

## REMOVAL OF RHODAMINE 6G DYE FROM WATER SOLUTION BY *alt*-MALEIC ANHYDRIDE-STYRENE-OCTENE-1 TERPOLYMER, CROSS-LINKED WITH TRIETHANOLAMINE

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**Abstract.** Batch sorption experiments were carried out for the removal of Rhodamine 6G dye (Rh6G) from aqueous solution using the *alt*-maleic anhydride-styrene-octene-1 terpolymer, cross-linked with triethanolamine. The operating variables studied were adsorbent dosage, solution pH, contact time, initial dye concentration and temperature. The Langmuir model successfully described the experimental data for the adsorption of the Rh6G onto *alt*-maleic anhydride-styrene-octene-1 terpolymer, cross-linked with triethanolamine. The calculated value of the maximum equilibrium sorption capacity is equal to be 20.28 mg g<sup>-1</sup>. The found value the sorption mean energy from D-R equation  $E_D=10.204 >8.0 \text{ kJ mol}^{-1}$ , indicated that, sorption process of the Rh6G dye by synthesized polymer-sorbent has chemical character. Adsorption data were modeled using the pseudo-first and pseudo-second order kinetic equations. It was found that the adsorption kinetics followed a pseudo-second order model. Also, the thermodynamic parameters of the adsorption process were calculated. The positive values of the  $\Delta G^0$  (3.718– 5.276 kJ mol<sup>-1</sup>) at 293–223 K and the positive value of the  $\Delta H^0$  (20.388 kJ mol<sup>-1</sup>) indicate that the sorption process is nonspontaneous and endothermic in nature. The positive value of  $\Delta S^0$  (0.052 kJ mol<sup>-1</sup> K<sup>-1</sup>) shows the increasing randomness during adsorption process.

**Keywords:** Adsorption, isotherms, kinetics, polymer sorbent, Rhodamine 6G, thermodynamic.

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### 1. Introduction

Dyes are widely used in industries such as textiles, paints, rubber plastic, paper, cosmetics, etc. Discharging dyes produced during various industrial activities can be harmful to aquatic life and human beings. The Rhodamine dyes are one of synthetic dyes and it is widely used as a colorant in the manufacturing of textiles, paper, cosmetics and food stuffs. When contacted with Rhodamine, it can cause serious health problems or signs such as increased allergy, dermatitis, heart rate, vomiting, skin cancer, lung cancer. Several treatment techniques of dye removal have been studied and developed, including physical, chemical, biological methods (Alizadeh *et al.*, 2016, Sadhasivam *et al.*, 2007, Gomes *et al.*, 2015, Dalvand *et al.*, 2016, Murugan *et al.* 2016, Hassan *et al.*, 2014). Adsorption processes belong to physical methods, which are found to be easier, more simply and more economical (Gomes *et al.*, 2015, Dalvand *et al.*, 2016, Chiew *et al.*, 2016, Anirudhan & Ramachandran, 2015). Various natural and synthetic polymer materials have been extensively explored and investigated for the adsorption removal of Rhodamine dyes. The chitosan-g-(N-vinyl pyrrolidone)/montmorillonite hydrogel composites was used to investigate the adsorption of a water-soluble cationic dye Rhodamine 6G (Vanamudan, 2014). The

