



Adsorption of rose Bengal dye from aqueous solution by amberlite Ira-938 resin: kinetics, isotherms, and thermodynamic studies

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ABSTRACT

In this study, the effectiveness of amberlite IRA-938 resin for Rose Bengal (RB) dye removal from aqueous phase was evaluated. For the RB dye removal, equilibrium was achieved within 45 min because rate of adsorption was fast. The adsorption equilibrium for RB dye onto amberlite IRA-938 resin was in good agreement with Langmuir adsorption isotherm. It was observed that amberlite IRA-938 resin had excellent RB dye adsorption capacity ($q_m = 142.86 \text{ mg g}^{-1}$ at 23°C). The environmental applicability of amberlite IRA-938 resin was performed in the separation of RB dye from the tap water sample spiked with 50 mg L^{-1} RB dye solution. The breakthrough and exhaustive capacity were 100 and 325 mg g^{-1} , respectively.

Keywords: Rose Bengal dye; Wastewater; Amberlite IRA-938 resin; Adsorption; Kinetics

1. Introduction

Nowadays, the release of various types of dyes into the environment is a big environmental problem [1–3]. There are various industries such as printing, textile, leather, cosmetic, dying, and petroleum which release the huge amount of dyes due to inappropriate processing [4–8]. Due to the carcinogenic nature, these dyes effluents create environmental problems and affect the aquatic life [9–11]. The inadequate management of harmful chemicals in textile waste water also has some severe effect on the health which creates diseases such

as ulcers, irritation, chemical burns and respiratory problems [12]. Therefore, it is obvious that the removal of these types of dyes from aqueous medium is an important environmental concern which can't be ignored. To remove the dyes from wastewater, various conventional treatments such as coagulation, biological treatment, membrane technology, oxidation, adsorption, and photodegradation have been utilized, but adsorption process is one of the most effective and inexpensive procedure [13–23]. Several authors have also used ion exchange resins for the removal of dyes, metals, and other types of inorganic/organic pollutants [24–30]. The retention of Methyl Green and Malachite Green dyes using amberlite XAD-4 and XAD-2 has

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been reported by Reis et al. [31]. Clinoptilolite and amberlite XAD-4 have been efficiently used for the removal of Basic Yellow 28 which is a cationic dye [32]. Amberlite IRA-958 which is an anion exchange resin was used for Acid Orange 7 dye removal from textile wastewater [33]. Renault et al. have synthesized starch based new ion exchanger and used for the removal of C.I. Acid Blue 25 from aqueous medium [34]. Karcher et al. [26] have shown that weakly and strongly basic anion exchange resins namely Lewatit MP-62 and Lewatit S6328A exhibited good sorption features for the reactive dyes (Reactive Red 198, Reactive Red 120 and Reactive Black 5) which were present in textile industries wastewaters. Rose Bengal is also an important dye which is extensively used in printing industries and insecticides although RB is used for the treatment of eczema and psoriasis at the low level. But, at higher concentration dosage, it has severe hazardous effects on the corneal epithelium of human being.

In this study, a polystyrene based anion exchanger resin amberlite IRA-938 was applied for RB dye removal from aqueous solutions. Various operating parameters, kinetic models, and isotherm models were investigated. The amberlite IRA-938 was practically used for the removal of RB dye from the tap water sample.

2. Experimental

2.1. Reagents

Rose Bengal ($C_{20}H_2Cl_4I_4Na_2O_5$; M.W. 973.67 g mol⁻¹) was purchased from Sigma-Aldrich (Germany). Polystyrene-divinyl benzene resin amberlite IRA-938 (with trimethyl ammonium groups, Cl⁻ form) was purchased from BDH chemical Ltd. (Poole, England).

2.2. Adsorption studies

For this study, 50 mg resin was shaken with 50 mL of RB dye solution of known concentration to achieve the equilibration time. After getting the equilibration time, the resin was filtered off and the concentrations of RB dye in the solution phase were determined using a double beam UV-vis spectrophotometer at 540 nm. The effect of several parameters such as temperature, initial concentration of RB dye, and pH were also performed. For the kinetics studies, different concentrations (25, 50, and 100 mg L⁻¹) of RB dye were taken and treated with the known amount of resin. The samples were collected at various time breaks until equilibrium achieved. Isotherm and thermodynamic studies were studied by changing the reaction temperature (23–45 °C) and RB dye concentration (25–300 mg L⁻¹).

The amount of RB adsorbed at equilibrium, q_e was evaluated as:

$$q_e = \frac{V(C_o - C_e)}{W \times 1000} \quad (1)$$

where W is the weight of resin, V is the volume of RB dye, C_o and C_e are the initial and final concentrations of RB dye in solution, respectively.

