

Removal of Rhodamine 6G dye from Water Solution by Alt-maleic anhydride-styrene Copolymer, Cross-linked with Glycerin

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ABSTRACT

alt-Maleic anhydride-styrene copolymer, crosslinked with glycerin has been used for removal of Rhodamine 6G dye from aqueous solution. Effects of pH solution, contact time, sorbent dosage, initial concentration of dye and temperature on removal degree have been evaluated. 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⁻¹. The found value of the mean sorption energy from D-R equation (5.472 kJ mol⁻¹) specifies that, sorption of the Rhodamine 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 measurement. The SEM image indicates that the surface of the sorbent non-homogeneous, which connected with accumulation of the Rhodamine 6G dye molecules on the sorbent surface. 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⁻¹), ΔH° (18.378 kJ mol⁻¹) and ΔS° (0.0374 kJ mol⁻¹K⁻¹) indicates that the adsorption process is non-spontaneous, endothermic and randomness in nature.

Key words: Adsorption, Cross-linked copolymer, Isotherms, Kinetic, Rhodamine 6G dye.

1. INTRODUCTION

A dye has synthetic origin and complex aromatic molecular structures that make them difficult to biodegrade when discharged in the ecosystem. These dyes are common water pollutants and they may be found in trace amounts in industrial wastewater. Even if a small number of dyes are present in water, it is visible and therefore undesirable and can affect the physicochemical properties of fresh water. It has been medically proven that drinking water contaminated with rhodamine dyes could lead to subcutaneous tissue borne sarcoma which is highly carcinogenic [1]. The physical, chemical, and biological methods applied for the removal of dyes from aqueous solutions include coagulation, flocculation, biological oxidation, solvent extraction, chemical precipitation, reverse osmosis, ion exchange, filtration, and membrane process [2]. The removal of rhodamine 6G (Rh 6G) from aqueous solutions was achieved by adsorption using poly (fumaric acid-co-acrylic acid) as adsorbent surface [3]. Several variables that affect the adsorption were studied including adsorbent dosage, contact time, pH, temperature, and ionic strength. The results indicate that hydrogel has a strong capability of removing Rh 6G dye directly from aqueous solutions. The equilibrium adsorption data have been analyzed using Langmuir, Freundlich, and Temkin models. The cross-linking poly (N-vinyl caprolactam-co-maleic acid) microparticles used in the adsorption of Rh 6G from aqueous solution [4]. The effect of different parameters such as initial pH, adsorbent dose, temperature, initial dye concentration, and contact time on their dye adsorption capacity was studied using the batch adsorption technique. The equilibrium adsorption data were better fitted with Langmuir isotherm model. The maximum adsorption capacities at pH = 10 were found 2012 mg/g for Rh 6G. The experimental data were well described by the pseudo-second-order model. The chitosan-g-(N-vinyl pyrrolidone)/

montmorillonite composites were used for the adsorption Rh 6G dye from water solution [5]. The results show that the adsorption capacity increased with increase sorbent dosage, contact time, but there was no change observed due to increase in temperature. The Rh 6G adsorption kinetics followed pseudo-second-order model and the equilibrium data were found to fit Freundlich model. Batch sorption experiments were carried out for the removal of Rh 6G from aqueous solution using palm shell powder as adsorbent [6]. The operating variables studied were adsorbent mass, solution pH, contact time, and initial dye concentration. To investigate the mechanism of sorption, adsorption data were modeled using the pseudo-first-order and pseudo-second-order equations. It was found that the adsorption kinetics followed a pseudo-second-order model. Equilibrium isotherm was analyzed using the Langmuir and the Freundlich isotherms. The parameters for each model have been determined. The exhaustive capacity was 105.0 mg g⁻¹ for Rh 6G at 25°C. The negative value of free energy change indicated the spontaneous nature of adsorption. Sulfonated poly (styrene [ST]-alt-maleic anhydride [MA]) microspheres were prepared from poly (St-alt-MA) by sulfonation reaction and its adsorption behavior as an efficient adsorbent for the removal of organic dyes was systematically studied [7]. Results indicated that

