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Research Article

Poly(Maleimide-alt-styrene) as a Sorbent for Remove of Rhodamine 6G dye from Aqueous Solutions

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ABSTRACT

This work presented results on the removal of Rh 6G dye from aqueous solutions using the alt-maleimide-styrene copolymer (MSC) as an adsorbent. The effects of pH, sorbent dosage, contact time, temperature, and initial dye concentration on the sorption degree and sorption capacity of the sorbent were investigated. The obtained experimental data have been analyzed using Langmuir and D–R models. Several kinetic and thermodynamic parameters of the adsorption process were determined and a possible sorption mechanism has been suggested.

Key words: Poly(Maleimide-alt-styrene), Remove of dyes, Rhodamine 6G, Langmuir, Water Purification

1. INTRODUCTION

A number of works on the sorption of Rhodamine 6G (Rh 6G) dye from aqueous solutions by sorbents with different compositions and structures have been published in the literature [1-9]. A copolymer fumaric acid with acrylic acid has been used as an adsorbent to remove Rh 6G dye from the aqueous solution [1]. The effect of adsorbent dosage, contact time, pH, temperature, and ionic strength on the sorption degree and sorption capacity has been studied. The experimental data obtained have been analyzed using Langmuir, Freundlich, and Temkin models. The results show that the polymer hydrogel has an effective sorbent for removing Rh 6G from aqueous solutions. The sulfonated alt-maleic anhydride (MA)-styrene copolymer was used as an effective adsorbent to remove organic dyes from aqueous solutions [2]. Cross-linked poly(N-vinyl caprolactam-co-maleic acid) microparticles were used as a sorbent for removing Rh 6G dye from an aqueous solution [3]. The effects of various parameters, such as pH, adsorbent dose, temperature, initial dye concentration, and contact time on sorbent adsorption capacity have been studied. The equilibrium adsorption data better corresponded to the Langmuir isotherm model. The maximum adsorption capacity at pH = 10 was 2012 mg/g. Experimental data have been well described by the pseudo-second-order model and has been synthesized magnetic manganese graphene oxide nanocomposite for Rh 6G dye removal from aqueous solutions [4]. The adsorbent was characterized by SEM, FTIR, and XRD. Experiments have been carried out at pH 6, the equilibrium time of 15 min, and the adsorbent amount of 0.6 g/L. Under this condition, the adsorption efficiency was investigated through Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich (D–R) isotherm models. The adsorption process was well fitted to Langmuir isotherm. The sorption capacity of the sorbent was 24.96 mg/g in 6 min. The high values of ΔH° (146.19 kJ/mol) and ΔG° (−0.04 kJ/mol) indicated that the adsorption mechanism was endothermic and physico-sorption in nature. Work [5] provides data on the removal of the Rh 6G dye from an aqueous solution by alt-MA-styrene copolymer (alt-MA-St), crosslinked with glycerin. Effects of pH, contact time, sorbent dosage, initial concentration of dye, and temperature on removal degree have been studied. The equilibrium sorption data were fitted to Langmuir, Freundlich, and D–R isotherms. The maximum equilibrium sorption capacity from the Langmuir equation is equal to 14.73 mg/g. The found value of the mean sorption energy from the D–R equation (5.472 kJ/mol) specifies that sorption of the Rh 6G dye by synthesized polymer sorbent has a physical character. The morphological features and surface characteristics of the dye-loaded sorbent after sorption have been studied using SEM method. The kinetic data were correlated well with the pseudo-second-order model. The positive values of the thermodynamic parameters ΔG° (7.45-6.04 kJ/mol), ΔH° (18.378 kJ/mol), and ΔS° (0.0374 kJ/mol/K) indicate that the adsorption process is endothermic and randomness in nature. Sorption experiments have been performed to remove the Rh6G dye from the aqueous solution using an alt-MA-St-octene-1 terpolymer, crosslinked with triethanolamine [6]. The working variables examined were adsorbent dosage, solution pH, contact time, initial dye concentration, and temperature. Langmuir's model successfully described the obtained experimental data. The design value of the maximum equilibrium sorption capacity is 20.28 mg/g. The found value of the mean sorption energy (10.204 kJ/mol) from equation D-R is more than 8.0 kJ/mol, which indicates the chemical nature of the sorption process of the Rh6G dye with the synthesized polymer sorbent. The adsorption data were modeled using pseudo-first and pseudo-second-order kinetic equations and the adsorption kinetics were found to correspond to the pseudo-second-order model. Furthermore, the thermodynamic parameters of the adsorption process have been calculated. The positive values of the ΔG° (3.718–5.276 kJ/mol) at 293–223 K and the positive value of the ΔH° (20.388 kJ/mol) indicate that the sorption process is non-spontaneous and endothermic in nature. The positive value of ΔS° (0.052 kJ/mol/K) shows the increasing randomness during the adsorption process. Waste-

