

UOT 541.64:543.544

REMOVAL OF RHODAMINE 6G DYE FROM WATER SOLUTION BY ALT-MALEIC ANHYDRIDE-STYRENE COPOLYMER, CROSS-LINKED WITH HEXAMETHYLENEDIAMINE**O.H. Akperov, F.M. Kamranzadeh, E.O. Akperov***Baku State University,
Z. Khalilov., 23, AZ1148 Baku, Azerbaijan, e-mail: oakperov@mail.ru**Received 28.10.2021**Accepted 10.12.2021*

Abstract: *The article provides data on the use of crosslinked with hexamethylenediamine alt-maleic anhydride-styrene copolymer, as a sorbent for the remove of the Rhodamine 6G dye from aqueous solution. The effect of the pH, sorbent amount, contact time, temperature and dye concentration on sorption was studied. The obtained data were processed in the coordinates of the Langmuir, Freundlich and D-R models equations and the values of the equilibrium sorption capacity and mean sorption energy were determined. The found value of the mean sorption energy from D-R equation $E_D=4.556 < 8.0 \text{ kJ mol}^{-1}$, indicated that the sorption of Rh6G by synthesized polymer-sorbent has physical character. Also, thermodynamic parameters, like standard Gibbs free energy (ΔG°), standart enthalpy change (ΔH°) and standart entropy change (ΔS°) were determined. The positive values of ΔG° confirm the nonspontaneous of adsorption process, and the positive value of ΔH° ($12.464 \text{ kJ mol}^{-1}$) suggested that the adsorption was endothermic in nature. The positive value of ΔS° ($0.0271 \text{ kJ mol}^{-1} \text{ K}^{-1}$) shows the increasing randomness during adsorption process.*

Keywords: *adsorption, cross-linked polymer, hexamethylenediamine, isotherms, rhodamine 6G*

DOI: *10.32737/2221-8688-2021-4-203-214*

1. Introduction

The physical, chemical and biological methods applied for removal of dyes from aqueous solutions include coagulation, flocculation, biological oxidation, solvent extraction, chemical precipitation, reverse osmosis, ion exchange, filtration and membrane process. Among these methods, the adsorption method is widespread in which complex process equipment is not required and is relatively easy to perform. [1]. The removal of Rhodamine 6G from aqueous solutions was achieved by adsorption using poly (fumaric acid-co-acrylic acid) as adsorbent surface [2]. Several variables that affect the adsorption were studied, including adsorbent dosage, contact time, pH, temperature and ionic strength. The equilibrium adsorption data were analyzed using Langmuir, Freundlich and Temkin models. The results indicate that hydrogel has a strong capability of removing Rhodamine 6G dye directly from aqueous solutions.

Sulfonated poly (styrene-alt-maleic

anhydride) microspheres were prepared from poly (styrene-alt-maleic anhydride) by sulfonation reaction and its adsorption behavior as an efficient adsorbent for the removal of organic dyes was systematically studied [3]. Results indicated that the adsorbent had more adsorption ability for cationic dyes as compared to poly (styrene-alt-maleic anhydride). The cross-linking poly (N-vinyl caprolactam-co-maleic acid) microparticles used in the adsorption of Rhodamine 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 was found 2012 mg/g for Rhodamine 6G. The experimental data were well described by the pseudo-second order model. 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 [5]. The effects of temperature, ionic strength, solution volume and the co-existing anions on the sorption behavior were also investigated. The results showed that the adsorption capacity increased as the sorbent dosage and contact time increased; however, there was no changes observed due to the increase in temperature. The Rh 6G adsorption kinetics followed pseudo-second order model and the equilibrium data were found to fit Freundlich model. Magnetic biochar-sorbent was prepared using Fe_3O_4 nanoparticle composites onto the surface of biochar derived from rice husk, and the removal of Rhodamine 6G dye by magnetic biochar was studied [6]. Kinetic, isotherms and thermodynamic studies were carried out to investigate the adsorption mechanism of Rhodamine 6G dye on magnetic biochar surface. Rhodamine 6G removal efficiency of Fe_3O_4 -composited biochar proved 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. Batch sorption

experiments were carried out for the removal of Rhodamine 6G from aqueous solution using Palm Shell Powder as adsorbent [7]. The operating variables studied were adsorbent mass, solution pH, contact time and initial dye concentration. In order 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 Rh6G at 25°C . The negative value of free energy change indicated the spontaneous nature of adsorption.