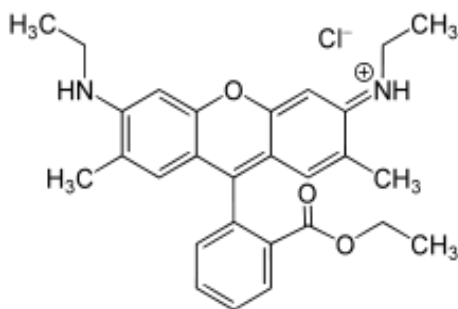
results show that the adsorption capacity for the dye increased with increase in dose, contact time, but there was no change observed with respect to increase in temperature. The adsorption kinetics of Rh 6G followed pseudo-second order model and the equilibrium data were found to fit Freundlich model. Batch sorption experiments were carried out for the removal of Rhodamine 6G from aqueous solution using Palm Shell Powder as adsorbent (Sreelatha & Padmaja, 2008). 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 kinetic equations. It was found that the adsorption kinetics followed a pseudo-second-order model, suggesting that the rate limiting step may be chemisorption. Equilibrium isotherm was analyzed using the Langmuir and the Freundlich isotherms. The characteristic parameters for each model have been determined. The exhaustive capacity was  $105.0 \text{ mg g}^{-1}$  for Rh6G at  $25 \text{ }^\circ\text{C}$ . The negative value of free energy change indicated the spontaneous nature of adsorption. 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 (Li *et al.*, 2016). Results indicated that the sulfonated poly (styrene-alt-maleic anhydride) had much more adsorb ability for cationic dyes compared to poly (styrene-alt-maleic anhydride). Exhausted coffee ground powder was proved to be an efficient adsorbent for the removal of Rhodamine dyes from aqueous solutions by batch adsorption experiments (Shen & Gondal, 2017). The adsorption kinetics and isotherm behaviors of Rhodamine molecules onto coffee ground powder was were studied and compared using pseudo-first, pseudo-second and Langmuir/Freundlich models, respectively. The effects of temperature, ionic strength, solution volume and the co-existing anions on the sorption behavior were also investigated. Furthermore, the adsorption mechanism responsible for the efficient removal of dyes is discussed in terms of adsorption process caused by electrostatic and intermolecular forces. Chemically modified chitosan-based super hydrophilic adsorbent was prepared and examined for removal of Rhodamine 6G dye from water solutions (Bhullar *et al.*, 2017). Adsorption parameters, such as adsorbent dose, initial concentration of pollutant, contact time and pH of the solutions were optimized for removal of Rh6G from aqueous solutions. The removal efficiency of sorbent for Rh6G was found to be 80.34% at pH 10 for constant sorbent dose  $1.0 \text{ g L}^{-1}$  and the data were subjected to adsorption isotherm analysis. The adsorption of the two cationic dyes, methylene blue and Rhodamine 6G, on the dry as well as equilibrium swollen superabsorbent polymers of acrylic acid, sodium acrylate, and acrylamide, crosslinked with ethylene glycol dimethyl acrylate, was investigated (Shukla *et al.*, 2012). The amount of the dye adsorbed at equilibrium per unit weight of the sorbent and the rate constants of adsorption were determined. The amount of the dye adsorbed at equilibrium by the sorbent decreased with increasing *mol %* of acrylamide. The amount of the dye adsorbed at equilibrium was almost equal for the dry and equilibrium swollen sorbent. However, the equilibrium swollen sorbent adsorbed dyes at a higher rate than the dry sorbent. The higher rate of adsorption was attributed to the availability of all the anionic groups present in the fully elongated conformation of the sorbent in the equilibrium swollen state. The effect of initial dye concentration on the adsorption was also investigated and the adsorption was described by Langmuir adsorption isotherms. The kinetics of adsorption of Rh6G on bentonite has been investigated in a batch adsorption process (Farham & Sameen, 2014). The adsorption of Rh6G 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 Rh6G on bentonite follows pseudo-second order rate kinetics. Magnetic biochar-sorbent was prepared using  $\text{Fe}_3\text{O}_4$  nanoparticle composites onto the surface of biochar derived from rice husk and the removal of Rhodamine 6G dye by magnetic biochar was studied (Suwunwong *et al.*, 2020). Kinetic, isotherms and thermodynamic studies were carried out to investigate the adsorption mechanism of rhodamine6G dye on magnetic biochar surface. The Rhodamine 6G removal efficiency of  $\text{Fe}_3\text{O}_4$ -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  $\text{Fe}_3\text{O}_4$ -biochar.

The present study details the removal of Rhodamine 6G dye from aqueous solutions by adsorption using an alt-maleic anhydride-styrene-octene-1 terpolymer, crosslinked with triethanolamine (MSOT) as an adsorbent. Various parameters affecting the adsorption process have been studied, such as pH, amount of sorbent polymer, contact time, initial dye concentration and temperature. In addition, kinetic and thermodynamic parameters were calculated and UV-spectroscopic study was conducted to determine a possible adsorption mechanism. The sorption properties of the alt-maleic anhydride-styrene-octene-1 terpolymer, crosslinked with triethanolamine toward Rh6G dye are executed for the first time and it defines the novelty of this work.

## 2. Experimental Materials

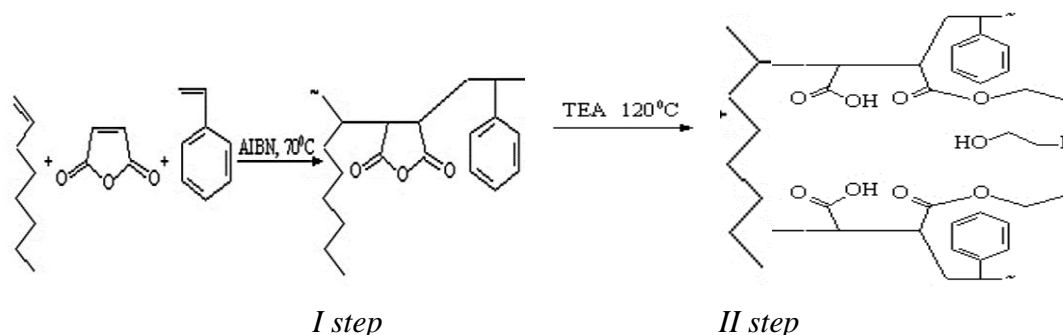
Maleic anhydride (MA) was purified before use by recrystallisation from benzene and by sublimation under vacuum. Octene-1 (OC), styrene (St) and triethanolamine (TEA) were distilled before use and had the following characteristics: OC: b.p. 120-122°C; St: b.p. 144-145°C, TEA: b.p. 161-162°C/15 mm Hg. Azobisisobutyronitrile (AIBN) was purified by recrystallisation from ethanol. UV-vis spectra were measured on a UV-vis SPECORD 210 PLUS (Germany) in the range 190–1100 nm. A pH-meter model pH-420 Akvilon, (Romania) was used for pH measurements. Rhodamine 6G (Rh 6G) was used as an adsorbate in the present study, is a monovalent cationic dye. Rh6G chloride is a bronze/red powder with the chemical formula  $\text{C}_{28}\text{H}_{31}\text{ClN}_2\text{O}_3$ . In dye classification it is classified as C.I. Basic Red 1, and the chemical structure of the dye is in the following form (Wikipedia)