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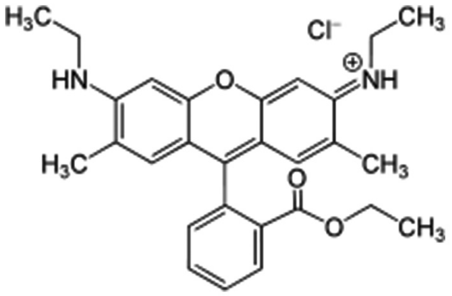
ground coffee powder was used as an effective adsorbent to remove Rh6G dye from the aqueous solution [7]. The effect of temperature, ionic strength, and coexisting anions on sorption results was investigated. The results showed that the adsorption capacity increased with increasing sorbent dosage, contact time, but no changes were observed with increasing temperature. The adsorption kinetics of Rh 6G followed the pseudo-second-order model, and it was found that the equilibrium data correspond to the Freundlich model. The magnetic biochar sorbent was obtained based on a composite of Fe_3O_4 nanoparticles on the surface of the biochar, obtained from rice husks, and the sorption of Rh 6G dye with a synthesized magnetic sorbent was investigated [8]. Kinetic and thermodynamic studies were carried out to study the adsorption mechanism. The efficiency of removing Rh 6G on a magnetic Fe_3O_4 composition is 94%. The adsorption isotherm and kinetic studies showed that the Langmuir model, pseudo-first-order, and pseudo-second-order models described the adsorption of Rh on magnetic Fe_3O_4-biochar well. Experiments were conducted on sorption Rh 6G from an aqueous solution using Palm Shell powder as an adsorbent [9]. To investigate the sorption mechanism, the adsorption data were modeled using pseudo-first- and pseudo-second-order equations. The adsorption kinetics were found to correspond to a pseudo-second-order model. The equilibrium isotherm was analyzed using Langmuir and Freundlich isotherms. Parameters have been defined for each model. The exhaustive capacity was 105.0 mg/g for Rh 6G at 25°C. The negative value of the free energy change indicates the spontaneous nature of the adsorption.

This work presented results on the removal of Rh 6G dye from aqueous solutions using the alt-maleimide-styrene copolymer (MSC) as an adsorbent. The effects of pH, sorbent dosage, contact time, temperature, and initial dye concentration on the sorption degree and sorption capacity of the sorbent were investigated. The obtained experimental data have been analyzed using Langmuir and D–R models. Several kinetic and thermodynamic parameters of the adsorption process were determined and a possible sorption mechanism has been suggested.

2. EXPERIMENTAL

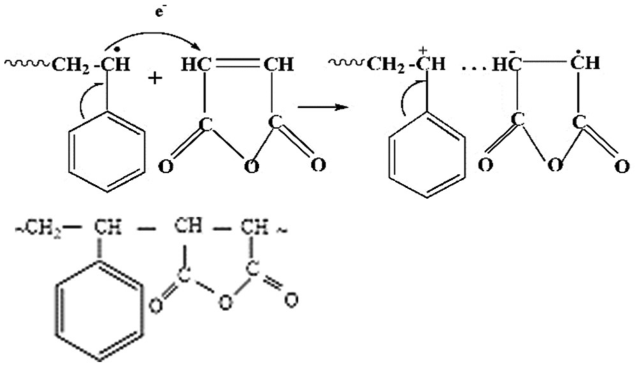
2.1. Materials

MA was recrystallized from benzene, styrene (St) was distilled again (temp.144–145°C), azobisisobutyronitrile was recrystallized from ethanol, urea (carbamide) $CO(NH_2)_2$, mol. massa 60.06 g/mol, and m.p.133–135°C (SOCAR Carbamide Plant Sumgait, Azerbajan). The cationic dye Rh 6G (mol. massa 479.02 g/mol and UV-absorption maximum 524 nm) with an empirical composition of $C_{28}H_{31}ClN_2O_3$ has the following structure (Wikipedia):

