

Decolorization of Rhodamine B Dye by Hydrogel Nanocomposite: Thermodynamic and Kinetic Studies

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ABSTRACT

Rhodamine B is used extensively in textile dyes and agricultural pesticides as fish pests. Hydrogel is a type of sorption technique used as a sorbent. As of now, adsorption is viewed as a cost-effective method that may be used as an alternative to traditional contamination treatment methods. Several techniques were utilized to determine the surface characteristics before and after the adsorption method, like fourier transform infrared (FT-IR) and field emission scanning electron microscopy (FESEM) techniques. The effect parameter of the adsorption method was studied, such as the effect of equilibrium time and weight. The data showed that the best removal percentage was (E%=96.546%) and adsorption capacity (188.0 mg/g) in the same order. Thermodynamic factor studies have shown that the reaction is spontaneous, exothermic, and convenient. The sorption isotherm of Rhodamine B onto sodium alginate-g-poly (acrylic acid)/GO composite hydrogel was analyzed utilizing two models First order and second order. The second order was the poorest in a fit of the liner curve and the better.

Keywords: Acrylic acid, Adsorption, Hydrogel, Removal, Rhodamine B, Sodium alginate.

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INTRODUCTION

Textile dyes are considered one of the utmost dangerous carcinogens and toxic substances, as carcinogenic dyes spread in drinking water and groundwater, are deposited on marine organisms, and cause poisoning.¹⁻³ Therefore, textile dyes are considered a dangerous and persistent water pollutant because they do not have the ability to biodegrade due to their complex aromatic structures. The adsorption technology was used as an easy, simple, and inexpensive technique for the complete removal of textile dyes because of their harmful effect on living organisms and their removal from drinking water.^{4,5} Rhodamine B (RhB) one of the utmost common dyes, is widely utilized in industries like dyeing, printing, textiles, paper, leather, etc. Poisoning and irritation of the skin. Rhodamine B (RhB) is a chemical compound that crystals powder soluble in water^{6,7} chemical composition is shown in Figure 1.

Sodium alginate (SA) is a natural anionic, bio-degradable, and renewable biopolymer that has drawn considerable interest in the last years. Alginate has been most utilized in various commercial implementations like food, pharmaceuticals, and cosmetics. Natural polymers' stability, solubility, and adsorbing ability can be manipulated via grafting.⁸⁻¹⁰ Recently, composite hydrogels have been of great use in many applications. Hydrogels are hydrophilic polymers and are considered three-dimensional networks that can absorb and retain a large amount of water.¹¹ Incorporation of graphite oxide into a hydrogel matrix increases the hydrogel's water absorption capacity, increases surface area and mechanical strength, and is also considered low cost and chemical stability.^{12,13}

This study used a readily available and eco-friendly absorbent material with low economic cost and high efficiency in removing the form from its aqueous solution. The thermodynamic factors and adsorption kinetics were studied.

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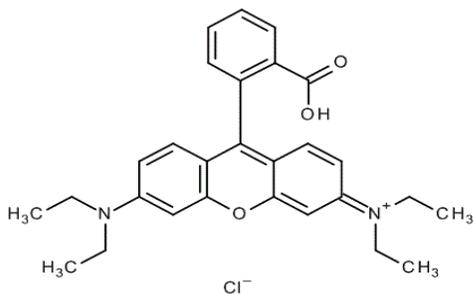


Figure 1: Chemical structure of Rhodamine B (RhB).

MATERIALS AND METHODS

Acrylic acid (AA), Graphene oxide (GO), potassium persulfate (KPS), N, N'-methylene-bisacrylamide (MBA), and Rhodamine B (RB) dye were purchased from Sigma Aldrich. A standard solution of Rhodamine B dye was prepared via dissolving 0.5 gm in 500 mL DW (500 mg/L). A series of Rhodamine B Dye concentrations about 10–100 mg/L. The solution pH of the Rhodamine B Dye natural is about 6.8.

Preparation of SA-g-poly(AA)/GO Composite

For the preparation of SA-g-poly(AA)/GO hydrogel, different steps begin with the preparation of the hydrogel (0.5 g in 20 mL) of Sodium alginate and (5 mL) of AA. The mixture is stirred very well by using an incubator shaker with the addition (0.8% w/v) of Graphene oxide via (1:10) a ratio of the mixture hydrogel. Then the cross-linker agent, MBA (0.05 g in 2 mL), is added, and the initiator KSP (0.03 g in 2 mL) passes the N₂ for one min. after placing the solution in the poly-ethylene test tubes. The tubes are then placed in a water bath control temperature of 65°C.