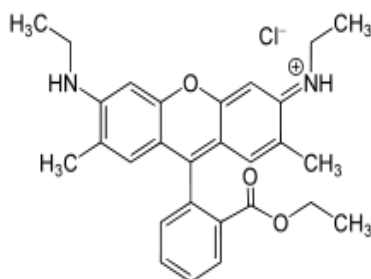
The current work provides results on removal of Rhodamine 6G dye from aqueous solutions using the cross-linked with hexamethylenediamine alt-maleic anhydride-styrene copolymer (HMSC) as an adsorbent. The effects of pH, sorbent dosage, contact time, temperature and initial dye concentration on the sorption degree were investigated. The equilibrium adsorption data were analyzed using Langmuir and Dubinin-Radushkevich models. Besides, kinetic and thermodynamic parameters of the adsorption process were determined and possible sorption mechanism suggested.

2. Experimental part

2.1. Materials and Methods

Maleic anhydride (MA) was recrystallized from benzene, styrene (St) - distilled (temp. $144\text{--}145^\circ\text{C}$), azobisisobutyronitrile (AIBN)-crystallized

from ethanol. The structure of cationic dye Rhodamine 6G-chlor dye with empirical composition $\text{C}_{28}\text{H}_{31}\text{ClN}_2\text{O}_3$, is as follows:



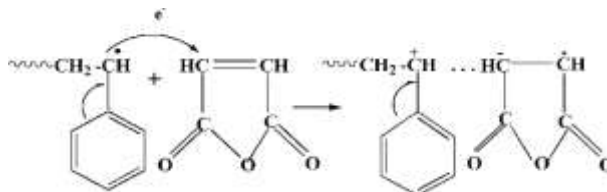
Its molecular weight is $479.02 \text{ g mol}^{-1}$, UV-absorption maximum is at 524 nm (Aldrich). UV-vis spectra were measured on a UV-vis SPECORD 210 PLUS (Germany) in the range of $190\text{--}800 \text{ nm}$. SEM measurements were

carried out by a model JEOL JSM-7600F (Japan) scanning electron microscope and pH was measured by the pH-meter pH-420 Akvilon (Romania).

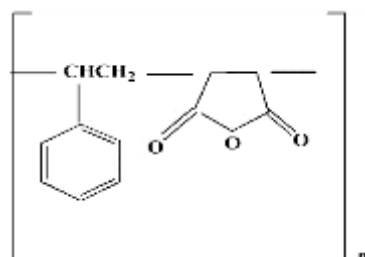
2.2. Sorbent preparation

Preparation of the HMSC was carried out in two stages: synthesis of the alternating maleic anhydride-styrene copolymer (*alt*-MA-St) and cross-linking of the copolymer with hexamethylenediamine (HMDA). The *alt*-MA-

St was synthesized according to the known procedure [8] by radical polymerization of MA and St in benzene at 80°C in the presence of AIBN as an initiator. Polymerization is followed by formation of donor-acceptor complex

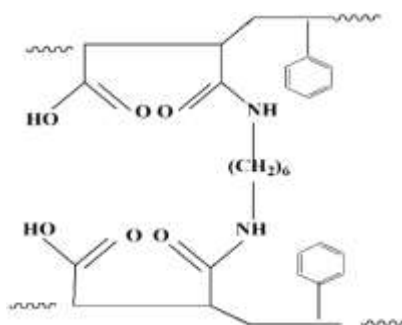


and forms the *alt*-MA-St:



Alt-MA-St was cross-linked with HMDA according to the following procedure: 2.0 g copolymer is mixed with 4.0 g HMDA at 60°C for 2 hours. After the obtaining solid mass is washed with distilled water and acetone, and

dried at 40°C in a vacuum oven. The structure and composition of the cross-linked *alt*-MA-St which used as a sorbent to remove the Rh 6G dye from water solution, is follows:



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 [9,10]. The sorption degree Rh 6G dye (%) and sorption capacity (mg g⁻¹) of the sorbent were calculated by the equations (1) and (2), respectively.

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

$$\text{Sorption capacity } (mq\ q^{-1}) = \frac{(C_0 - C_e) \times V_{sol}}{m_{sorb}} \quad (2)$$

C_0 and C_e ($mg\ L^{-1}$) are initial and equilibrium concentrations of Rh 6G, respectively. 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 Rh6G 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 $20^\circ\ C$. Under these conditions, the pH of the solution changed in the range 3-9. The results show that in a strongly acidic medium (pH=3) the sorption degree is low (7.4%). For cationic dyes, the lower adsorption of the dye at strong acidic medium is likely due to the presence of excess H^+ ions which compete with cationic groups of the dye at the active sites of the

adsorbent [11]. Thus, the high values of the sorption degree at above pH=3 are explained by electrostatic attraction forces between the immobilized negatively charged sorbent and the positively charged dye. It revealed that the maximum estimate of sorption degree (25.2%) is observed in pH= 6. In considering the relatively high sorption rate in pH 6, a series of subsequent experiments were performed in pH 6. likely due to the presence of an excess H^+ ions.

3.2. 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 Rh 6G sorption by sorbent was investigated at different contact time varying between 10 and 120 *min* at $20^\circ\ C$

(Table 1). These results indicated that as time increases the removal of Rh 6G increases to a certain point of equilibrium. During the first 20 *min* of the sorption 8.7% of the total amount of Rh 6G was immobilized.