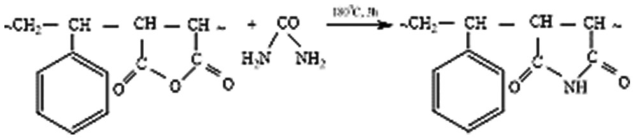


2.2. Preparation of the Sorbent

The preparation of MSC was carried out in two steps: Synthesis of the alt-MA-St copolymer and its reaction with urea. In the first step, alt-MA-St was synthesized by radical copolymerization of MA and St in benzene under 80^0C in the presence of AİBN as an initiator. The copolymerization proceeds to form a donor-acceptor complex resulting in the formation of alt-MA-St copolymer macromolecules.



The second step of synthesis of the MSC was carried out according to the known method [10]: A mixture of 4.04 g (0.02 mol) of alt-MA-St and 0.6 g (0.01 mol) of urea was placed in an oven at 180°C for 3 h. After cooling to room temperature, the obtained solid mass was washed with bidistilled water, then with acetone, and dried at 40°C in a vacuum drying oven. The MSC formation scheme is shown below:



UV-spectra were taken on a spectrophotometer SPECORD 210 PLUS (Germany), the SEM image was taken on a scanning electron microscope JEOL JSM-7600F (Japan), and the pH was measured by a pH- meter pH-420 Akvillon (Romania).

2.3. Adsorption Experiments

A stock solution of Rh 6G dye with a concentration of 500 mg/L was prepared in double-distilled water and the experimental solutions with the desired concentration were obtained by dilutions stock solution. Experiments to study the adsorption of the Rh 6G dye by synthesized sorbent were carried out according to the procedure, described in the works previously published by us [5,6]. The sorption degree (%) Rh 6G dye and sorption capacity (mg/g) of the sorbent have been calculated by Eqs (1) and (2), respectively:

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

$$\text{Sorption capacity (mg/g)} = \frac{(C_0 - C_e) \times V_{sol}}{m_{sorb}} \quad (2)$$

Where C_0 and Ce (mg/L) are initial and equilibrium concentrations of Rh 6G, respectively, $Vsol$ (L) is the volume of the dye solution subjected to sorption, and m_{sorb} (g) is the mass of sorbent.

3. RESULTS AND DISCUSSION

3.1. Effect of pH

The pH effect on the degree of Rh 6G sorption was studied under the following conditions: Initial dye concentration 75 mg/L, sorbent weight 3.0 g/L, sorption time 30 min, and 20°C. Under these conditions, the pH of the solution changed in the range 3–9. The results show that in a highly acidic medium (pH=3), the sorption rate is low (7.4%). It is known that for cationic dyes, lower adsorption in a strongly acidic medium is due to the presence of an excess of H^+ ions, which compete with the cationic groups of the dye at the active sites of the adsorbent [11]. Thus, high sorption values at pH above three are explained by electrostatic attractive forces between the immobilized negatively charged sorbent and the positively charged dye. It was found that a high sorption value (30.72%) was observed at pH = 6. Since a high sorption rate is observed at pH 6, subsequent experiments were carried out at pH 6.

3.2. Effect of Sorbent Dosage

The sorbent amount for sorption varied from 1.0 to 4.0 g/L at Rh 6G concentration 200 mg/L, V_{sol} = 0.04 L, 20°C, 30 min, and pH 6. The obtained results show that the sorption degree increases when the sorbent amount increases from 1.0 to 3.0 g/L. A further increase in the amount of sorbent practically does not lead to a change in the sorption degree. Therefore, the amount of sorbent 3.0 g/L^{-1} was taken as the working amount and used in subsequent experiments.

3.3. Effect of the Rh6G Initial Concentration

The sorption degree of the Rh 6G and the sorption capacity of the sorbent strongly depend on the dye's initial concentration. The dye concentration was varied in the range of 75–225 mg/L at the sorbent dosage 3.0 g/L, 30 min, 20°C, V_{sol}=0.04 L, and pH 6, The results show that the sorption degree decreased from 30.72 to 12.49%. This can be explained by the saturation of the sorbent-specific sites with an increase in the initial dye concentration. At the same time, the sorption capacity of the sorbent increases from 7.68 to 9.37 mg/g. Therefore, it can be concluded that the experimental maximum sorption capacity (q_{exp}) of the sorbent under the studied conditions is 9.37 mg/g. The results obtained by the dependence of the sorption degree and sorption capacity on the initial concentration of the dye were processed in the coordinates of the isotherm equations: Langimur and D–R and the values of the sorption process parameters have been calculated.