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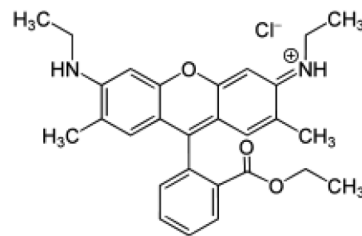
the adsorbent had more adsorption ability for cationic dyes compared to poly (St-alt-MA). The spent ground coffee powder was used as an effective adsorbent to remove rhodamine dyes from aqueous solutions, and the adsorption kinetics and isotherm behaviors were studied and compared [8]. The effects of temperature, ionic strength, solution volume, and the coexisting anions on the sorption behavior were also investigated. Furthermore, the adsorption mechanism responsible for the efficient removal of dyes is discussed in terms of chemically modified chitosan-based superhydrophilic adsorbent was prepared and examined for the removal of Rh 6G dye from water solutions [9]. Adsorption parameters, such as adsorbent dose, initial concentration of the dye, contact time, and pH of the solutions, were optimized. The dye removal efficiency was found to be 80.34% at pH 10 and sorbent dose 1.0 g L^{-1} . The adsorption of methylene blue and Rh 6G on a dry and swollen mixture of acrylic acid, sodium acrylate, and acrylamide polymers, cross-linked with ethylene glycol and dimethyl acrylate was investigated [10]. The equilibrium sorption capacity and adsorption rate constants were determined. The amount of dye adsorbed at equilibrium decreased with increasing mole% acrylamide. The sorption capacity was almost equal for the dry and swollen sorbent. However, the swollen sorbent adsorbed the dyes at a higher rate than the dry sorbent. The higher adsorption rate was due to the presence of all anionic groups present in the fully elongated conformation of the swollen sorbent. The effect of the initial dye concentration on adsorption was also studied and adsorption was described by the Langmuir adsorption isotherm. The kinetics of adsorption of Rh 6G on bentonite has been investigated in a batch adsorption process [11]. The adsorption of Rh 6G was found to be dependent on pH, initial concentration, adsorbent dose, contact time, and temperature. The Langmuir, Freundlich, and Temkin isotherm models were analyzed for the equilibrium adsorption data and the various isotherm parameters were evaluated. The Rh 6G on bentonite follows pseudo-second-order rate kinetics. Magnetic biochar sorbent was prepared using Fe_3O_4 nanoparticle composites onto the surface of biochar derived from rice husk and the removal of Rh 6G dye by magnetic biochar was studied [12]. Kinetic, isotherms, and thermodynamic studies were carried out to investigate the adsorption mechanism of Rh 6G dye on magnetic biochar surface. The Rh 6G removal efficiency of Fe_3O_4 -composited biochar is higher than that of pristine biochar with maximum efficiency of 94% removal. The adsorption isotherm and kinetic studies indicated that the Langmuir model, pseudo-first-order and pseudo-second-order models described well the rhodamine adsorption onto magnetic Fe_3O_4 -biochar.

The present study was undertaken to evaluate the efficiency of cross-linked with glycerin maleic anhydride–styrene copolymer for the removal of the Rh 6G dye from water solution. The effects of pH, sorbent dosage, contact time, initial dye concentration, and temperature on the sorption degree were investigated. The equilibrium adsorption data have been analyzed using Langmuir, Freundlich, and Dubinin-Radushkevich (D-R) models. In addition, kinetic and thermodynamic parameters of the adsorption process were determined and possible sorption mechanism has been suggested.

2. EXPERIMENTAL

2.1. Materials and Methods

MA was purified before use by recrystallization from benzene. Styrene (St) was distilled before use (b.p. $144\text{--}145^\circ\text{C}$). Azobisisobutyronitrile (AIBN) was purified by recrystallization from ethanol. Rh 6G chloride was used as an adsorbate in the present study, is a monovalent cationic dye. Rh 6G is a bronze/red powder with chemical formula $\text{C}_{28}\text{H}_{31}\text{ClN}_2\text{O}_3$. It has been classified as C.I. Basic Red 1 in dye classification, and the chemical structure of the dye has the following form (Wikipedia).

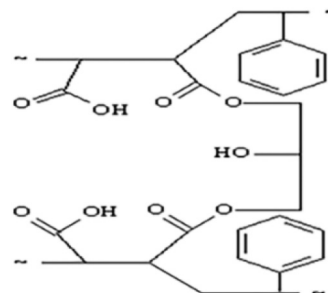


It has a molecular weight of $479.02 \text{ g mol}^{-1}$. Absorption maximum at 524 nm (Aldrich). AQ2

Sorption process of the Rh 6G dye was carried out using a batch experiment method. UV–Vis spectra were measured on a UV–Vis SPECORD 210 PLUS (Germany) in the range of $190\text{--}1100 \text{ nm}$. SEM measurements were carried out by a model JEOL JSM-7600F (Japan) scanning electron microscope. A pH meter model pH-420 Akvilon (Romania) was used for pH measurements.

2.2. Preparation of Adsorbent

The polymer sorbent alt-MA-St copolymer, cross-linked with glycerin (MSG), containing various functional groups ($-\text{COOH}$, OCO , $-\text{OH}$, and $\text{C}=\text{O}$) was synthesized in two steps: In the first step, 4.9 g MA, 4.16 g St (molar ratio MA/St = 1:1), and 0.1 g AIBN were dissolved in benzene (50 ml) and mixture was heated at 80°C for 1 h . The obtained copolymer (CPL) has been precipitated in ethanol or heptane and dried at 40°C in the vacuum oven (yields 6.7 g , 72.6%). The contents of SPL have been determined by chemical analysis and equal $51.5 \text{ mol}\%$, MA and $48.5 \text{ mol}\%$ St, respectively. In the second step, a mixture of SPL (4.08 g) and GL (5.0 g) was heated at 120°C for 3 h . Then, the obtained functional cross-linked polymer was washed repeatedly with double-distilled water and acetone for the removal of unreacted GL and SPL. The polymer sorbent has been dried at 30°C in the vacuum oven. The prepared adsorbent has the following cross-linked structure:



2.3. Adsorption Experiments

A stock solution dye with concentration 500 mg L^{-1} 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 with a synthesized sorbent were carried out according to the procedure, described in the works previously published by us [13,14]. The sorption degree Rh 6G dye (%) and sorption capacity (mg g^{-1}) of the sorbent have been calculated by the Equations (1) and (2), respectively.