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

Time, <i>min</i>	20	30	40	60	80	100	110	120
Sorption degree, %	8.7	12.2	15.4	19.1	24.3	28.5	30.6	31.1

The state of dye equilibrium in the HMSC structure is reached after 110-120 *min*. At that time, 30.6-31.21% of Rh 6G were removed by

sorbent. Therefore, the contact time equal to 110 *min* was considered to be sufficient for sorption of Rh 6 G by sorbent.

3.3. Effect of sorbent dosage

The sorbent amount for sorption is changed from 1.0 to $4.0\ g\ L^{-1}$. The obtained results show that noticeable change of extent of sorption happens when there is rise in quantity of a sorbent up to $3.0\ g\ L^{-1}$. A further increase in the amount of sorbent practically not lead to a

change in the degree of sorption. Therefore, the amount of sorbent $3.0\ g\ L^{-1}$ was taken as the working amount and used in subsequent experiments. The experimental results of removing Rh 6G dye from sulfur depending on the amount of sorbent are shown in Table 2.

Table 2. Effect of sorbent dosage (Rh6G concentration 200 mg L⁻¹, V=0.04 L, 20°C, 110 min)

Sorbent dosage, gL ⁻¹	1.0	1.5	2.0	2.5	3.0	3.5	4.0
Sorption degree, %	11.5	17.3	21.2	27.3	30.6	31.1	31.0

3.4. Temperature effect

The purpose of this research is to ascertain the effect of temperature on the sorption of Rh6G dye by the HMSC. The effect of temperature on the removal of Rh6G dye in aqueous solution by HMSC was studied by varying the temperature between 20 and 60° C at the initial dye concentration of 200 mg L⁻¹, pH 6, sorbent dosage 3.0 g L⁻¹ and contact time 110 min. The data presented in Table 3 showed that adsorption of dye by the HMSC increased

as the temperature increased. This behavior confirms that the adsorption of dye had an endothermic nature. This is because with increasing temperature, the attractive forces adsorbent surface and Rh6G are weakened and the sorption decreases. The results of the temperature dependence of sorption are used to determine the thermodynamic parameters of the sorption process.

Table 3. Effect of temperature on sorption degree (initial Rh 6G concentration 200 mg L⁻¹, sorbent dosage 3,0 g L⁻¹, V=0.04 L, 110 min.

Temperature, °C	20	30	40	50	60
Sorption degree, %	30.6	36.3	40.0	43.7	45.1

3.5. Effect of the Rh6G initial concentration

Experimental results relating to the change in sorption rate and sorbent content at retardation

of the dye layer Rh 6G from 75 mg L to 220 mg L-1 are shown in Table 4.

Table 4. Effect of dye concentration on sorption degree and sorption capacity (sorbent dosage 3.0 g L⁻¹, 110 min, 20°C, V=0.04L)

Initial concentration, mg L ⁻¹	75	100	125	150	175	200	220
Sorption degree, %	44.5	42.4	38.0	34.9	32.0	30.6	29.5
Sorption capacity, mg g ⁻¹	11.12	14.13	15.83	17.45	18.67	20.4	21.6

The results showed that the Rh 6G sorption onto sorbent were strongly affected by the initial dye concentration and as the initial Rh6G concentration increases, sorption degree decreases. The Rh 6G removal degree decreases from 44.5 to 29.5% when its initial concentration increases from 75 to 220 mg L⁻¹. It is explained as being due to the fact that as dye concentration increased, the specific sites of a sorbent were saturated and exchange sites filled. Equilibrium sorption capacity of the sorbent was calculated in the initial Rh 6G

concentration range 75–220 mg L⁻¹ at 20°C and for 110 min contact time. It revealed that the sorption capacity of the sorbent increased rapidly as the equilibrium concentration of Rh 6G increased. When the Rh6G concentration the constant value. It can be concluded that the experimentally maximum sorption capacity (q_{exp}) of the sorbent at the equilibrium conditions is 20.4–21.6 mg g⁻¹. The results obtained from the dependence of the sorption degree and the sorption capacity from initial concentration of the dye were developed in the

coordinates of the Langmuir and Dubinin-Radushkevich isotherm equations and

calculated the values of sorption process.

3.6. Langmuir and Dubinin-Radushkevich isotherms

Langmuir isotherm describes monolayer adsorption based on the assumption that all the adsorption sites have equal adsorbate affinity and that adsorption at one site does not affect adsorption at an adjacent site. The Langmuir isotherm can be described by Eq (3)

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

Where 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 MSOT ($mg g^{-1}$) and K_L is the Langmuir equilibrium constant ($L g^{-1}$).