3.4. Langmuir and D–R Isotherms

The Langmuir isotherm describes monolayer adsorption and the linear form of the isotherm equation is as follows:

$$C_e/q_e=1/(q_{max}\,K_L)+C_e/q_{max} \tag{3}$$

Where C_e is the equilibrium concentration of sorbate (mol/L), q_e is the amount of the sorbate adsorbed at equilibrium (mol/g), q_{max} is the monolayer maximum adsorption capacity of the sorbent (mol/g), and K_L is the Langmuir equilibrium constant (L/g).

The D–R isotherm equation, which is used to distinguish between physical and chemical adsorption, is given by Eq (4)

$$ln\ q_e=-K_D\varepsilon^2+lnB_{DR} \tag{4}$$

Where K_D is the D–R equation constant, B_{DR} is theoretical isotherm capacity (mol/g), q_e is the sorption capacity (mol/L), and ε is Polanyi potential, which is defined by Eq (5)

$$\varepsilon=RT\ ln\ (1+1/Ce)$$

Where Ce is equilibrium concentration of sorbate (mol/L) and R is universal gas constant (8.314 J/mol).

The D-R equation constant is related to the mean adsorption energy (E) by Eq. (6)

$$E=1/(2\ K_D)^{½} \tag{6}$$

The obtained experimental equilibrium data were examined with Langmuir and D–R isotherm models. The plot equations of the Langmuir and D-R equations are given in Figures 1 and 2, respectively. The Langmuir and D-R isotherm parameters were calculated from the slope-intercept of the plots and were given in Table 1. The calculated value of the maximum experimental sorption capacity from the Langmuir equation [Figure 1] is equal to 10.67 mg/g, which is close to the experimentally obtained value of the equilibrium sorption capacity (9.37 mg/g). The obtained data show the applicability of the Langmuir model, showing the formation of monolayer coverage. The favorability of the adsorption process can be expressed by a dimensionless constant called separation factor (R_L). The separation factor R_L has been calculated using the Eq (7)

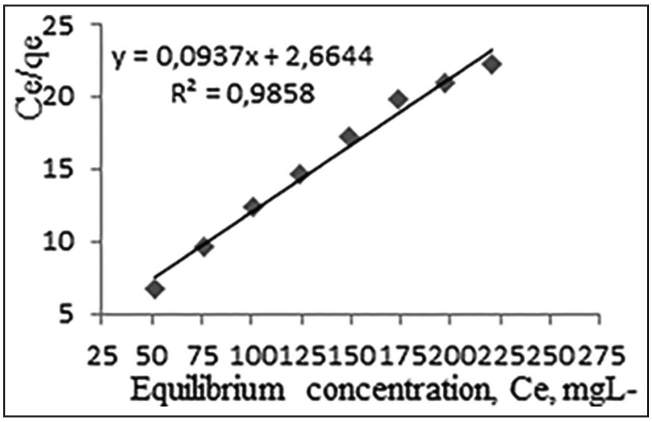


Figure 1: Langmuir and D-R equations at equilibrium concentration.

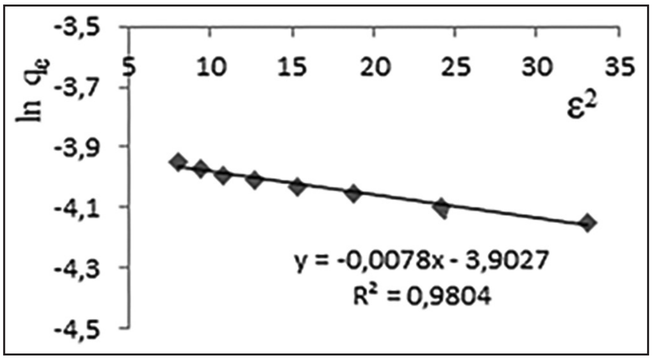


Figure 2: The Langmuir and D-R isotherm.