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

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

C_0 and C_e (mg L^{-1}) are initial and equilibrium concentrations of Rh 6G, respectively, V_{sol} (L) is the volume of the dye solution subjected to sorption, and m_{sorb} (g) is the weight of sorbent.

3. RESULTS AND DISCUSSION

3.1. Effect of pH

The effect of pH on the Rh 6G dye sorption degree was investigated at an initial dye concentration 75 mg L^{-1} , sorbent weight of 3.0 g L^{-1} , sorption time of 30 min, and temperature of 20°C . Under these conditions, the pH of the solution changed in the range of 3–9. The results show that in a strongly acidic medium, the sorption degree is low (5.6%); the maximum sorption degree (21.0%) is observed at $\text{pH} = 6$. However, increase in solution pH results in reduction of sorption degree to 16.2%. The low adsorption of Rh 6G at acidic pH was suggested to be due to the presence of excess H^+ ions in solution. For cationic dyes, the lower adsorption of the dye at strong acidic medium is likely due to the presence of an excess H^+ ions, which compete with the cationic groups of the dye at the active sites of the adsorbent [15]. As surface charge density decreases with an increase in the pH solution, the electrostatic repulsion between the positively charged dye and the surface of the adsorbent is lowered, which may result in an increase in the extent of adsorption [16]. With an increase in the pH of solution, the electrostatic repulsion between the positively charged cationic dyes and the surface of adsorbent is lowered and consequently the removal efficiency is increased [17]. Thus, the larger values found at pH above 3 are explained by electrostatic attraction forces between the immobilized negatively charged sorbent and the positively charged dye ions. In view of the relatively high sorption degree of the Rh 6G by the synthesized adsorbent at pH 6, subsequent experiments were carried out at pH 6.

3.2. Effect of Sorbent Dosage

The dye removal degree from the aqueous solution versus the amount of sorbent under fixed experimental conditions is shown in Table 1.

The sorbent amount taken for sorption ranged from 1.0 to 4.0 g L^{-1} . The obtained results show that a noticeable change in the removal degree is observed as the amount of sorbent increases to 3.0 g L^{-1} . With a further increase, the amount of sorbent practically does not change the sorption degree. It can be considered that the amount of sorbent 3.0 g L^{-1} is optimal under the selected experimental conditions. Therefore, 3.0 g L^{-1} sorbent was used in further experiments.

3.3. Effect of Contact Time

Contact time is an important parameter because this factor determines the sorption kinetics of a sorbate at its given initial concentration. The effect of contact time on the sorption process Rh 6G dye by the

Table 1: Effect of sorbent dosage (rhodamine 6G concentration 200 mg L^{-1} , $V=0.04 \text{ L}$, 20°C , 30 min)

| | | | | | | | |
|-----------------------------------|-----|-----|------|------|------|------|------|
| Sorbent dosage, g L^{-1} | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 | 3.5 | 4.0 |
| Removal degree, % | 1.5 | 5.5 | 10.2 | 12.3 | 12.6 | 13.0 | 13.1 |

Table 2: Effect of time on sorption degree (initial rhodamine 6G concentration 200 mg L^{-1} , $V=0.04 \text{ L}$, sorbent dosage 3.0 g L^{-1} , 20°C)

| | | | | | | | | |
|-------------------|-----|------|------|------|------|------|------|------|
| Time, min | 20 | 30 | 40 | 60 | 80 | 100 | 120 | 150 |
| Removal degree, % | 3.7 | 12.6 | 14.6 | 19.1 | 22.3 | 25.5 | 28.8 | 29.5 |

synthesized sorbent was investigated under fixed conditions with a change in contact time from 20 to 150 min (Table 2).

The results indicated that with the increase of time, the removal of Rh 6G increased to a certain point of equilibrium. During the first 20 min of the sorption, 3.7% of the total amount of Rh 6G was immobilized. The state of dye equilibrium in the MSG structure is reached after 120–150 min. During this time, 28.8–29.5% of Rh 6G was removed by sorbent. Therefore, the contact time equal to 120–150 min was considered to be sufficient for sorption of Rh 6G dye onto sorbent.

3.4. Effect of Dye Concentration on Sorption Degree and Sorption Capacity

When studying the effect of the concentration of the solution Rh 6G on the dye sorption degree and the sorption capacity of the sorbent, dye solutions with an initial concentration of 75 – 250 mg L^{-1} were experimented with constant values of the remaining parameters. The results are shown in Table 3.