The Dubinin-Radushkevich (D-R) isotherm equation, which is more generally used to distinguish between physical and chemical adsorption, is given by the Eq (4)

$$\ln q_e = -K_D \varepsilon^2 + \ln B_{DR} \quad (4)$$

Where K_D is the D-R equation constant, B_{DR} theoretical isotherm saturation capacity ($mole g^{-1}$), q_e is the sorption capacity ($mol L^{-1}$) and ε is Polanyi potential, which is defined

by Eq (5)

$$\varepsilon = RT \ln (1 + 1/C_e) \quad (5)$$

Where C_e is equilibrium concentration of the Rh6G ($mol L^{-1}$), R is universal gas constant ($8.314 J mol^{-1}$). The D-R constant can give the valuable information regarding the mean energy (E) of adsorption by the Eq (6)

$$E = 1 / (2 K_D)^{1/2} \quad (6)$$

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 Fig.3 and Fig.4, respectively. The Langmuir and D-R isotherm parameters were calculated from the slope intercept of the plots and shown in Table 5. The calculated value of the maximum experimental sorption capacity from the Langmuir equation, (Fig.3) is equal to be $31.15 mg g^{-1}$, which are close to experimentally obtained value of equilibrium sorption capacity from sorption isotherm ($21.6 mg g^{-1}$).

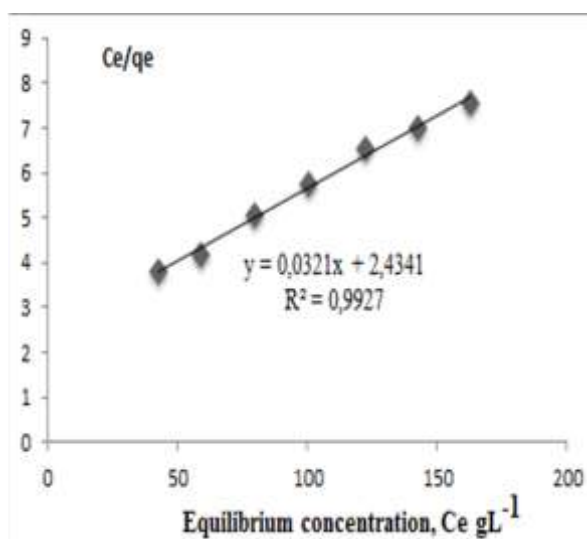


Fig. 3. Langmuir plot for sorption (pH 6, 30 min, $C_0 = 75 - 220 mg L^{-1}$, $V = 0.04 L$, sorbent dosage $3.0 g L^{-1}$, $20^\circ C$).

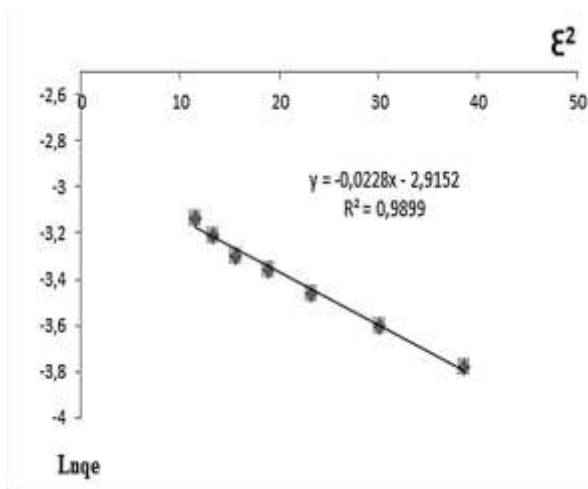


Fig. 4. D-R plot for sorption (pH 6, 110 min, $C_0 = 75 - 220 mg L^{-1}$, $V = 0.04 L$, sorbent dosage $3.0 g L^{-1}$, $20^\circ C$).

Table 5. Langmuir and D-R equations parameters

Langmuir equation				D-R equation			
$q_{max}, mg\ g^{-1}$	$K_L, L\ mg^{-1}$	R_L	R^2	$K_D, kCmol^{-1}$	$B_{DR}, mol\ g^{-1}$	$E, kCmol^{-1}$	R^2
31.15	0.0132	0.503-0.256	0.9927	0.024	0.08318 (39.84mq ⁻¹)	4.556	0.9899

Obtained data shows the applicability of the Langmuir model indicating the formation of monolayer coverage of the dye molecules at the surface of the adsorbent. The essential feature of the Langmuir isotherm to identify the feasibility and favorability of the adsorption process can be expressed by a dimensionless constant called separation factor (R_L). The separation factor R_L was calculated using the Eq (7)

$$R_L = 1 / (1 + K_L C_o) \quad (7)$$

Where C_o -is the initial Rh6G concentration ($mg\ L^{-1}$). If $1 > R_L > 0$, adsorption is favorable while $R_L > 1$ represent unfavorable adsorption, and $R_L = 1$ represent linear adsorption while the

adsorption process is irreversible if $R_L = 0$ [12]. The calculated values of R_L for different initial concentration of the Rh6G ($75-220\ mg\ L^{-1}$) were equal to be 0.503– 0.256 to indicate highly favorable adsorption for the Rh6G onto HMSC.