3. Results and discussion

3.1. Adsorption parameters

The adsorption of RB onto resin was studied at different contact time (5–100 min). In the beginning, the adsorption of RB dye was rapid and the equilibrium was achieved in 45 min (Fig. 1(a)). In 45 min, 96% RB dye was adsorbed onto the resin. But, after 45 min, no significant change in the adsorption of RB dye was observed. The fast adsorption of RB at the initial stages indicated the presence of freely accessible ion exchange sites on the amberlite IRA-938 resin surface. The high adsorption of RB onto amberlite IRA-938 resin (Fig. 2) might be due to:

- (1) Hydrogen bonding between the nitrogen of quaternary ammonium groups and the hydroxyl group of RB
- (2) π - π interaction between the aromatic rings of amberlite IRA-938 resin and RB

The effect of pH for the adsorption of RB onto resin was performed in the pH range from 2 to 10. The RB dye adsorption was enhanced from 31.4 to 96.8% as the pH increased from 2 to 8 (Fig. 1(b)), while further increase in pH up to 10 did not change the percent removal of RB dye. In the acidic solution, the H⁺ ions were adsorbed on the surface of the resin due to the high concentration and high mobility of these H⁺ ions, and RB molecules were left in the aqueous medium [35,36]. The adsorption of RB dye onto resin was also studied by taking different RB concentration (25–300 mg L⁻¹) at pH 8 for 45 min. The removal of RB dye was decreased from 98.5 to 79.5% when RB dye concentration was increased from 25 to 300 mg L⁻¹ which might be due to the lesser number of adsorption sites for the higher dose of RB dye (Fig. 1(c)). The temperature study for the adsorption of RB was also performed at diverse temperatures, i.e. 23, 35, 40, and 45 °C. It was observed (Fig. 1(d)) that the RB dye adsorption was increased from 62 to 97.4% with the increase in temperature from 23 to

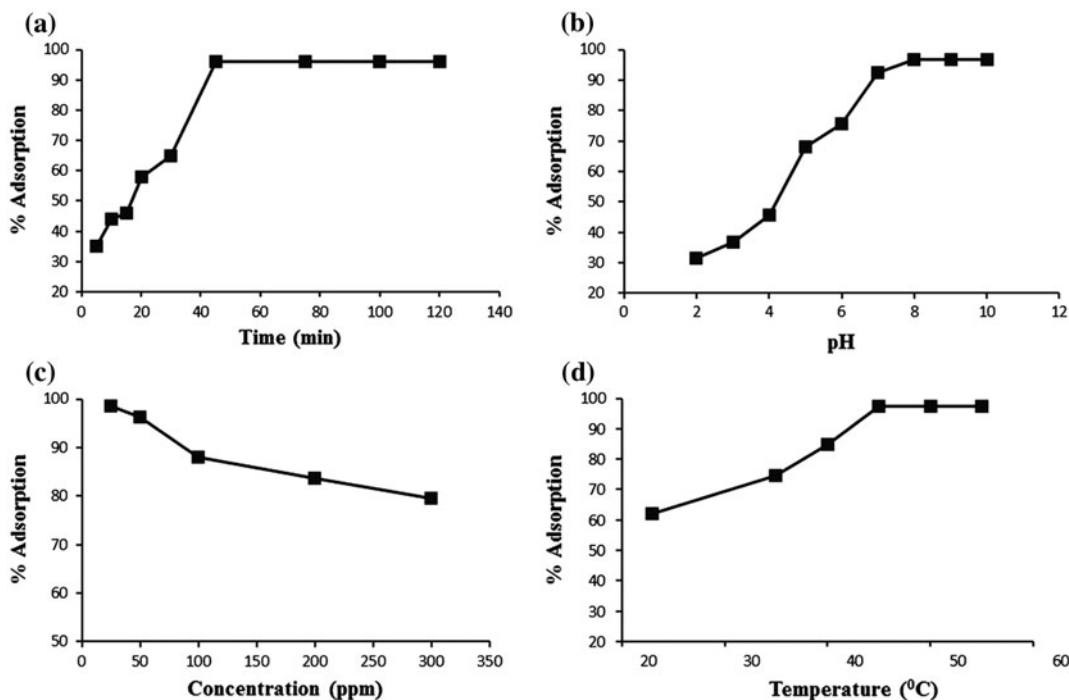


Fig. 1. Percent removal of RB dye using amberlite IRA-938 resin at different (a) time, (b) pH, (c) Initial RB concentration and (d) temperature.