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

### Preparation of Adsorbent

Polymer-sorbent, containing various functional groups (-COOH, OCO, -CH<sub>2</sub>OH, =N-, and =C=O) was synthesized in following two steps:



In the first step 4.9 g, (0.04 mol) MA), 2.24 g (0.02 mol) OC and 2.08 g (0.02 mol) St (molar ratio MA/OC/St =2:1:1) and 0.1 g AIBN were dissolved in acetic anhydride (30 ml) and mixture was heated at 70°C for 1 h. The obtained terpolymer (TPL) has been precipitated in ethanol or heptane and dried at 40°C in the vacuum oven (yields 6.7 g, 72.6%). The monomer contents of TPL have been determined by chemical analysis and equal 51.5; 17.8; 30.7 mol %, MA, OC and St respectively. In the second step a mixture of TPL (4.12 g) and triethanolamine (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 removal of unreacted TEA and TPL. The polymer-sorbent has been dried at 30°C in the vacuum oven.

### 3. Adsorption Experiments

Sorption of Rh 6G on MSOT was carried out using a batch experiment method. A stock solution of 500 mg L<sup>-1</sup> was prepared in double distilled water and the experimental solutions of the desired concentration were obtained by successive dilutions.

A quantity of 40 ml of Rh 6G dye solution of a certain concentration was placed in a 100-ml Erlenmeyer flask containing the sample of sorbent and was agitated in a thermocontrolled water bath. At the end of the experiment the mixture of adsorbent and adsorbate was immediately separated using glass fiber filter and residual Rh 6G in solution was defined by a photometric method. For this purpose, 1 ml of the filtered dye solution placed in the 25 ml graduated flask, diluted with the buffer solution CH<sub>3</sub>COOH/NH<sub>4</sub>OH with pH6 and the optical density has been defined. According to the obtained value of the optical density, the residual amount of Rh 6G has been determined using a calibration curve. The sorption degree R (%) and sorption capacity q (mg g<sup>-1</sup>) of the sorbent have been calculated by the Eq's (1) and (2):

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

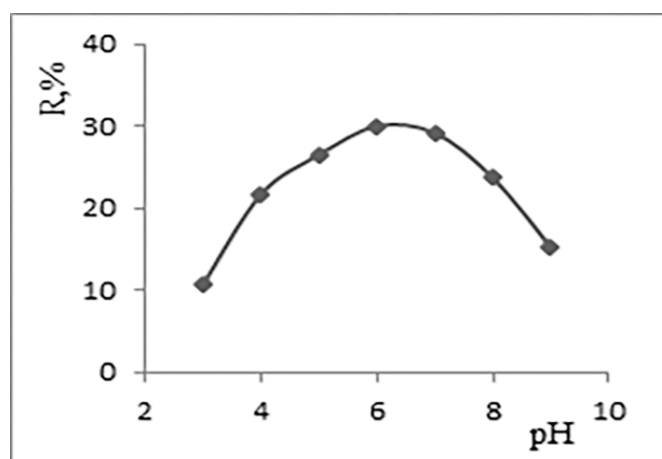
$$\text{Sorption capacity } (q) = \frac{(C_0 - C_e) \times V_{sol}}{m_{sorb}} \quad (2)$$

where:  $C_0$  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.

#### 4. Result and discussion

##### *Effect of pH*

The pH factor is very important in the adsorption process especially for dye adsorption. The effect of pH on the adsorption of Rh6G with MSOT was studied. It was observed that the pH has a significant influence to the adsorption process (Fig. 1). Fig.1 show that the maximum uptake of Rh6G dye was observed at pH 6 (30.0%). At pH between range 3-6 the removal degree was increased from 10.7% up to 30.0%. With a further increase in pH, a decrease in the sorption degree of the dye is observed.