The found value of the mean sorption energy from D-R equation $E_D = 4.556 < 8.0\ kJ\ mol^{-1}$ indicated that sorption of Rh6G by synthesized polymer-sorbent has physical character [13]. The theoretical isotherm saturation capacity of the sorbent (B_{DR}) from D-R equation is equal to be $0.08318\ mmol\ g^{-1}$ ($39.84\ mg\ g^{-1}$).

3.7. Sorption kinetics

Kinetic studies were carried out under optimized conditions from 10 to 100 min. The kinetic data obtained were fitted to linear form of Lagergren pseudo-first and pseudo-second order kinetic models [14]. The pseudo-first order kinetic model known as Eq (8)

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

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 pseudo-first order adsorption process (min^{-1}). The pseudo-second order kinetic model is expressed by the Eq (9)

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

Where q_t and q_e -are the amounts of Rh6G sorbed at time τ and at equilibrium ($mol\ g^{-1}$), 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 Fig.5 and Fig.6, respectively.

Calculated parameters are placed in Table 6. Obtained data shows that the sorption process of the Rh6G from aqueous solutions with HMSC is better described by the pseudo-second kinetic model with determination coefficient 0.9907. Due to the fact that the correlation coefficient for the pseudo-second reaction is higher, it can be recognized that the sorption process occurs according to a pseudo-second reacting order. It should be noted that the value calculated for sorption capacity ($38.2\ mg\ g^{-1}$) from the pseudo-second order reaction graph is consistent with values obtained from the Langmuir (31.15 $mg\ g^{-1}$) and D-R (39.84 $mg\ g^{-1}$) isotherms.

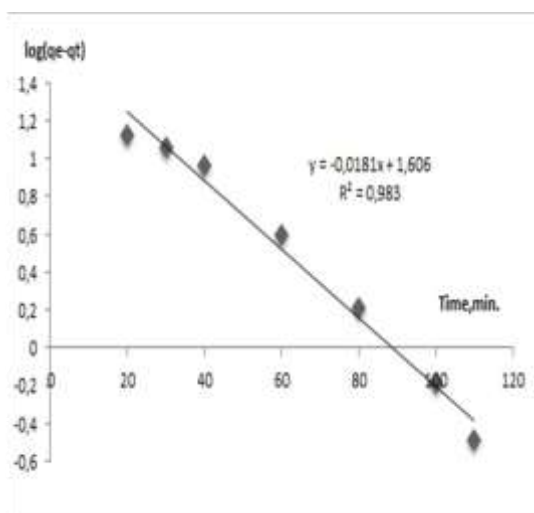


Fig. 5. Plot pseudo–first order model ($C_0 = 200 \text{ mg L}^{-1}$, $\text{pH}=6$, sorbent dosage 3.0 mg L^{-1} , $V= 0.04 \text{ L}$, 20°C).

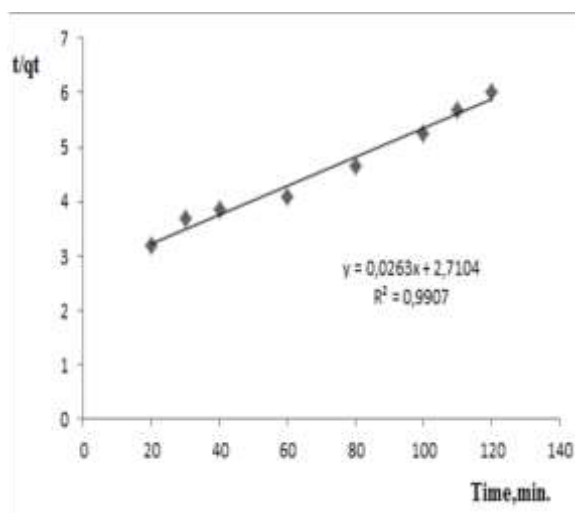


Fig.6. Plot of pseudo–second order model ($C_0 = 200 \text{ mg L}^{-1}$, $\text{pH}=6$, sorbent dosage 3.0 mg L^{-1} , $V= 0.04 \text{ L}$, 20°C).