Adsorption Studies

Adsorption experiments were performed in batch Shaker water bath shaker in 10 mL conical flasks. The effect of several adsorption factors, like equilibrium time, the weight of the hydrogel, thermodynamics, and Kinetics, were studied. Adsorption experiments were conducted at 25 °C and agitation

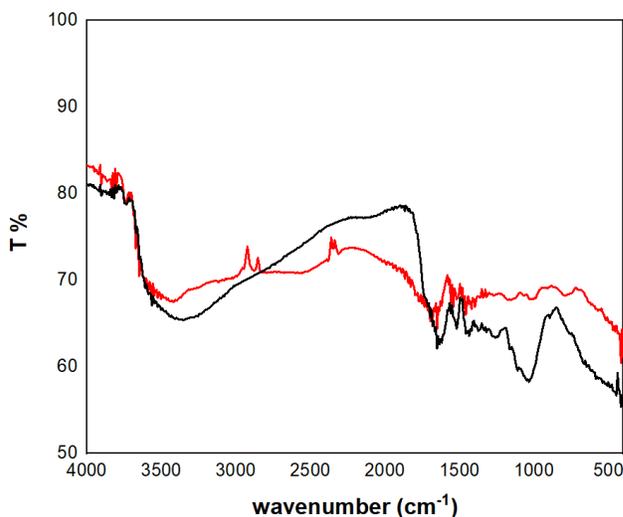


Figure 2: FT-IR spectra to determine Rhodamine B (RB) dye onto SA-g-poly(AA)/GO hydrogel before and after adsorption.

of 120 rpm. The residual dye concentration in each aliquot was estimated via a UV-visible spectrophotometer. The adsorption capacity (Q_e) and removal percentage ($E\%$) adsorption was calculated in Eq. (1,2).

$$E\% = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (1)$$

$$Q_e = \frac{(C_0 - C_e)V_{ml}}{(W \text{ gm})} \quad (2)$$

RESULTS AND DISCUSSIONS

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra of SA-g-poly(AA)/GO hydrogel before adsorption and after dye-loading on the surface show that some peaks were shifted, as shown in Figure 2. In the SA-g-poly(AA)/GO hydrogel spectrum before adsorption, a strong peak at 3430 cm⁻¹ represents the -OH stretching of the phenol group. The peak at 3004 cm⁻¹ indicates-CH₂ stretching of an aliphatic compound. Therefore the spectrum of SA-g-poly(AA)/GO hydrogel after dye-loading notes that no new peak appears on the surface after the adsorption method, but there is a variance only in the intensity of adsorption, and this is evidence of the occurrence of the physical adsorption.^{14,15}

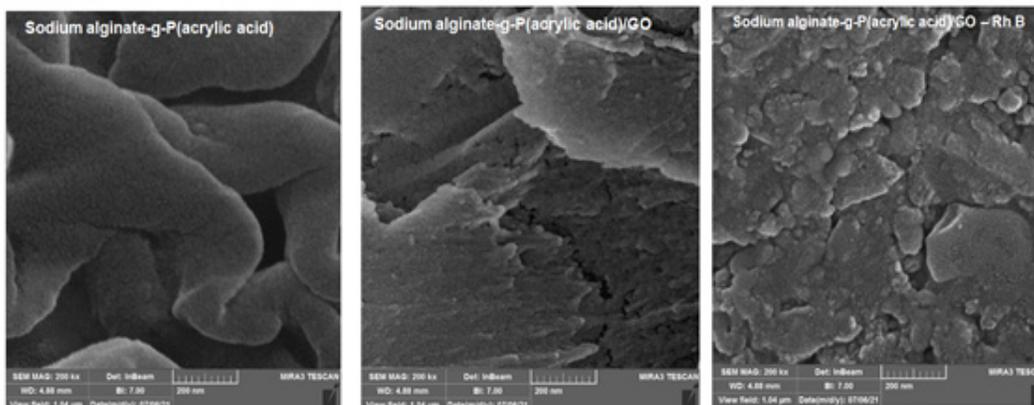


Figure 3: FESEM image of SA-g-poly(AA) hydrogel and SA-g-poly(AA)/GO hydrogel before and after adsorption.

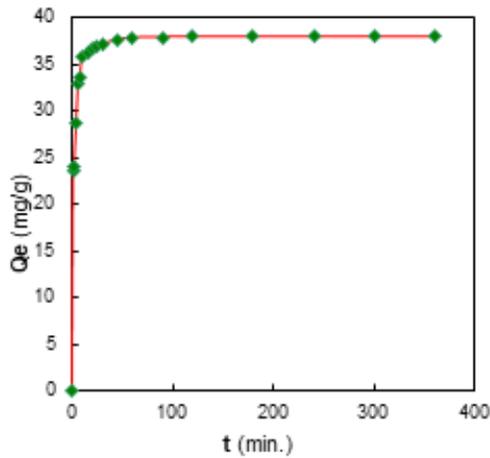


Figure 4: Effect of equilibrium time of Rhodamine B

Field emission scanning electron microscopy (FESEM)