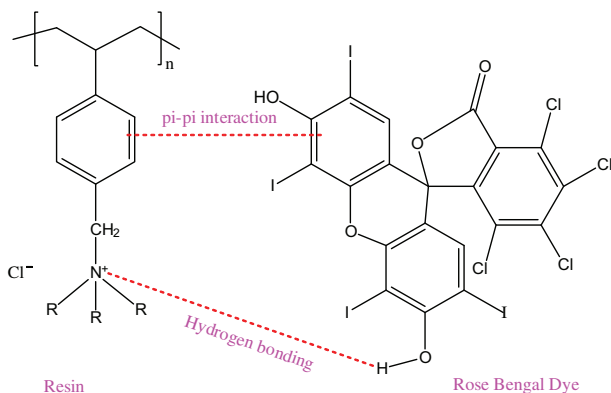


Fig. 2. Mechanism for the adsorption of RB dye onto amberlite IRA-938 resin.

45°C, respectively. There was no further change in the adsorption of RB up to 55°C. The increase in the adsorption of RB with the increase in temperature showed the endothermic nature of adsorption process.

3.2. Adsorption kinetics

The kinetics of RB adsorption onto amberlite IRA-938 resin were analyzed using pseudo-first-order,

pseudo-second-order, and intraparticle diffusion kinetic models.

The pseudo-first-order equation was given by Lagergren [37]:

$$\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (2)$$

The pseudo-second-order equation was given by Ho et al. [38]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

where q_t and q_e are the amounts of RB adsorbed at time t , and at equilibrium, respectively. The values of pseudo-first-order rate constant k_1 and pseudo-second-order rate constant k_2 were determined from the slope of the plot $\log (q_e - q_t)$ vs. t and the intercepts of the plot t/q_t vs. time, respectively.

The intraparticle diffusion model is given as [39]:

$$q_t = k_{id} t^{1/2} + C \quad (4)$$

where (C is the intercept and K_{id} is the intraparticle diffusion rate constant). If the plot passes through the

origin, then the rate-limiting process is only due to the intraparticle diffusion [40,41]. Otherwise, some other mechanism is also included along with intraparticle diffusion [38]. The values of different constant parameters and correlation coefficients are given in Table 1. From the results, it was found that the experimental data were well fitted to the pseudo-second-order model with better value of correlation coefficient ($R^2 > 0.990$). The intraparticle diffusion plot for the adsorption of RB onto amberlite IRA-938 did not pass through the origin. Consequently, intraparticle diffusion was not the only rate determining step for the RB adsorption mechanism.

3.3. Adsorption isotherms

Langmuir and Freundlich isotherm models are given as [42,43]:

$$\frac{1}{q_e} = \frac{1}{Q_m} + \frac{1}{bQ_m C_e} \quad (5)$$

$$\log q_e = \log K_f + \frac{1}{n} \ln C_e \quad (6)$$

where (q_e is the amount of adsorbed RB, C_e is the equilibrium concentration of RB, Q_m and b are the Langmuir constants and K_f and n are the Freundlich constants).

The values of Q_m and b (Table 2) were calculated from the intercept and slope of linear plots of $1/q_e$ vs. $1/C_e$, respectively. As the temperature was enhanced from 23 to 45°C, Q_m values were increased from 142.86 to 285.71 mg g⁻¹. It was also noted that amberlite IRA-938 had better monolayer adsorption capacity in comparison with the previously studied adsorbents [44,45]. The values of b were also increased with the increase in temperature which showed the

endothermic adsorption process. The K_f and n parameters were evaluated from the intercept and slope of the linear plots of $\log q_e$ vs. $\log C_e$, respectively. The values of R^2 were higher for Langmuir isotherm which confirmed the better applicability of this model.

The values of separation factor (R_L) can be evaluated as [46]:

$$R_L = \frac{1}{1 + bC_0} \quad (7)$$

The values of R_L in this study were lesser than one which showed the favorable nature of adsorption for RB onto amberlite IRA-938 resin (Table 2).

3.4. Thermodynamic studies

The values of thermodynamic parameters, ΔH° and ΔS° , were evaluated from the slopes and intercepts of the plots of $\ln K_c$ vs. $1/T$ using the equation:

$$\ln K_c = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (8)$$

The ΔG° was calculated as:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (9)$$

The values of K_c were calculated by q_e/C_e . The values of all thermodynamic parameters are given in Table 3. The adsorption of RB dye onto amberlite IRA-938 resin was endothermic due to the positive values of ΔH° . The negative values of ΔG° designated the degree of spontaneity of the RB adsorption onto amberlite IRA-938 resin.