Table 6. Regression parameters for kinetic models

Kinetic model Parameters	Pseudo-first order			Pseudo-second order		
	$q_e, \text{mg g}^{-1}$	K_1, min^{-1}	R^2	$q_e, \text{mg g}^{-1}$	$K_2, \text{L g}^{-1} \text{min}^{-1}$	R^2
	41.50	0.0417	0.9768	38.2	0.0006	0.9907

3.8. Adsorption thermodynamics

Thermodynamic parameters, like standard Gibbs free energy (ΔG°), standard enthalpy change (ΔH°) and standard entropy changes (ΔS°) were determined in order to explain the

effect of temperature on the adsorption of Rh 6G by HMSC. These parameters can be calculated from the Eq's (10-12)

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

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

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

Where R –is the gas constant ($8.314 \text{ J mole}^{-1} \text{ K}^{-1}$), T –is absolute temperature, 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 (Fig.8) and are placed in Table 7. The positive values of ΔG° confirm the nonspontaneous of

adsorption process, and the positive value of ΔH° ($12.464 \text{ kJ mol}^{-1}$) suggested that the adsorption is endothermic in nature. The positive value of ΔS° ($0.0271 \text{ kJ mol}^{-1} \text{ K}^{-1}$) shows the increasing randomness during adsorption process.

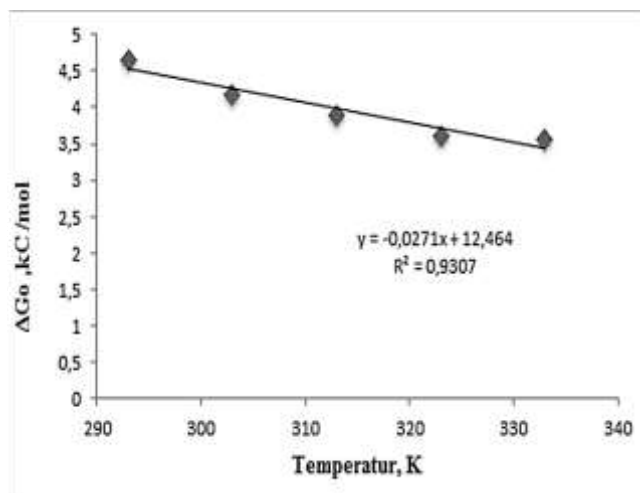


Fig. 8. Plot of ΔG° versus T (pH 6, 110 min, $C_0 = 200 \text{ mg L}^{-1}$, $V = 0.04 \text{ L}$, sorbent dosage 3.0 g L^{-1})

Table 7. Sorption thermodynamic parameters

Temperature, TK	Thermodynamic parameters		
	$\Delta G^\circ, kJ mol^{-1}$	$\Delta H^\circ, kJ mol^{-1}$	$\Delta S^\circ, kJ mol^{-1} K^{-1}$
293	+4.664		
303	+4.184		
313	+3.917	+ 12.464	+0.0271
323	+3.628		
333	+3.584		

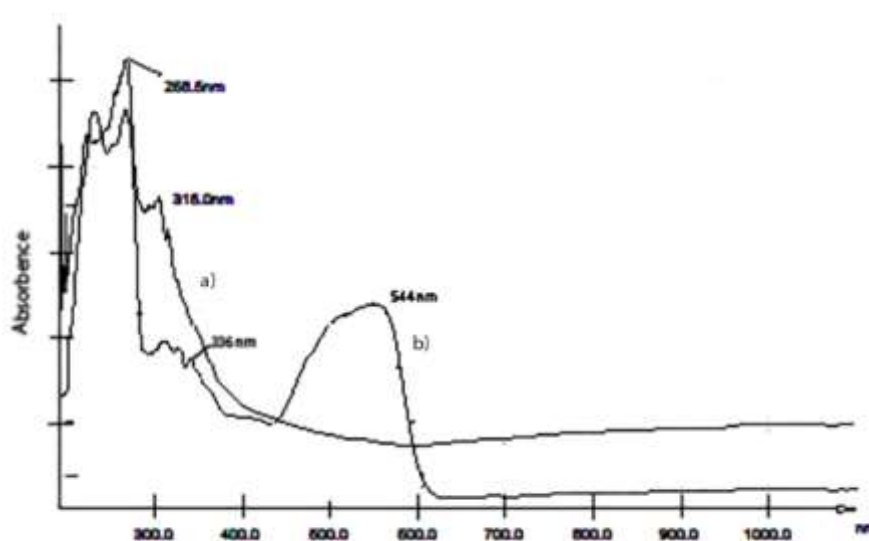


Fig. 9. UV-vis spectra of the HMSC a) before and b) after sorption.

3.9. Adsorption mechanism

The assumption of the possible adsorption mechanism has been made on the basis of the UV–spectra of the sorbent before and after adsorption and on the mean sorption energy, calculated from the D-R isotherm. UV–spectra of the HMSC before and after sorption have been illustrated in Fig.9.

Fig. 9 shows that the UV–spectra of the sorbent before and after sorption are different. In the UV– spectra of the sorbent after sorption (Fig.9b) there new absorption maximum

appears which is not observed in the spectra of the sorbent before sorption (Fig.9a). The maximum 544 nm in the UV–vis spectra of the sorbent after adsorption corresponds to Rh 6G dye which is adsorbed onto surface of the sorbent.