$$R_L = 1/(1+K_LC_o) \tag{7}$$

Where Co is the initial concentration of Rh 6G (mg/L^{-1}). If $1 > R_L > 0$, adsorption is favorable, whereas $R_L > 1$ represents unfavorable adsorption, $R_L = 1$ represents linear adsorption, and the adsorption process is irreversible if $R_L = 0$ [12]. The calculated R_L values for the different initial Rh6G concentrations (75–225 mg/L) were 0.274–0.113, indicating a high favorability of Rh6G adsorption to MSC. The found value of the mean sorption energy from the graph of equation D-R is 8.1 kJ/mol <8.0 kJ/mol, indicating that sorption Rh6G with synthesized polymer-sorbent is chemical in nature [13-17]. The theoretical sorbent capacity (B_{DR}) from the graph of equation D-R is 0.0202 mol/g (9.676 mg/g).

3.5. Effect of Contact Time and Sorption Kinetics

Sorption contact time is an important parameter of the sorption process since the sorption kinetics can be analyzed from the obtained data at different contact times. The contact time for the sorption of Rh6G dye with the synthesized sorbent was examined in the range of 20–80 min at 20°C. The results show that under the selected conditions, with increasing contact time, the Rh 6G removal degree increases, and equilibrium is observed after 70–80 min (sorption degree 18.3–18.6%).

The obtained data were fitted to the linear form of Lagergren pseudo-first- and pseudo-second-order kinetic models [14-17]. The pseudo-first-order kinetic model known as Eq (8)

Table 1: Langmuir and D–R equations parameters (initial concentration of the Rh6G 75–225 mg/L sorbent dosage 3.0 g/L, 30 min, 20°C, *Vsol*=0.04 *L*).

Langmuir equation				D-R equation			
q_{max}, mg/g	K_L, L/mg	R_L	R^2	K_D, kC/mol	B_{DR}, mol/g	E, kC/mol	R^2
10.67	0.035	0.274-0.113	0.9858	0.0078	0.0202	8.1	0.9804

Table 2: Regression parameters for the kinetics models (Rh 6G initial concentration 200 mg/L, *Vsol*=0.04 *L*, sorbent dosage 3.0 g/L, 20°C, and sorption time 20–80 min).

	Kinetics model		Pseudo-first order		Pseudo-second order	
	q_e, mg/g	K_1, min^{-1}	R^2	q_e, mg/g	K_2, Lg^{-1}/min	R^2
Parameters	25.03	6.24×10^{-2}	0.9185	17.36	1.845×10^{-3}	0.9912

Table 3: Sorption thermodynamic parameters (Rh 6G initial concentration 200 mg/L, *Vsol*=0.04 *L*, sorbent dosage 3.0 g/L, and 30 min).

Temperature, TK	Thermodynamic parameters		
	ΔG°, k J/mol	ΔH°, k J/mol	ΔS°, k J/mol/K
293	+7.272	+ 15.962	+0.0296
303	+7.051		
313	+6.545		
323	+6.452		

$$\log (q_e - q\tau) = \log q_e - 0.434 K_1 \tau \quad (8)$$

Where q_t and q_e are the amounts of dye adsorbed at time τ and at equilibrium (mg/g^{-1}), respectively, and K_1 is the rate constant of the pseudo-first-order adsorption process (min^{-1}). The pseudo-second-order kinetic model is expressed by the Eq (9)

$$\tau/q_\tau = 1/(K_2 q_e^2) + \tau/q_e \quad (9)$$

Where q_t and q_e are the amounts of Rh6G sorbed at time τ and at equilibrium (mol/g), respectively, K_2 is the pseudo-second-order equilibrium rate constant ($mole^{-1}$ min^{-1}). Plots of the equation of the pseudo-first and pseudo-second models are illustrated in Figures 3 and 4, respectively. Calculated parameters are placed in Table 2.

The obtained data show that the sorption process of the Rh6G from aqueous solutions with SMC is better described by the pseudo-second kinetic model. Since the correlation coefficient for the pseudo-second reaction (0.9912) is higher than the correlation coefficient for the pseudo-first reaction (0.9185), it can be assumed that the sorption process proceeds according to the pseudo-second reaction order.