The results show that with an increase the initial dye concentration from 75 to 250 mg L^{-1} , the degree of removal decreases from 19.0 to 11.8%, while the sorption capacity of the sorbent increases from 4.74 to 9.83 g g^{-1} , and the establishment of practical equilibrium is observed at concentration of 200 mg L^{-1} . A decrease in sorption degree with increasing the initial dye concentration can be explained by filling and saturating the active sites of the sorbent. In this connection, 9.83 g g^{-1} can be considered the experimental equilibrium capacity of the sorbent.

3.5. Effect of Temperature

The effect of temperature on the Rh 6G dye adsorption with MSG was studied in the range of 20 – 60°C at an initial dye concentration 200 mg L^{-1} , pH 6, and contact time 30 min (Table 4).

As shown from Table 4, with increasing temperature, the sorption degree increases to 25.5% at 60°C . The increase of sorption with increasing temperature can be explained by an increase in the mobility of the dye molecules, which leads to a more intensive interaction with the active sites of the sorbent. The observed dependence of temperature sorption degree confirms that the Rh 6G dye adsorption process with MSG has endothermic character in nature.

3.6. Langmuir, Freundlich, and DR Isotherms

Langmuir isotherm describes monolayer adsorption based on the assumption that all the adsorption sites have equal adsorbate affinity

Table 3: Effect of dye concentration on sorption degree and sorption capacity (sorbent dosage 3.0 g L^{-1} , 30 min, 20°C , $V=0.04 \text{ L}$)

| | | | | | | | | |
|---|------|------|------|------|------|------|------|------|
| Initial concentration, mg L^{-1} | 75 | 100 | 125 | 150 | 175 | 200 | 225 | 250 |
| Sorption degree, % | 19.0 | 18.0 | 15.8 | 14.5 | 13.2 | 12.6 | 12.1 | 11.8 |
| Sorption capacity, g g^{-1} | 4.74 | 6.0 | 6.58 | 7.26 | 7.7 | 8.4 | 9.07 | 9.83 |

Table 4: Effect of temperature on sorption degree (initial Rh 6G concentration 200 mg L^{-1} , $V=0.04 \text{ L}$, 30 min)

| | | | | | |
|-------------------------------|------|------|------|------|------|
| Temperature, $^\circ\text{C}$ | 20 | 30 | 40 | 50 | 60 |
| Removal degree, % | 12.6 | 15.0 | 19.1 | 23.0 | 25.5 |

and that adsorption at one site does not affect adsorption at an adjacent site. The Langmuir isotherm can be described by Equation (3)

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

C_e is the equilibrium concentration of Rh 6G (mg L^{-1}), q_e is the amount of the Rh 6G adsorbed at equilibrium (mg g^{-1}), q_{max} is the monolayer maximum adsorption capacity of the MSG (mg g^{-1}), and K_L is the Langmuir equilibrium constant (L g^{-1}). Freundlich isotherm equation considers heterogeneous surfaces and is based on the idea that the adsorption depends on the energy of the adsorption sites. Freundlich isotherm is expressed by the Equation (4)

$$\log q_e = \log K_F + (1/n) \log C_e \quad (4)$$

K_F is the Freundlich constant and $1/n$ is the heterogeneity factor.

The obtained experimental equilibrium data were examined with Langmuir and Freundlich isotherm models. The linear curve of specific sorption versus equilibrium concentration of Rh 6G in solution and

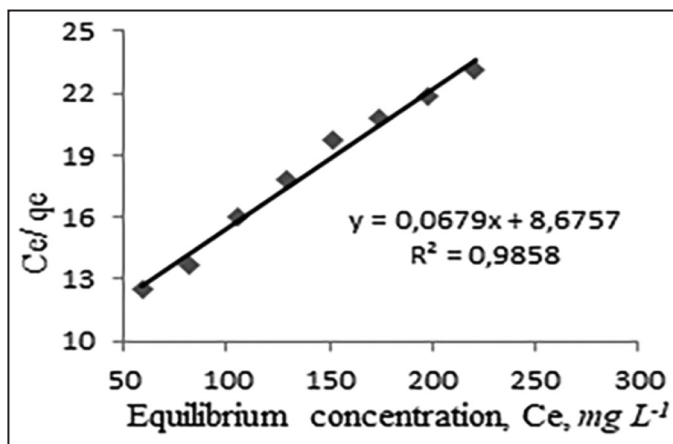


Figure 1: Langmuir plot for the rhodamine 6G sorption.

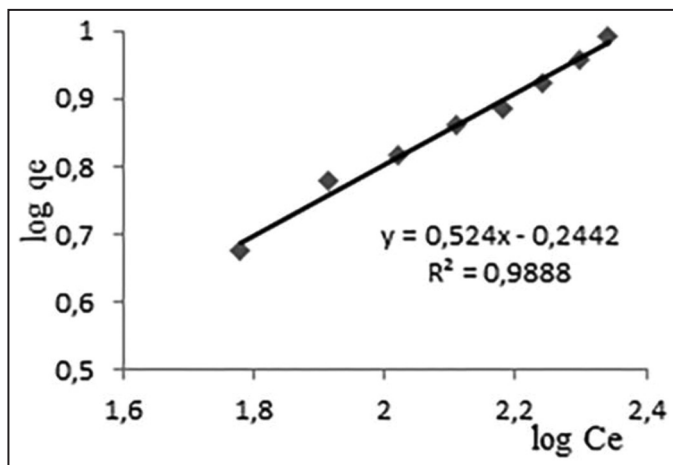


Figure 2: Freundlich plot for the rhodamine 6G sorption.