The obtained data for mean energy $E=4.256 \text{ kJ mol}^{-1} < 8.0 \text{ kJ mol}^{-1}$ from the D-R isotherm also indicated that the sorption of Rh 6G by synthesized polymer sorbent has physical character.

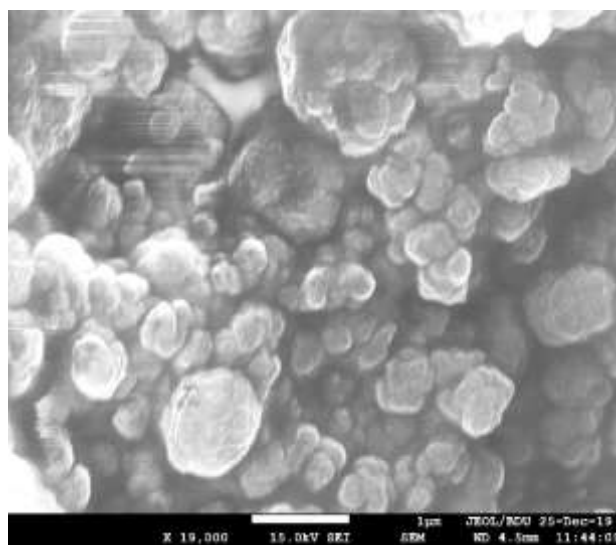


Fig. 10. SEM image of sorbent after sorption (x19.000)

The SEM image in figure 10 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).

References

1. Vilar VJP, Botelho CMS, Boaventura RAR. Methylene blue adsorption by algal biomass, based materials: biosorbents characterization and process behavior. *Journal of Hazardous Materials*, 2007, vol. 147(1-2), pp. 120-132.
2. Wissam L. Benyan. The Adsorptive Removal of Rhodamine 6G Dye from Aqueous Solution by Using Poly (Fumaric Acid-Co-Acrylic Acid) Hydrogels. *Journal of Global Pharma Technology*, 2019, vol. 11(3), pp. 263-272.
3. Yaping Li, Wangyan Nie, Peng Peng Chen, Yifeng Zhou. Preparation and characterization of sulfonated poly (styrene-alt-maleic anhydride) and its selective removal of cationic dyes. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2016, vol. 499, pp. 46-53. <https://doi.org/10.1016/j.colsurfa.2016.04.009>.
4. Popescu I., Suflet DM. Poly (N-vinyl caprolactam-co-maleic acid) microparticles for cationic dye removal. *Polym. Bull.* 2016, vol.73 (5), pp. 1283–1301. <https://doi.org/10.1007/s00289-015-1549->

5. Kai Shen, Gondal, MA. Removal of hazardous Rhodamine dye from water by adsorption onto exhausted coffee ground. *Journal of Saudi Chemical Society*, 2017, vol. 21, pp. 120–127.
6. Thitipone Suwunwong, Pimchanok Patho, Patcharanan Choto and Khampho Phoungthong. Enhancement the rhodamine 6G adsorption property on Fe₃O₄-composited biochar derived from rice husk. *Materials Research Express*, 2020, vol. 7(2), 025511. <https://doi.org/10.1088/2053-1591/ab6b58>.
7. Sreelatha G., Padmaja P. Study of Removal of Cationic Dyes using Palm Shell Powder as Adsorbent. *Journal of Environ. Protection Sci.*, 2008, vol. 2, pp. 63-71.
8. Akperov O.H., Akperov E.O. Practicum in the chemistry of high molecular weight compounds. BSU Publishing House, Baku, 2014, p. 31.
9. Akperov O.H., Akperov E.O., Kamranzadeh F.M. Removal of Rhodamine 6G dye from water solution by alt-maleic anhydride-octene-1terpolomer, crosslinked with triethanolamin. *New Materials, Compounds and Applications*, 2020, vol. 4, no.3, pp. 188-202.
10. Akperov O.H., Kamranzadeh F.M., Akperov E.O., Abbasov M.E., Durmazucar L. Removal of Rhodamine 6G dye from water solution by alt-maleic anhydride-styrene copolymer, cross-linked with Glycerin. *Indian Journal of Advances in Chemical Science*, 2021, vol. 9, no. 3, pp. 166-173.
11. Salleh M. A. M., Mahmoud D. K., Karim W. A., Idris A. Cationic and anionic dye adsorption by agricultural solid wastes: A comprehensive review. *Desalination*, 2011, vol.280, issues 1-3, pp. 1-13.
12. Sumanjit S. R., Mahajan R. K. Kinetic and equilibrium studies of adsorption of dye Congo red from aqueous solutions on bagasse charcoal and banana peels. *Journal of Surface Science and Technology*, 2012, vol. 28, pp. 133-147.
13. Monika J., Gard V., Kadirvelic K. Chromium (VI) removal from aqueous solution, using sunflower stem waste. *Journal of Hazardous Materials*, 2009, vol. 162, pp. 365-372.
14. Sunday A., Akolo S.A., Kovo A.S. Comparative study of adsorption of copper ion onto locally developed and commercial chitosan. *Journal of Encapsulation and Adsorption Sciences*. 2015, vol. 5, pp. 21-37.