Figure 3 shows that the surface of SA-g-poly(AA) hydrogel contains many inactive active sites and has a cloud-like shape, whereas SA-g-poly(AA)/GO hydrogel before the adsorption process shows an increase in surface area, random agglomerations, and filling of all active sites. This indicates that the adsorption process has occurred.⁹

Effect of Equilibrium Time

Figure 4 shows the effect of equilibrium time on dye adsorption by SA-g-poly(AA)/GO hydrogel. The amount of dye adsorbed increase rapidly and is noticeable during the 10 min, then the amount of dye adsorbed increases gradually until the contact time is reached. It was found that the better time for adsorption of Rhodamine B is 60 minutes.¹²

Weight of SA-g-poly (AA)/GO Hydrogel

Percentage removal E% of Rhodamine B was studied via varying the adsorbent dosage. The E% of adsorption increased

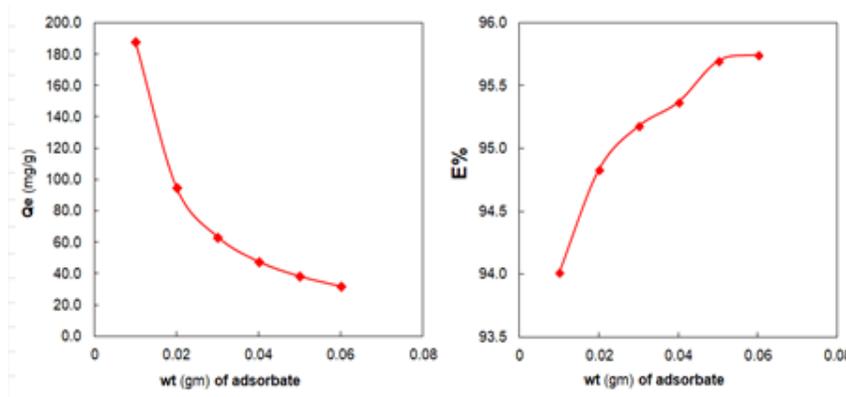


Figure 5: Effect of SA-g-poly(AA)/GO hydrogel weight on the adsorption capacity and percentage removal of Rhodamine B

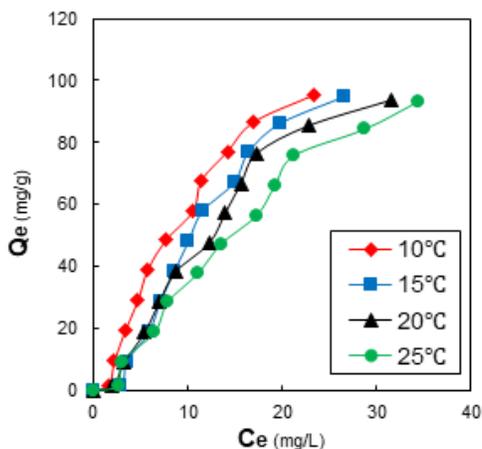


Figure 6: Adsorption isotherms of dye onto SA-g-poly (AA)/GO hydrogel at different temperatures

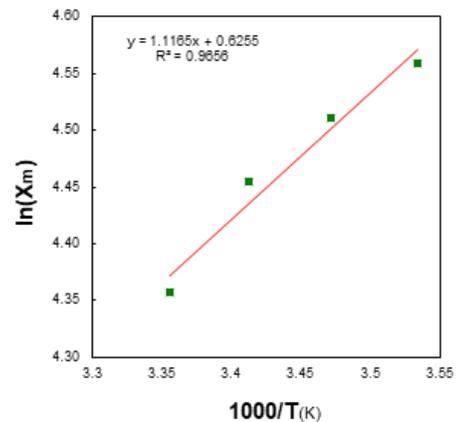


Figure 7: Plot $\ln X_m$ against the absolute temp. of the adsorption of Rhodamine B onto surface

Table 1: Influence of temperature on the maximum adsorbed amount for adsorption of dye onto surface

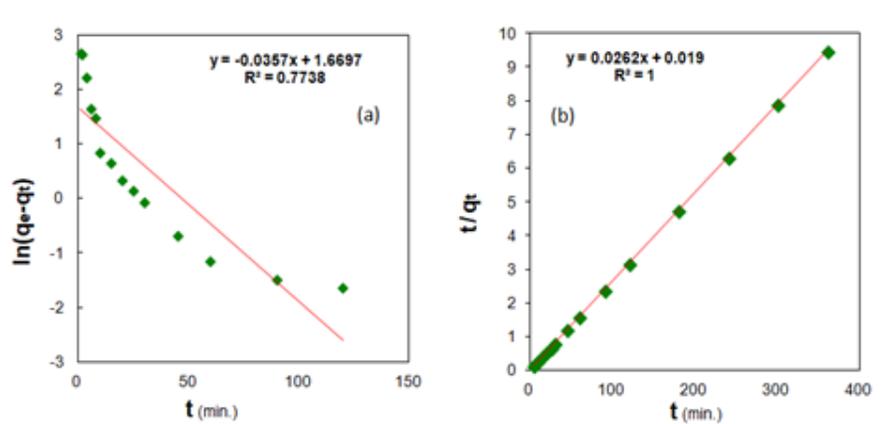
Temp. (°)	Temp. (K)	1000/T(K)	Ce	Xm	ln (Xm)
10	283	3.533	23.3	95.5	4.559
15	288	3.472	23.3	91	4.510
20	293	3.412	23.3	86	4.454
25	298	3.355	23.3	78	4.356