Table 5: Langmuir, Freundlich, and D-R equations parameters (initial Rh 6G concentration 75–250 mg L^{-1} , $V=0.04$ L, sorbent dosage 3.0 g L^{-1} , 30 min, 20°C)

| Langmuir equation | | | | Freundlich equation | | | | D-R equation | | | |
|--------------------------------|----------------------------|------------|--------|---------------------|-------|-------|--------|-----------------------------|---------------------------------|---------------------------|--------|
| q_{max} , mg g^{-1} | K_L , L mg^{-1} | R_L | R^2 | $1/n$ | n | K_F | R^2 | K_D , kJmol^{-1} | B_{DR} , mmol g^{-1} | E , kJmol^{-1} | R^2 |
| 14.73 | 0.00783 | 0.63–0.338 | 0.9858 | 0.524 | 1.908 | 3.342 | 0.9888 | 0.0334 | 0.0254 (12.17 mg/g) | 5.472 | 0.9695 |

D-R: Dubinin-Radushkevich

the curve of the logarithmic equilibrium adsorption capacity versus logarithmic equilibrium concentration are given in Figures 1 and 2 (pH6, 60 min, $C_0=75\text{--}250$ mg L^{-1} , $V=0.04$ L, sorbent dosage 3.0 g L^{-1} , 20°C), respectively.

The Langmuir and Freundlich isotherm parameters were calculated from the slope intercept of the plots and are given in Table 5. The calculated value of the maximum equilibrium sorption capacity from the Langmuir equation is equal to 14.73 mg g^{-1} , which is closer to the experimentally found value of the sorption capacity (9.83 mg g^{-1}).

The favorability of the adsorption process can be expressed by the separation coefficient (R_L), which is calculated using the equilibrium constant (K_L) in the Langmuir isotherm equation. The dimensionless value of the separation coefficient R_L can be calculated using Equation (5)

$$R_L = 1/(1+K_L C_0) \quad (5)$$

C_0 is the initial concentration of the adsorbate. If $1 > R_L > 0$, adsorption is favorable, at $R_L > 1$ adsorption is unfavorable, $R_L = 1$ represents linear adsorption, and if $R_L = 0$ adsorption process is irreversible [18]. The R_L values, calculated by us for the Rh 6G initial concentrations 75–250 mg L^{-1} are 0.630–0.338, indicate, that Rh 6G dye adsorption with MSG is favorable.

The D-R isotherm equation, which is more generally used to distinguish between physical and chemical adsorption, is given by the Equation (6)

$$\ln q_e = -K_D \epsilon^2 + \ln B_{DR} \quad (6)$$

K_D is the D-R equation constant, B_{DR} theoretical isotherm saturation capacity (mol g^{-1}), q_e is the equilibrium adsorption capacity (mol g^{-1}), and ϵ is Polanyi potential, which is defined by Equation (7)

$$\epsilon = RT \ln (1+1/C_e) \quad (7)$$

C_e is equilibrium concentration of the Rh 6G (mol L^{-1}), R is universal gas constant (8.314 J mol^{-1}). The D-R constant K_D can give the valuable information regarding the mean energy (E_D) of adsorption, which is calculated by the Equation (8)

$$E_D = 1/(2 K_D)^{1/2} \quad (8)$$

By the E_D value, the adsorption type can be determined: If $8.0 > E_D > 16.0$ kJ mol^{-1} , the adsorption process can be assumed to involve chemical sorption, on the other hand, if $E_D < 8.0$ kJ mol^{-1} indicates that the adsorption process is physical in nature [19].

Plot of the D-R equation function $\ln q_e = f(\epsilon^2)$ illustrated in Figure 3 (pH 6, contact time 30 min, $C_0=75\text{--}250$ mg L^{-1} (0.1566–0.5279 mmol L^{-1}), $V = 0.04$ L, sorbent dosage 3.0 g L^{-1} , 20°C) and calculated D-R equation parameters are placed in Table 5.

The theoretical isotherm saturation capacity of the sorbent (B_{DR}) from D-R equation is equal to 0.0254 mmol g^{-1} (12.17 mg g^{-1}). The found value of the mean sorption energy $E_D = 5.472$ $\text{kJ mol}^{-1} < 8.0$ kJ mol^{-1} indicated that sorption of Rh 6G by synthesized polymer sorbent has physical character.