УДАЛЕНИЕ КРАСИТЕЛЯ РОДАМИНА 6G ИЗ ВОДНОГО РАСТВОРА С АЛЬТ-СОПОЛИМЕРОМ МАЛЕИНОВЫЙ АНГИДРИД-СТИРОЛ, СШИТОГО С ГЕКСАМЕТИЛЕНДИАМИНОМ

О.Г. Акперов, Ф.М. Камранзаде, Е.О. Акперов

*Бакинский государственный университет
AZ 1148, Баку, ул. 3.Халилова, 23; e-mail: oakperov@mail.ru*

В статье представлены результаты по использованию альт-сополимера малеиновый ангидрид-стирол, сшитого гексаметилендиамином, в качестве сорбента для удаления красителя Родамина 6G из водного раствора. Было изучено влияние pH раствора, количества сорбента, времени контакта, концентрации красителя и температуры на степень сорбции красителя и равновесной сорбционной емкости сорбента. Полученные экспериментальные данные были обработаны в координатах уравнений изотермы Ленгмюра, Фрейндлиха и Дубинина-Радушкевича и определены аналитические параметры сорбции. Из графика уравнения Ленгмюра было определено значение сорбционной емкости (31.95 мг г⁻¹). Рассчитанное значение энергии адсорбции из графика уравнения D-R составляет 4.556 кДж моль⁻¹, что указывает на физическую природу сорбции красителя из водного раствора синтезированным сорбентом. Определены некоторые кинетические и термодинамические параметры процесса сорбции. Сорбция описывается псевдоторым порядком взаимодействия, положительные значения изменения энтальпии ΔH°(12,464 кДж моль⁻¹) указывают на эндотермический характер сорбции, а положительное значение изменения энтропии ΔS° (0.0271кДж моль⁻¹ K⁻¹) доказывает об увеличении хаотичности при адсорбции.

Ключевые слова: адсорбция, сополимер, изотермы, гексаметилендиамин, Родамин 6G

HEKSAMETİLENDİAMİNLƏ TİKİLMİŞ ALT-MALEİN ANHİDRİDİ- STİROL BİRGƏ POLİMERİ İLƏ RODAMİN 6G BOYAQ MADDƏSİNİN SULU MƏHLULDAN SORBSİYASI

O.H. Əkbərov, F.M. Kamranzadə, E.O. Əkbərov

Bakı Dövlət Universiteti,
Bakı Z. Xəlilov, 23, AZ 1148 Bakı, e-mail: oakperov@mail.ru

Məqalədə Rodamin 6G boyaq maddəsinin sulu məhluldan çıxarılması üçün heksametilendiaminlə tikilmiş alt-malein anhidridi-stirol birgə polimerindən istifadə olunmasına aid nəticələr verilmişdir. Sorbsiya dərəcəsinə pH-ın, kontakt müddətinin, sorbentin miqdarının, temperaturun və boyaq maddəsinin ilkin qatılığının təsiri öyrənilmişdir. Alınan təcrübi nəticələr Ləngimür, Freyndlix və Dubinin-Raduşkeviç izoterm tənliklərinin koordinatlarında işlənmiş, tarazlıq sorbsiya tutumunun qiyməti $31.95 \text{ mq } q^{-1}$ alınmışdır. D-R tənliyinin qrafikindən adsorbsiya enerjisi üçün hesablanmış qiymət $E_D=4.556 < 8.0 \text{ kC mol}^{-1}$ -dur, bu isə Rodamin-6G boyaq maddəsinin sintez olunmuş sorbentlə sulu məhluldan sorbsiyasının fiziki xarakterli olduğunu göstərir. Sorbsiyanın standart Gibbs enerjisi (ΔG°), entalpiya dəyişməsi (ΔH°) və entropiya dəyişməsinin (ΔS°) qiymətləri təyin olunmuşdur. ΔH° -ın müsbət qiyməti ($12.464 \text{ kC mol}^{-1}$) və ΔG° -nin müsbət qiymətləri isə adsorbsiyanın spontan getmədiyini və endotermik xarakterli olduğunu göstərir. ΔS° -in müsbət qiyməti ($0.0271 \text{ kC mol}^{-1} \text{ K}^{-1}$) isə adsorbsiyanın gedişində xaotikliyin artdığını sübut edir.

Açar sözlər: adsorbsiya, birgə polimer, izotermilər, heksametilendiamin, Rodamin 6G