**Figure 1.** Dependence sorption degree from pH (Rh 6G initial concentration  $100 mg L^{-1}$ ,  $V=0.04 L$ ,  $20^{\circ}C$ ,  $30 min$ )

Generally, at low pH solution, the percentage of dye removal will decrease for cationic dye adsorption, while for anionic dyes the percentage of dye removal will increase (Salleh et al 2011). At low pH, the lower dye adsorption onto MSOT can be linked to the large amount of  $H^+$  ions present, which compete with the dye positive groups for the adsorption sites of the sorbent. With the increase of the pH of the solution (above 3), the active sites of the surface of the sorbent were deprotonated and the competition for the adsorption sites between the dye cations and  $H^+$  decreased, which increased the amount of dye adsorbed (Hassan *et al.*, 2014). 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.

##### *Effect of sorbent dosage*

The effect of adsorbent dosage on the Rh 6G sorption process has been investigated at initial Rh 6G concentration  $100 mg L^{-1}$ , contact time  $30 min$ ,  $20^{\circ}C$ . The result shows that, the removal efficiency increases with increasing of the sorbent dosage. The increase of the sorbent dosage from  $0.05 g$  ( $1.0 g L^{-1}$ ) up to  $0.2 g$  ( $4.0 g L^{-1}$ ) causes the increase in the sorption degree of Rh 6G from 6.9 up to 32.6% (Table 1).

**Table 1.** Effect of sorbent dosage on sorption degree (Rh 6G initial concentration  $100 \text{ mg L}^{-1}$ , sorbent dosage  $3.0 \text{ g L}^{-1}$ ,  $V=0.04 \text{ L}$ ,  $20^\circ\text{C}$ ,  $30 \text{ min}$ )

Sorbent dosage, $\text{gL}^{-1}$	1.0	1.5	2.0	2.5	3.0	3.5	4.0
Sorption degree R, %	6.9	14.3	20.8	26.3	30.0	32.0	32.6

The sorption degree rapid increased with the increasing of the sorbent dosage up to  $1.0\text{--}3.0 \text{ gL}^{-1}$ , beyond which it attained almost a practical constant value (30.0–32.6%). Hence, sorbent amount equal to  $3.0 \text{ g L}^{-1}$ . Therefore, in further experiments with  $3.0 \text{ g L}^{-1}$  of sorbent was used.

#### ***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 has been investigated at different contact time varying between 10 and  $100 \text{ min}$  at  $20^\circ\text{C}$  (Table 2).

**Table 2.** Effect of time on sorption degree (Rh 6G initial concentration  $100 \text{ mg L}^{-1}$ ,  $V=0.04 \text{ L}$ , sorbent dosage  $3.0 \text{ g L}^{-1}$ ,  $20^\circ\text{C}$ )

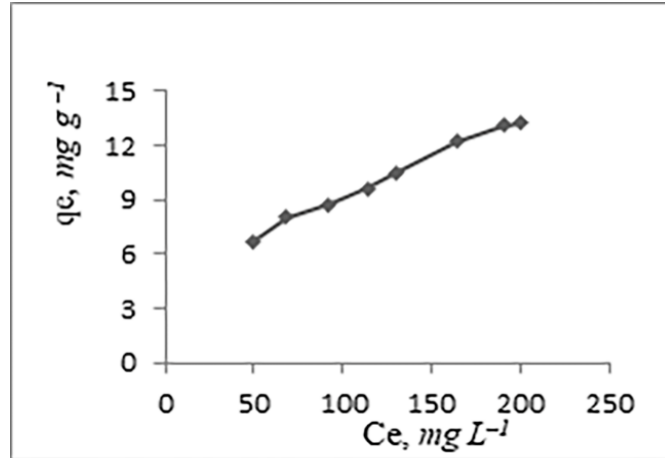
Time, <i>min</i>	10	20	30	40	60	80	100
Sorption degree R, %	20.1	25.7	30.0	33.6	35.2	36.0	36.3

These results indicated that with the increase of time the removal of Rh 6G increased to a certain point of equilibrium. During the first  $10 \text{ min}$  of the sorption 20.1% of the total amount of Rh 6G was immobilized. The state of dye equilibrium in the MSOT structure is reached after  $60 \text{ min}$ . At that time, 33.6–35.2% of Rh 6G were removed by sorbent. Therefore, the contact time equal to 40–60 *min* was considered to be sufficient for sorption of Rh 6 G by sorbent.