3.7. Sorption Kinetics and Thermodynamics

Kinetic studies were carried out under the optimized conditions from 20 to 150 min. The kinetic data obtained were fitted to linear form of Lagergren pseudo-first-order and pseudo-second-order kinetic models [20]. The pseudo-first-order kinetic model known as Equation (9)

$$\log(q_e - q_\tau) = \log q_e - 0.434 K_1 \tau \quad (9)$$

q_τ and q_e are the sorption capacity at time τ and at equilibrium (mol g^{-1}), respectively, K_1 is the rate constant of pseudo-first-order kinetic model (min^{-1}). The pseudo-second-order kinetic model is expressed by the Equation (10)

$$\tau/q_\tau = 1/(K_2 q_e^2) + \tau/q_e \quad (10)$$

q_τ and q_e are the sorption capacity at time τ and at equilibrium (mol g^{-1}), respectively, K_2 is the pseudo-second-order equilibrium rate constant ($\text{mol}^{-1} \text{min}^{-1}$). Plots of the pseudo-first and pseudo-second order equations are illustrated in Figures 4 and 5 ($C_0 = 200 \text{ mg L}^{-1}$, $\text{pH} = 6$, sorbent dosage 3.0 g L^{-1} , $V = 0.04 \text{ L}$, 20°C), respectively. The obtained values of kinetic parameters are placed in Table 6.

The correlation coefficient for the pseudo-second-order model is higher compared to the pseudo-first-order model and therefore it can be considered that the adsorption process of the Rh 6G dye with MSG is better described by the pseudo-second-order model equation.

The obtained data on adsorption of the Rh 6G dye with the synthesized sorbent MSG have been compared with some literature data (Table 7) [21-24]. It can be seen that the data presented in our work

Table 6: Regression parameters for the kinetics models (initial Rh 6G concentration 200 mg L^{-1} , $V=0.04 \text{ L}$, sorbent dosage 3.0 g L^{-1} , 20°C)

| Kinetic model parameters | | | | | |
|--------------------------|------------------------|--------|-------------------------|------------------------|--------|
| Pseudo-first order | | | Pseudo-second order | | |
| $q_e, \text{mg g}^{-1}$ | K_1, min^{-1} | R^2 | $q_e, \text{mg g}^{-1}$ | K_2, min^{-1} | R^2 |
| 32.48 | 0.003 | 0.8892 | 31.545 | 0.00071 | 0.9894 |

Table 7: Comparison of Rh 6G dye uptake data with other adsorbents

| Sorbent | $q_{\text{max}}, (\text{mg g}^{-1})$ | pH | Adsorbent, Model | Source |
|--|--------------------------------------|------|------------------|---------------|
| Activated carbon | 44.7 | 7 | 0.02 Langmuir | [24] |
| Palm shell powder | 105.0 | 5.75 | 0.4 Langmuir | [23] |
| Biological sludge | 16.3 | 7 | 10.0 Langmuir | [22] |
| Coffee ground | 17.37 | — | 1.0 Langmuir | [8] |
| Trichoderma harzianum mycelial biomass | 3.40 | 8 | 2.0 Langmuir | [24] |
| Chitosan-g-(N-vinylpyrrolidone)/montmorillonite hydrogel | 36.6 | 10 | 0.05 Freundlich | [5] |
| Bentonite clay | 111.11 | 6 | 4.0 g Langmuir | [11] |
| Cross-linked maleic anhydride-styrene copolymer | 14.73 | 6 | 3.0 Langmuir | In this study |

are comparable with data on adsorption Rh 6G dye with other different adsorbents.

Thermodynamic parameters, such as standard Gibbs free energy (ΔH°), standard enthalpy change (Δ°), and standard entropy change (Δ°), were determined to explain the effect of temperature on the adsorption of Rh 6G on MSG. These parameters can be calculated from the Equations (11–13)

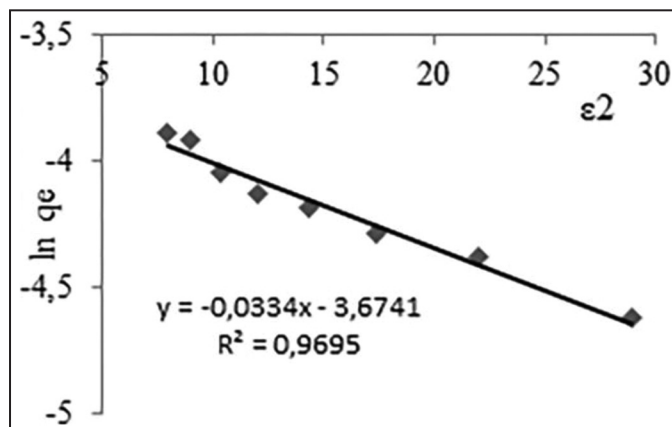


Figure 3: Dubinin-Radushkevich plot for the rhodamine 6G sorption.

