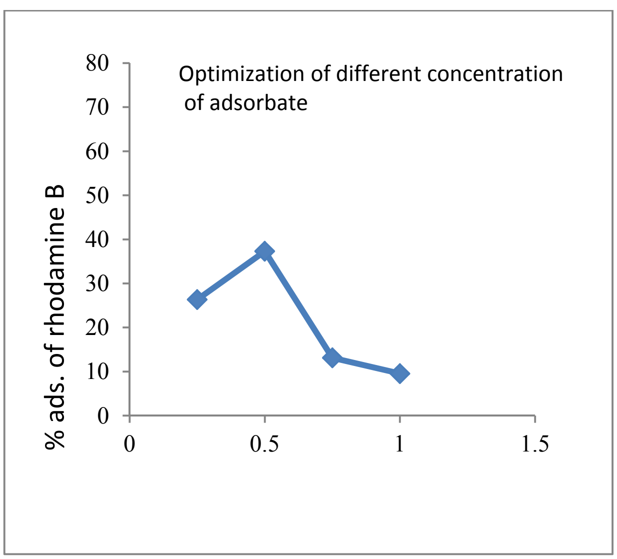

Fig. 4: Effect of concentration on adsorption of rhodamine B with modified chitosan

3.5 Effect of Temperature

It was observed that low temperature favour the high removal efficiency. In this study, the maximum percentage removal 45.0% was obtained at 25°C.

3.6 Adsorption Isotherms

An adsorption isotherm describes the relationship between the amount of adsorbate taken up by the adsorbent with concentration. The isotherms applied in this study are Freundlich and Langmuir isotherms.

3.6.1 Langmuir isotherm: The Langmuir isotherm equation is given as

$Ce/(qe)=1/qmK+Ce/qm$

Here, Ce: equilibrium concentration (mg/l), qe: the amount adsorbed at equilibrium (mg/g)

qm and K are Langmuir constants and are calculated from slope and intercept respectively of the plots (C_e/qe vs. C_e).

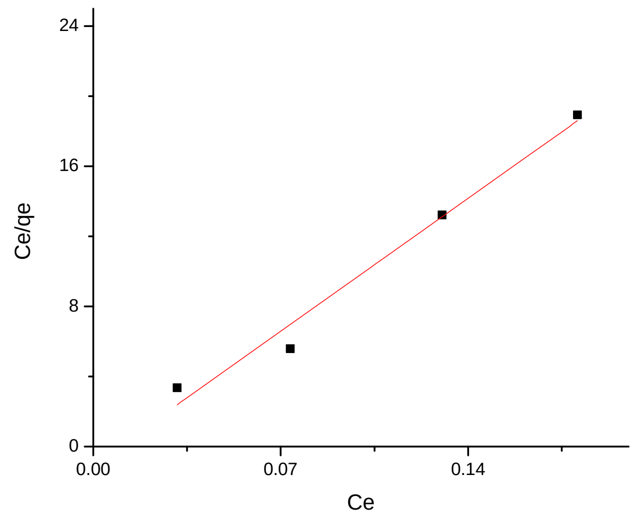

Fig. 5: Langmuir Adsorption Isotherm

3.6.2 Freundlich adsorption isotherm: The Freundlich equation is dependent on sorption at the heterogeneous surface. The equation can be calculated by assuming a decrease in logarithmic in the adsorption enthalpy with the increase in the adsorption enthalpy with the increase in the fraction of occupied sites.

The Freundlich equation is:

$q_e=K_fC_e^n$

Here, qe: the amount of dye sorbed at equilibrium per gram of sorbent (mg/g)

C_e: equilibrium concentration of dye

K_f, n are the Freundlich constants.

The graph is plotted between q_e and C_e. The Freundlich equation can be rearranged in linearized and logarithmic form in order to determine Freundlich constants. This can be shown as

$Log (q_e) = Log (K_f) + 1/n \; Log (C_e)$

K_f and 1/n are Freundlich constant.1/n is heterogeneity factor and K_f indicates the adsorption capacity. The value of n>1, indicates the favorable adsorption. The value of n and K_f are calculated from slope and intercepts of the plots of log qe vs. log C_e.

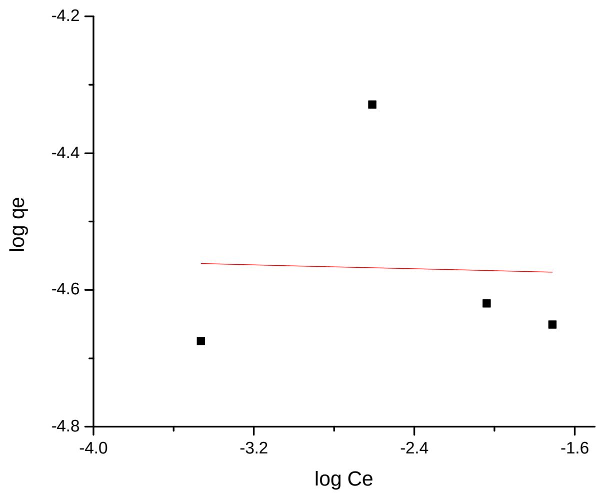

Fig. 6: Freundlich adsorption Isotherm

The value of R indicates the nature of isotherm, if the conditions are R>1, R=1, R<1 and R=0, the adsorption process is unfavorable, linear, favorable and irreversible respectively.