#### ***Effect of the Rh6G initial concentration and sorption isotherm of sorbent***

Rh 6G solutions with several initial concentrations in the range of  $49.9\text{--}200 \text{ mg L}^{-1}$  and at  $20^\circ\text{C}$  were equilibrated using  $3.0 \text{ g L}^{-1}$  adsorbent dosage. The results showed that the Rh 6G sorption onto sorbent were strongly affected by the initial dye concentration and with increasing of initial Rh6G concentration, sorption degree is decreasing. The Rh 6G removal degree decreases from 33.5 to 19.2% when its initial concentration increases from  $49.9$  to  $200 \text{ mg L}^{-1}$ . It is explained that with increasing dye concentration, the specific sites of a sorbent were saturated and exchange sites were filled. In Fig.2 it is illustrated sorption isotherm, which was constructed on dependence of sorption capacity of a sorbent on equilibrium concentration of the Rh 6G. Equilibrium sorption capacity of the sorbent was calculated in the initial Rh 6G concentration range  $49.9\text{--}200 \text{ mg L}^{-1}$  at  $20^\circ\text{C}$  and for  $30 \text{ min}$  contact time. It is shown that the sorption capacity of the sorbent increases rapidly with the increasing of equilibrium concentration of Rh 6G. When the Rh6G concentration reached a certain extent the increasing of adsorption capacity became slower and comes nearer to constant value. It can be concluded that the experimentally maximum sorption capacity ( $q_{exp}$ ) of the sorbent at the equilibrium conditions is  $13.5 \text{ mg g}^{-1}$ .





**Figure 2.** Sorption isotherm of sorbent (pH 6, 30 min,  $C_0=49.9\text{--}200\text{ mg L}^{-1}$ ,  $V=0.04\text{ L}$ , sorbent dosage  $3.0\text{ g L}^{-1}$ ,  $20^\circ\text{C}$ )

**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 (3)

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

where  $C_e$  -is the equilibrium concentration of Rh 6G ( $\text{mg L}^{-1}$ ),  $q_e$ - is the amount of the Rh 6G adsorbed at equilibrium ( $\text{mg g}^{-1}$ ),  $q_{max}$ -is the monolayer maximum adsorption capacity of the MSOT ( $\text{mg g}^{-1}$ ) and  $K_L$ -is the Langmuir equilibrium constant ( $\text{L g}^{-1}$ ).

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

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

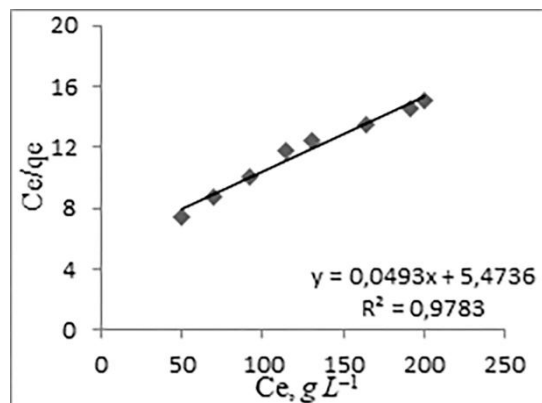
where  $K_D$  – is the D–R equation constant,  $B_{DR}$ –theoretical isotherm saturation capacity ( $\text{mole g}^{-1}$ ),  $q_e$ -is the sorption capacity ( $\text{mol L}^{-1}$ ) and  $\varepsilon$  – is Polanyi potential, which is defined by (5)

$$\varepsilon = RT \ln (1 + 1/C_e) \tag{5}$$

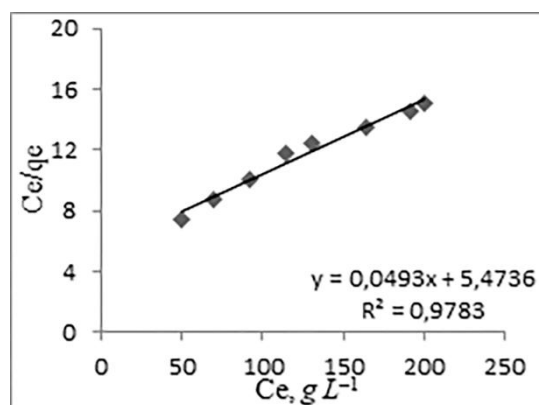
where  $C_e$  –is equilibrium concentration of the Rh6G ( $\text{mol}^{-1}$ ),  $R$ - is universal gas constant ( $8.314\text{ J mol}^{-1}$ ). The D–R constant can give the valuable information regarding the mean energy ( $E$ ) of adsorption by the (6)

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

The obtained experimental equilibrium data were examined with Langmuir and D–R isotherm models. The plots 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 were given in Table 3. The calculated value of the maximum experimental sorption capacity from the Langmuir equation, (Fig.3) is equal to be  $20.28\text{ mg g}^{-1}$ , which are close to experimentally obtained value of equilibrium sorption capacity from sorption isotherm ( $13.5\text{ mg g}^{-1}$ )