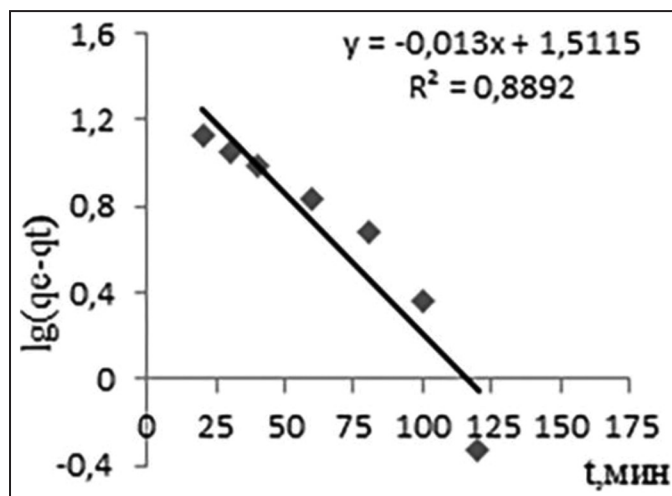


Figure 4: Plots of pseudo-first-order models.

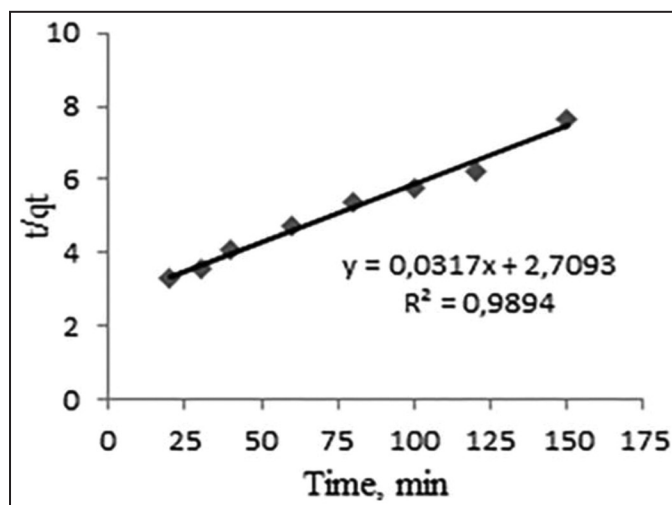


Figure 5: Plots of pseudo-second order.

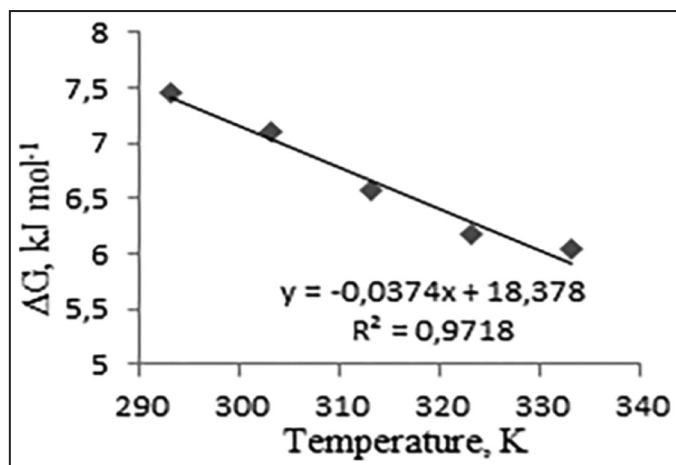


Figure 6: Plot of ΔG° versus T.

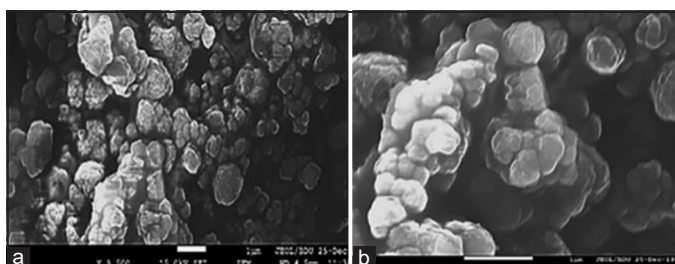


Figure 7: SEM image of the rhodamine (Rh) 6G-loaded sorbent: (a) $\times 9500$ and (b) $\times 25,000$ (light sites the adsorbed Rh 6G dye).

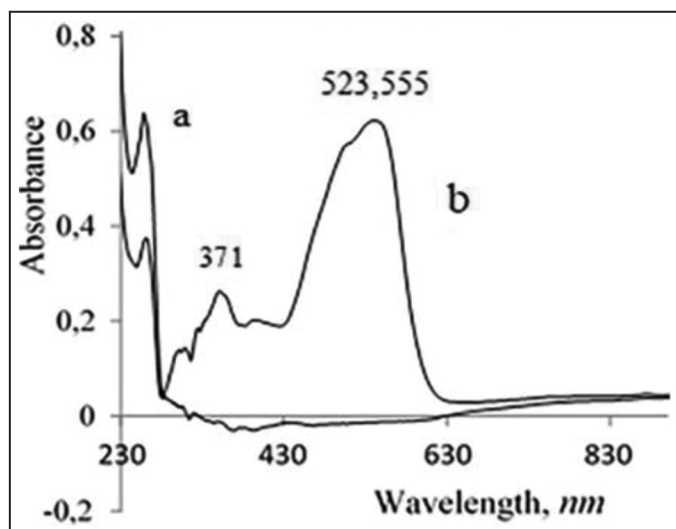


Figure 8: UV-visible spectra of the MSG: (a) Before and (b) after sorption.