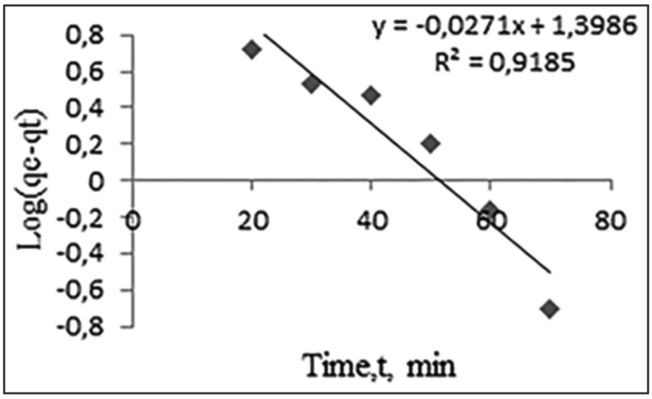


Figure 3: Pseudo-first model.

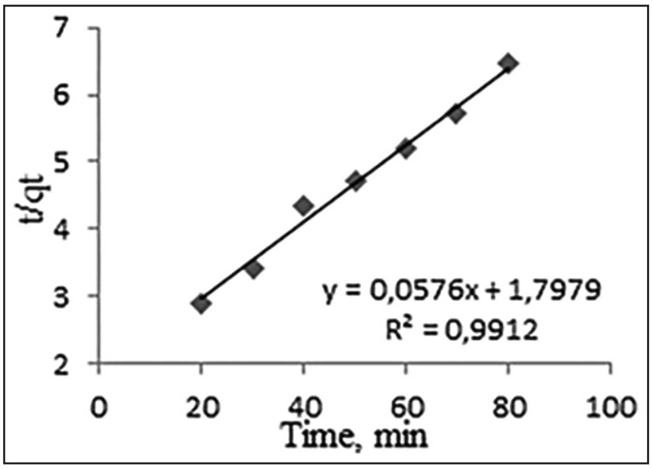


Figure 4: Pseudo-second models.

3.6. Effect of Temperature and Thermodynamics of the Adsorption

The effect of temperature on the removal degree of the Rh6G dye from the aqueous solution by the synthesized polymer sorbent has been studied, varying the temperature in the range of 20–50°C. The sorption conditions were as follows: Initial dye concentration 200 mg/L, pH 6, sorbent dosage 3.0 g/L, and contact time 30 min. The obtained experimental data show that dye adsorption degree decreases with increasing temperature, which confirms the endothermic nature of the process. The results on dependence of the sorption degree from temperature have been used to determine the thermodynamics parameters of the sorption process. Thermodynamic parameters such as Gibbs standard free energy ($\Delta G°$), standard enthalpy change ($\Delta H°$), and standard entropy change ($\Delta S°$) were determined using the following thermodynamic equations (10-12)

$$\Delta G^o = -2,3\ RT \log K_d \quad (10)$$

$$K_d = q_e/C_e \quad (11)$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \quad (12)$$

Where R is the gas constant (8.314 J/mol/K), T is the absolute temperature, and K_d is the equilibrium constant. The values of $\Delta H°$ and $\Delta S°$ were calculated from the plot of ΔGo = f (T) [Figure 5] and placed in Table 3. The positive values of $\Delta G°$ (6.452–7.272) confirm the non-spontaneous adsorption process, and the positive value of $\Delta H°$ (15.962 kJ/mol) suggested that the adsorption is endothermic in nature. The positive value of $\Delta S°$ (0.0296 kJ/mol/K) shows the increasing randomness during the adsorption process.

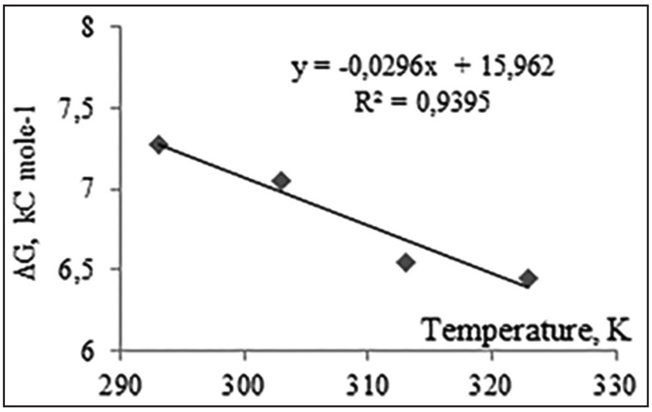


Figure 5: Effect of temperature and thermodynamics of the adsorption.