**Figure 3.** Langmuir plot for sorption (pH 6, 30 min,  $C_o = 49.9 - 200 \text{ mg L}^{-1}$ ,  $V = 0.04 \text{ L}$ , sorbent dosage  $3.0 \text{ g L}^{-1}$ ,  $20^\circ\text{C}$ )



**Figure 4.** D-R plot for sorption (pH 6, 30 min,  $C_o = 49.9 - 200 \text{ mg L}^{-1}$ ,  $V = 0.04 \text{ L}$ , sorbent dosage  $3.0 \text{ g L}^{-1}$ ,  $20^\circ\text{C}$ )

**Table 3.** Langmuir and D-R equations parameters

<u>Langmuir equation</u>				<u>D-R equation</u>				
$q_{max}, \text{mg g}^{-1}$	$K_L, \text{L mg}^{-1}$	$R_L$	$R^2$	$K_D, \text{kJ mol}^{-1}$	$B_{DR}, \text{mg g}^{-1}$	$E, \text{kJ mol}^{-1}$	$R^2$	
20.28	0.009	0.537-0.258	0.9783	0.0048	72.66	10.204	0.9781	

Obtained data shows the applicability of the Langmuir model, showing 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 ( $R_L$ ) was adopted. The separation factor  $R_L$  was calculated using the (7)

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

where  $C_o$  is the initial Rh6G concentration ( $\text{mg L}^{-1}$ ). 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  $R_L = 0$  (Sumanjit & Mahajan, 2012). The calculated values of  $R_L$  for different initial concentration of the Rh6G ( $49.9 - 200 \text{ mg L}^{-1}$ )



were equal to be 0.537– 0.258, indicates highly favorable adsorption for the Rh6G onto MSOT.

The found value of the mean sorption energy from D–R equation  $E_D=10.204 >8.0 \text{ kJ mol}^{-1}$  indicated that, sorption of Rh6G by synthesized polymer-sorbent has chemical character (Monika *et al.*, 2009). The theoretical isotherm saturation capacity of the sorbent ( $B_{DR}$ ) from D–R equation is equal to be  $0.1517 \text{ mmol g}^{-1}$  ( $72.66 \text{ mg g}^{-1}$ ).

### Sorption kinetics

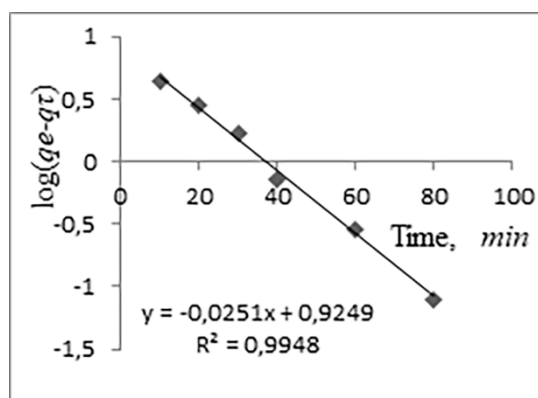
Kinetic studies were carried out under the optimized conditions from 10 to 100 *min*. The kinetic data obtained were fitted to linear form of Lagergren pseudo–first and pseudo–second order kinetic models (Sunday *et al.*, 2015). The pseudo–first order kinetic model known as (8)

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

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

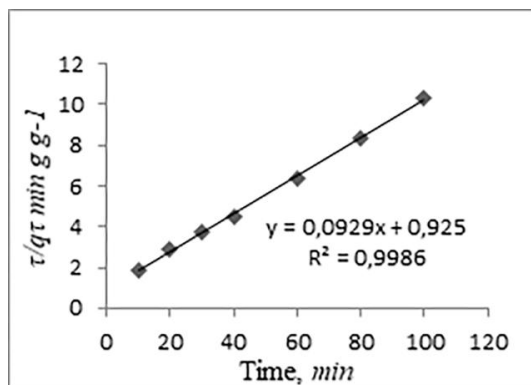
$$\tau / q_t = 1/(K_2 q_e^2) + \tau/q_e \quad (9)$$

where  $q_t$  and  $q_e$ –are the amounts of Rh6G sorbed at time  $\tau$  and at equilibrium ( $\text{mol g}^{-1}$ ), respectively,  $K_2$ –is the pseudo–second order equilibrium rate constant ( $\text{mole}^{-1} \text{ min}^{-1}$ ). Plots of the equation of the pseudo–first and pseudo–second models are illustrated in Fig.5 and Fig.6, respectively.



**Figure 5.** Plot pseudo–first order model ( $C_0 = 100 \text{ mg L}^{-1}$ ,  $\text{pH}=6$ , sorbent dosage  $3.0 \text{ mg L}^{-1}$ ,  $V= 0.04 \text{ L}$ ,  $20^\circ\text{C}$ ).