Table 1
Kinetic parameters for RB adsorption of onto amberlite IRA-938 resin

Kinetic models	Parameters	25 ppm	50 ppm	100 ppm
Pseudo-first-order	q_e (mg g ⁻¹)	15.4	33.8	69.2
	k_1 (min ⁻¹)	1.81×10^{-2}	1.93×10^{-2}	2.00×10^{-2}
	R^2	0.940	0.900	0.899
Pseudo-second-order	q_e (mg g ⁻¹)	27.10	58.48	126.58
	k_2 (g mg ⁻¹ min ⁻¹)	26.4×10^{-4}	9.36×10^{-4}	3.5×10^{-4}
	R^2	0.991	0.990	0.990
Intraparticle diffusion	k_{id} (mg g ⁻¹ min ^{-1/2})	3.12	6.85	13.81
	C (mg g ⁻¹)	1.47	1.48	3.17
	R^2	0.937	0.941	0.947

Table 2
Isotherm model parameters for RB adsorption of onto amberlite IRA-938 resin

Equilibrium model	Parameters	23°C	35°C	40°C	45°C
Langmuir isotherm	q_m (mg g ⁻¹)	142.86	161.29	200	285.71
	b (L mg ⁻¹)	7.69×10^{-2}	9.01×10^{-2}	14.1×10^{-2}	37.8×10^{-2}
	R_L	0.84	0.81	0.74	0.20
	R^2	0.989	0.990	0.993	0.990
Freundlich isotherm	K_f (L mg ⁻¹)	1.21	1.57	3.18	11.2
	n	1.11	1.043	1.02	1.02
	R^2	0.988	0.987	0.976	0.973

Table 3
Thermodynamics parameters for RB adsorption of onto amberlite IRA-938 resin (RB concentration 25 mg L⁻¹; temperature range 23–45°C)

C_o (mg L ⁻¹)	ΔH° (J mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)	ΔG° (J mol ⁻¹)			
			296 K	308 K	313 K	318
25	73.48	0.25	-0.52	-3.52	-4.77	-6.02

3.5. Breakthrough study

Hundred milligram of amberlite IRA-938 resin was taken in the glass column and 1.0 L of RB dye solution (50 mg L⁻¹) was passed through the column at the flow rate of 1 mL min⁻¹. The eluted RB dye solution was collected in 50 mL fractions and its concentration was evaluated by UV-visible spectrophotometer. The breakthrough curves (Fig. 3) showed that 200 mL Milli-Q water was eluted through the column without identifying RB dye in the effluent. The breakthrough and the exhaustive capacities in Milli-Q water was calculated 100 and 325 mg g⁻¹, respectively.

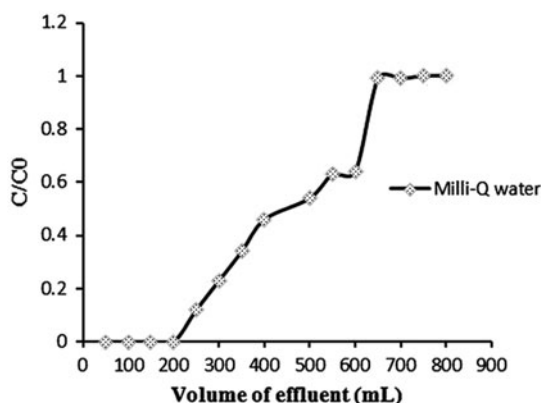


Fig. 3. Breakthrough curves for the adsorption of RB dye onto amberlite IRA-938 resin.

3.6. Environmental applications

In order to explore the environmental application of the amberlite IRA-938 resin, removal of RB was performed in a tap water sample by batch process. The tap water sample was taken from the Department of Chemistry, KSU, Saudi Arabia. Fifty gram RB dye was spiked in 1.0 L of tap water sample and the solution pH was kept 8. In a conical flask, 50 mL of tap water sample was shaken with 50 mg of amberlite IRA-938 resin for 45 min. After 45 min, the RB dye concentration of in the solution phase was determined. It was noted that the adsorption of RB onto amberlite IRA-938 resin was 92.3% which concluded that there was no much more effect of the matrix on the adsorption of RB by amberlite IRA-938 resin.

4. Conclusion

Amberlite IRA-938 resin was found to be an excellent material for the RB dye removal from aqueous solution. The adsorption of RB dye onto amberlite IRA-938 resin was dependent upon parameters such as pH, contact time, RB concentration, and temperature. Langmuir isotherm and pseudo-second-order kinetic models were obtained as the most suitable models for describing RB removal through the adsorption. It was observed that the resin had outstanding RB dye adsorption capacity ($q_m = 142.86$ mg g⁻¹ at 23°C) which was considerably high. Besides, the

results of thermodynamic study exhibited that RB adsorption onto amberlite IRA-938 was endothermic and spontaneous.

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