$$\Delta^\circ = -2,3 RT \log K_d \quad (11)$$

$$K_d = q_e / C_e \quad (12)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (13)$$

R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T is absolute temperature, and K_d is equilibrium constant at the temperature T. The values of ΔH° and ΔS° were obtained from the slope and intercept of the plots of ΔG° versus T (Figure 6) and are placed in Table 8. The positive value of ΔH° ($18.209 \text{ kJ mol}^{-1}$) suggests that the adsorption is endothermic in nature. The positive value of ΔS° ($0.369 \text{ kJ mol}^{-1} \text{ K}^{-1}$) shows the increase of randomness during adsorption process.

Table 8: Sorption thermodynamic parameters (pH 6, 30 min, $C_0 = 0.365 \text{ mmol L}^{-1}$, $V = 0.04 \text{ L}$, sorbent dosage 3.0 g L^{-1})

| Temperature, TK | Thermodynamic parameters | | |
|-----------------|---------------------------------------|---------------------------------------|--|
| | $\Delta G^\circ, \text{ kJ mol}^{-1}$ | $\Delta H^\circ, \text{ kJ mol}^{-1}$ | $\Delta S^\circ, \text{ kJ mol}^{-1} \text{ K}^{-1}$ |
| 293 | 7.45 | | |
| 303 | 7.11 | | |
| 313 | 6.57 | 18.378 | 0.0374 |
| 323 | 6.19 | | |
| 333 | 6.04 | | |

3.8. Mechanism of the Adsorption

The conclusion about the possible mechanism of the Rh 6G dye adsorption by the MSG has been made on the basis of SEM image and UV spectrum of the adsorbent after sorption. The SEM image (Figure 7) shows that the surface of the sorbent is not homogeneous, which is associated with the accumulation of Rh 6G dye molecules on the surface of the adsorbent. The UV spectra of MSG before and after sorption are illustrated in Figure 8.

The maximum 523–555 nm (Figure 8b) in UV spectrum of the sorbent after adsorption corresponds to Rh 6G dye adsorbed on a sorbent surface, and the maximum of 371 nm has been attributed to dye sorbent complex. The complexation of Rh 6G with carboxyl polymers, including maleic acid copolymers, is reported in works [25,26]. It is noted that Rh 6G can form complexes with copolymers of maleic acid, which give highs in the region of 350–370 nm. Taking into account the obtained data on SEM analysis, UV spectroscopy of the sorbent after sorption, and values of kinetic and thermodynamic parameters, it can be concluded that Rh 6G dye interacts with active sites of the MSG and adsorption process is connected with electrostatic interaction forces. The found value of the mean sorption energy from D-R equation $E_D = 5.472 \text{ kJ mol}^{-1} < 8.0 \text{ kJ mol}^{-1}$ indicated that sorption of Rh 6G by synthesized polymer sorbent has physical character.

4. CONCLUSIONS

The effects of pH, contact time, sorbent dosage, temperature, and dye initial concentration have been tested and optimum conditions of the sorption process of the Rh 6G dye from aqueous solution with MSG were evaluated. The equilibrium sorption data were fitted to Langmuir, Freundlich, and D-R models. The calculated value of the maximum equilibrium sorption capacity from the Langmuir equation is equal to 14.73 mg g^{-1} . Separation factor R_L values at different initial concentration of the Rh 6G were less than 1 and greater than 0 ($1 > R_L > 0$), indicated that adsorption is favorable. It was found that the pseudo-second-order model was the most appropriate model, describing the sorption kinetics. The positive value of the ΔH° ($18.378 \text{ kJ mol}^{-1}$) indicates that the sorption process is endothermic in nature. The positive value of ΔS° ($0.0374 \text{ kJ mol}^{-1} \text{ K}^{-1}$) shows the increasing randomness during adsorption process. Taking into account the obtained data on SEM analysis, UV spectroscopy of sorbent before and after sorption, and values of kinetics and thermodynamics parameters, it can be concluded that Rh 6G dye interacts with active sites of the MSG and process is connected with electrostatic interaction forces. The found value of the mean sorption energy from D-R equation $E_D = 5.472 \text{ kJ mol}^{-1} < 8.0 \text{ kJ mol}^{-1}$ also indicated that sorption of Rh 6G by synthesized polymer sorbent has physical character. To summarize, it could be concluded that cross-linked with glycerin alt-MA-St copolymer is an efficient adsorbent, which can be successfully applied for Rh 6G dye removal from aqueous solutions.

5. ACKNOWLEDGMENTS

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6. COMPLIANCE WITH ETHICAL STANDARDS

6.1. Funding

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6.2. Conflicts of Interest

The authors declare that they have no conflicts of interest.

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