Langmuir Isotherm			Freundlich Isotherm		
R^2	qm (mg/g)	K(L/mg)	R^2	n	K_f
0.970	0.00922	108.15	0.4983	141.64	2.947×10^{-5}

The R^2 value indicates that Langmuir adsorption isotherm is being followed.

3.7 Adsorption Kinetics

Kinetic model is very useful to understand the mechanism of adsorption of dye and behavior of adsorbent for dye removal.

3.7.1 Pseudo-first order kinetics

This model was derived by Lagergren. If adsorption continues by diffusion through a boundary; it follows pseudo first order equation.

$$dqtdt=k_{ad}(q_e\text{-}q_t)$$

Where q_e (mg/g) is the adsorption capacity at equilibrium time and q_t (mg/g) is the adsorption capacity at time t..k_{ad} (min^{-1}) is the rate constant. The integrated rate law equation (at qe=0 at t=0) becomes

$$\log (q_e\text{-}q_t) = \log q_e\text{-}k_{ad}2.303t$$

The rate constant i.e. k_{ad} can be computed from the linear plots between log (q_e-q_t) versus t.

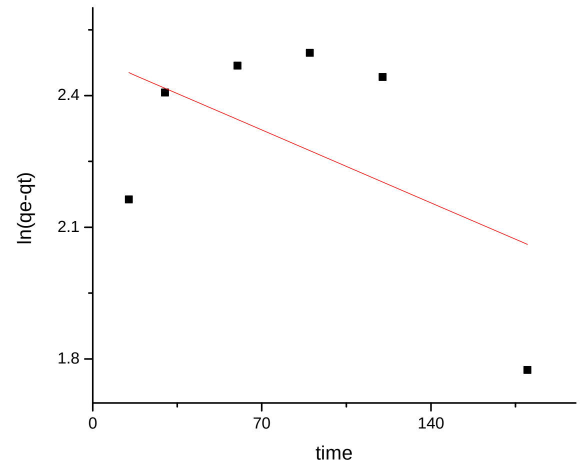

Fig. 7: Pseudo-first-order kinetics

3.7.2 Pseudo-second order kinetics

The equation of the pseudo-second order kinetics is:

$$dqt/dt=k_2(q_e\text{-}q_t)^2$$

Where, k_2 is rate constant (g mg^{-1} min^{-1}) The integrated rate law equation (at qt=0 at t=0) becomes

$$t/qt=1/kq_e^2+1/q_e t$$

qe and k_2 are calculated from slope and intercept from linear plots of t/qt vs. t.

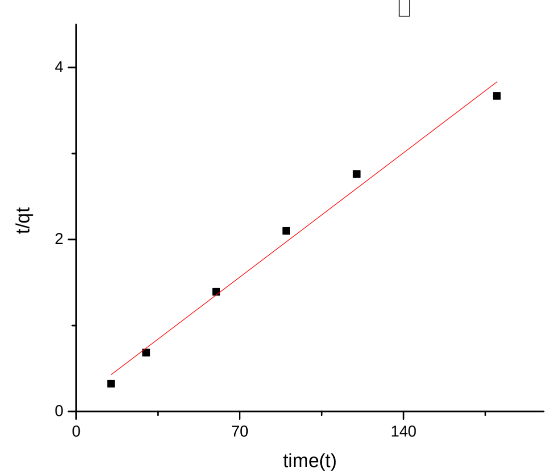

Fig. 8: Pseudo-second order kinetics

Pseudo first order kinetics			Pseudo second order kinetics		
R^2	k_{ad}	qe	R^2	Qe	K_2
0.08606	0.00237	307.397	0.9865	48.4730	0.0036

The R^2 value indicates that pseudo-second order kinetics is followed.

3.8 Thermodynamic studies

Enthalpy change (ΔH°), entropy change (ΔS°), free energy change (ΔG°) are thermodynamic parameters. The Langmuir constant K (L/mole) was used to calculate changes in Gibbs free energy according to following equations.

$\Delta G° = -RT \ln K$

$\Delta G° = \Delta H° - T\Delta S°$

Thus, we get $\ln K = -\Delta H/RT + \Delta S/R$

ΔH° and ΔS° values can be determined from the slope and intercept respectively from the linear plots of ΔG° vs. Temperature (T).

Temp.(K)	ΔG(KJ/mol)	ΔH°(KJ/mol)	ΔS°(KJ/mol)
298	-497.17	-515.56	3.5091
303	-850.63		
313	-567.35		

4. CONCLUSION

The adsorption of Rhodamine B dye onto modified chitosan was studied. It was concluded that

i) The adsorption of dye increases with increase in pH, contact time, adsorbent dosage and decreases with concentration of adsorbate and temperature.

ii) The adsorption isotherm show that based on the R^2 value, Langmuir adsorption isotherm is followed.

iii) The adsorption isotherm followed second order kinetics.

iv) The thermodynamic parameters indicate that the process is spontaneous and exothermic.

5. ACKNOWLEDGEMENT

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