Calculated parameters are placed in Table 4. Obtained data shows that the sorption process of the Rh6G from aqueous solutions with MSOT is better described by the pseudo–second kinetic model with determination coefficient 0.9986. Conformity between calculated ( $10.76 \text{ mg g}^{-1}$ ) and experimental ( $13.25 \text{ mg g}^{-1}$ )  $q_e$  values, suggesting that chemisorption is a defining stage in the Rh6G adsorption process on a synthesized sorbent.



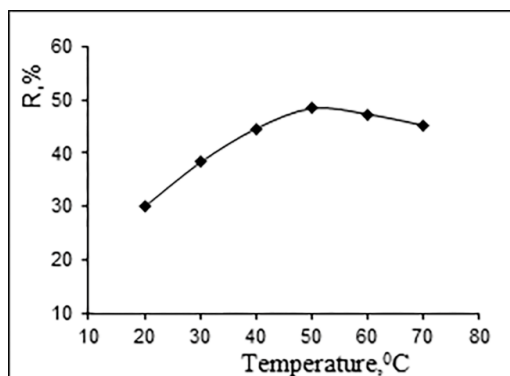
**Figure 6.** Plot pseudo-second order model ( $C_0 = 100 \text{ mg L}^{-1}$ , pH=6, sorbent dosage  $3.0 \text{ mg L}^{-1}$ ,  $V = 0.04 \text{ L}$ ,  $20^\circ\text{C}$ )

**Table 4.** Regression parameters for the kinetics models

Kinetic model	Pseudo-first order			Pseudo-second order		
Parameters	$q_e, \text{mg g}^{-1}$	$K_1, \text{min}^{-1}$	$R^2$	$q_e, \text{mg g}^{-1}$	$K_2, \text{L g}^{-1}\text{min}^{-1}$	$R^2$
	8.414	$5.78 \times 10^{-3}$	0.9948	10.76	$9.33 \times 10^{-4}$	0.9986

#### *Effect of temperature and thermodynamics of the adsorption*

The purpose of this research is to ascertain the effect of temperature on the sorption of Rh6G dye by the MSOT. The effect of temperature on the removal of Rh6G dye in aqueous solution by MSOT was studied by varying the temperature between 20 and  $60^\circ\text{C}$  at initial dye concentration of  $100 \text{ mg L}^{-1}$ , pH 6, sorbent dosage  $3.0 \text{ g L}^{-1}$  and contact time  $30 \text{ min}$ . The data presented in Fig.7 showed that adsorption of dye by the MSOT increased with increase in temperature. This behavior confirms that the adsorption of dye has an endothermic nature. However, the magnitude of such increase continues to decline as temperatures are increased from 50 to  $70^\circ\text{C}$ . This is because with increasing temperature, the attractive forces adsorbent surface and Rh6G are weakened and the sorption decreases. Examination of the Fig.7 revealed that most of the dye were removed between the temperatures of 20 to  $50^\circ\text{C}$ .



**Figure 7.** Dependence sorption degree from temperature (pH 6,  $30 \text{ min}$ ,  $C_0 = 49.9 - 200 \text{ mg L}^{-1}$ ,  $V = 0.04 \text{ L}$ , sorbent dosage  $3.0 \text{ g L}^{-1}$ )

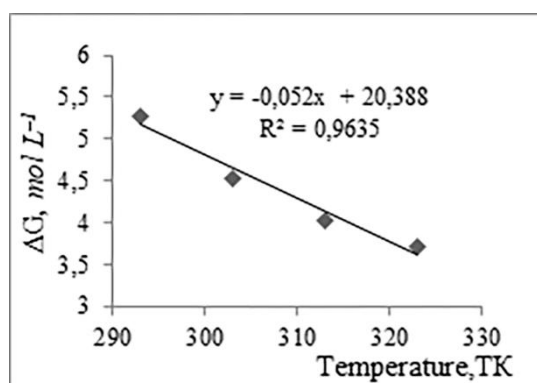
Thermodynamic parameters, like standard Gibbs free energy ( $\Delta G^\circ$ ), standard enthalpy change ( $\Delta H^\circ$ ) and standard entropy change ( $\Delta S^\circ$ ) were determined in order to explain the effect of temperature on the adsorption of Rh 6G by MSOT. These parameters can be calculated 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  $\Delta H^\circ$  and  $\Delta S^\circ$  were obtained from the slope and intercept of the plots of  $\Delta G^\circ$  versus  $T$  (Fig.8) and are placed in Table 5.