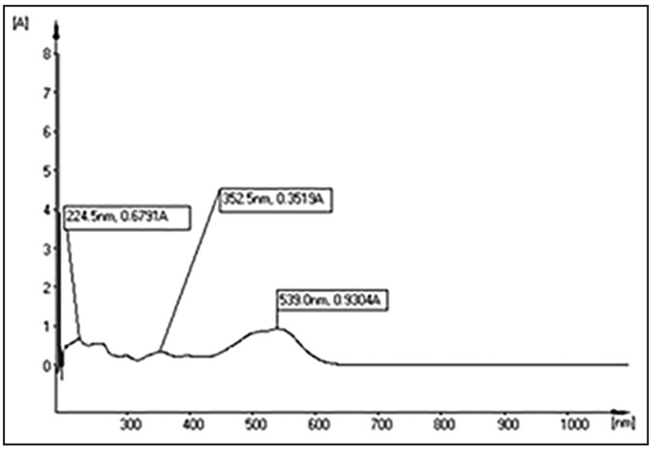


Figure 6: UV-spectra of the sorbent after adsorption.

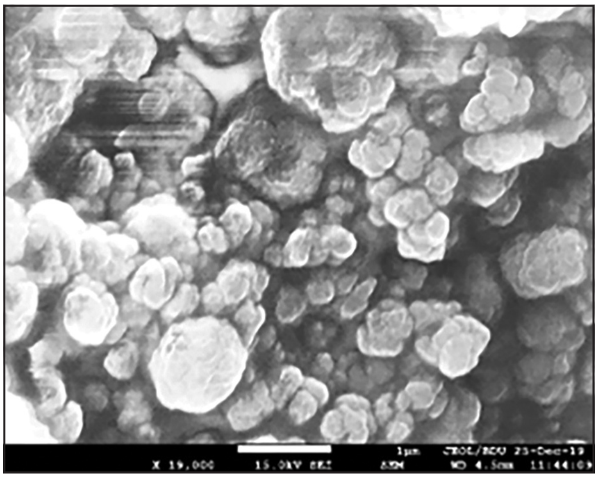


Figure 7: SEM image of the sorbent after adsorption.

3.7. Adsorption Mechanism

The assumption of the possible adsorption mechanism has been made based on the UV-spectra [Figure 6] and SEM image [Figure 7] of the sorbent after adsorption, and on the mean sorption energy, calculated from the D-R isotherm. The maximum 539 nm in the UV-vis spectra of the sorbent after adsorption corresponds to Rh 6G dye, adsorbed onto the surface of the sorbent. The SEM image in Figure 7 shows that the sorbent surface is not homogeneous after sorption. This is most likely due to the sorption of the dye on the sorbent surface during the sorption process (the light areas correspond to the Rh 6G dye on the sorbent surface). The calculated value for mean energy E from isotherm D-R (8.1 kJ/mol) is <8.0 kJ/mol, indicating the chemical nature of Rh 6G sorption by the synthesized polymer sorbent.

4. CONCLUSIONS

In this study, the efficiency of a sorbent for the removal of Rh 6G dye from aqueous solutions was investigated. Batch mode sorption studies indicate that the sorption process was dependent on the initial pH solution, sorbent dose, dye concentration, contact time, and temperature. The equilibrium sorption data obtained at different initial concentrations of dye fitted well in the Langmuir and D–R isotherms model. The maximum monolayer sorption capacity was found to be 10.67 mg/g, which is close to the value of equilibrium sorption capacity experimentally obtained from sorption isotherm (9.37 mg/g). The calculated value for mean energy E from isotherm D-R (8.1 kJ/mol) is <8.0 kJ/mol, indicating the chemical nature of Rh 6G sorption by the synthesized polymer sorbent. Kinetic studies show that the dye removal followed a pseudo-second-order rate equation. The positive value of ΔH° (+15.962 kJ/mol) suggested that the adsorption is endothermic in nature. The positive value of *ΔS*° (+0.0296 kJ/mol/K) shows the increasing randomness during the adsorption process. Finally, it can be concluded that the MSC can be used as a sorbent for the removal of Rh 6G from aqueous solutions.

5. ACKNOWLEDGMENTS

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6. COMPLIANCE WITH ETHICAL STANDARD

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7. CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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Author Queries???
AQ4: Kindly provide the text part