Table 2: thermodynamic parameter of dye onto SA-g-poly (AA)/GO hydrogel

ΔH (kJ.mol ⁻¹)	ΔG (kJ/mol)	ΔS (J/mol.K)	Equilibrium Constant (K)
-9.283	-7.106	-7.691	18.455

Table 3: Kinetic parameters for the adsorption of Rhodamine B

First-order			Second-order		
K ₁	q _e	R ²	K ₂	q _e	R ²
0.032	5.131	0.7738	0.036	38.163	1.0000

**Figure 8:** Kinetic models: (a) PFO (b) PSO

with an increase in the weight of SA-g-poly (AA)/GO Hydrogel. However, the quantity of dye adsorbed per unit weight of adsorbent decreased with an increase in adsorbent dose by about 0.01–0.06 g, as shown in Figure 5. As the amount of adsorbent increases, the number of active sides available for adsorption increases; thus, the removal percentage is too high.^{16,17} Hence, the best removal percentage E% of rhodamine dye (95.666%) and the adsorption efficiency (40.432 mg/g) at the adsorption dose of 0.05 g. thus, the adsorption of Rhodamine B increased with the sorbent dosage and reached an equilibrium value after a certain sorbent dosage (0.06 g) for the adsorbent.

Thermodynamic Parameter

Figure 6 appear increases in the quantity of Rhodamine B adsorbed with the solution temperature increase. This indicates that the adsorption process is endo-thermic; the kinetic energy of molecules Rhodamine B rise with the increased temperature, therefore facilitating the diffusion of the Rhodamine B adsorbed within the pores of the SA-g-poly(AA)/GO hydrogel that the rate of adsorption diffusion in surface pores would contribute to adsorption of Rhodamine B at rising temperatures.^{18,19}

Table 1 shows the thermodynamic parameter of Rhodamine

B dye adsorption on the surface SA-g-poly(AA)/GO hydrogel; Free Gibbs energy (ΔG) has a negative value indicating that the adsorption process is (spontaneous), entropy (ΔS) with a positive value for Rhodamine B dye leads to an increase in the degrees of freedom of the dye molecules, (ΔH) with a negative value that the adsorption process of Rhodamine B dye is exothermic, (ΔH) with a negative value for Rhodamine B dye indicates that the adsorption process is an exo-thermic process.²⁰

The basic thermodynamic quantities of adsorption of Rhodamine B on composite were estimated via calculating values X_m at several solution temperatures (Figure 7). The heat of adsorption enthalpy may be found from Van't Hoff equation (equation (2)), free change energy (ΔG) could be calculated by equation (3), and entropy (ΔS) was calculated from Gibb's equation (equation (2)). Table (1) and Figure (7) demonstrate these calculations.

$$\ln X_m = (-\Delta H)/RT + \text{constant} \quad (3)$$

$$\Delta G = -RT \ln K_{eq} \quad (4)$$

$$\Delta G = \Delta H - T \cdot \Delta S \quad (5)$$

Table 2 shows the basic thermodynamic values of the adsorption of dye on composite. Adsorption of vander Waals kind is suggested as indicated via these values.

Kinetics Studies

Table 3 shows the kinetic factors obtained from the Pseudo First order (PFO) and pseudo-second-order (PSO) equations. Regardless of the convergence of the pseudo-second-order q_{cal} value to q_{exp} , the ($R^2=1$) value of the PSO is obtained equal to one for the studied dye concentrations.^{21,22} These results confirm that the spurious second-order Kinetics describes the adsorption process best than the first-order model, where the value of ($R^2 = 0.7738$) was as shown in Figure 8.²³

CONCLUSION

Here, it was adopted that material prepared have high efficiency in removal pollutants, including dyes from drinking water, the absorbent material is available and inexpensive, high ability to swell and retain the pollutant inside, and Graphene oxide was loaded to increase the surface area and also increase the surface capacity in the removal the pollutant. The best removal percentage (96.54%) and the adsorption kinetics were studied through the results. It was found that it conforms to a second model depending on the (R^2) value.

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