**Figure 8.** Plot of  $\Delta G^\circ$  versus  $T$  (pH 6, 30 min,  $C_0 = 100 \text{ mg L}^{-1}$ ,  $V = 0.04 \text{ L}$ , sorbent dosage  $3.0 \text{ g L}^{-1}$ )

**Table 5.** Sorption thermodynamic parameters

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	5.276		
303	4.532		
313	4.01	20.388	0.052
323	3.718		

The positive values of  $\Delta G^\circ$  confirm the nonspontaneous of adsorption process, and the positive value of  $\Delta H^\circ$  ( $20.388 \text{ kJ mol}^{-1}$ ) suggested that the adsorption is endothermic in nature. The positive value of  $\Delta S^\circ$  ( $0.052 \text{ kJ mol}^{-1} \text{ K}^{-1}$ ) shows the increasing randomness during adsorption process.

For the purpose of assessment scientific and practical significance of our work, we compared the obtained by us data on adsorption of Rh6G dye with MSOT a with some literature data on sorption Rh6G dye by other adsorbents (Table 6).

**Table 6.** Comparison of Rh 6G dye uptake data with other adsorbents

Sorbent	$q_{max}$ ( $mg\ g^{-1}$ )	pH	Adsorbent, ( $g\ L^{-1}$ )	Model	Source
Activated carbon	44.7	7	0.02	Langmuir	Anna durai et al, 2001
Palm shell powder	105.0	5.75	0.4	Langmuir	Sreelatha, Padmaja, 2008
Biological sludge	16.3	7	10.0	Langmuir	Anna durai et al 2003
Coffee ground	17.37	—	1.0	Langmuir	Kai Shen, Gondal, 2017
<i>Trichoderma harzianum</i> mycelial biomass	3.40	8	2.0	Langmuir	Sadhasivam et al 2007
Chitosan-g-(N-vinyl pyrrolidone)	36.6	10	0.05	Freundlich	Vanamudan et al 2014
montmorillonite hydrogel	111.11	6	4.0 g	Langmuir	Anirudhan, Ramachandran, 2015
Bentonite Clay	111.11	6	4.0 g	Langmuir	Anirudhan, Ramachandran, 2015
Cross-linked maleic anhydride terpolymer	20.28	6	3.0	Langmuir	In this study

From Table 6, the adsorption parameters on removal of Rh6G dye from water solution by MSOT is comparable with data on adsorption of Rh6G dye from water solution, using other adsorbents.

### ***Mechanism adsorption***

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 MSOT before and after sorption have been illustrated in Fig.9.

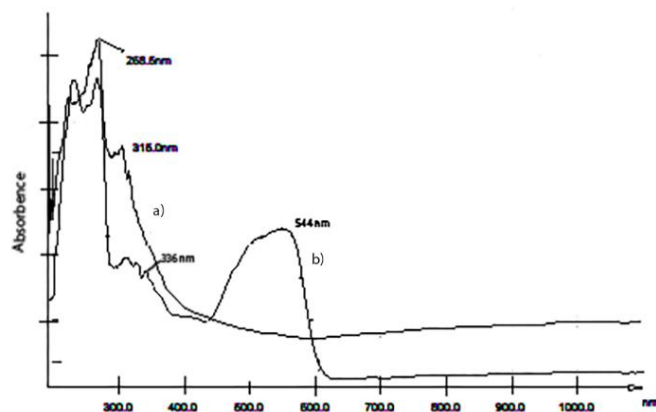
**Fig. 9.** UV–vis spectra of the MSOT a) before and b) after sorption

Fig. 9 shows that the UV–spectra of the sorbent before and after sorption differ. In the UV– spectra of the sorbent after sorption (Fig.9b), new absorption maximum appears, that are 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, adsorbed onto surface of the sorbent. This spectrum also contains maxima in the average 336 nm, which can be attributed to donor-acceptor complexes of Rh6G dye with MSOT. The complexation of Rh 6G with maleic acid copolymers is reported in the works (Oikonomou *et al.*, 2008, Rivas *et al.*, 2001). It is noted that Rh 6G can be

form complexes with maleic acid copolymers, which give maximum in the region 350-370 nm.

The obtained data for mean energy  $E=10.204 \text{ kJ mol}^{-1} > 8.0 \text{ kJ mol}^{-1}$  from the D-R isotherm also indicated that, sorption of Rh 6G by synthesized polymer sorbent has chemical character.

## 5. Conclusions

The cross-linked maleic anhydride-styrene-octene-1 terpolymer has been used for the removal of Rh 6G from aqueous solution. Effects of contact time, sorbent dosage, temperature and copper ions initial concentration were tested and optimum conditions of the sorption process were evaluated. The calculated value of the maximum sorption capacity from the Langmuir equation is equal to  $20.28 \text{ mg g}^{-1}$ . Separation factor  $R_L$  values at different initial concentration of the Rh 6G were less than 1 and greater than zero, ( $1 > 0.537 - 0.258 > 0$ ) indicating favorable adsorption. The found value of the mean sorption energy from D-R equation  $E=10.204 \text{ kJ mol}^{-1} > 8.0 \text{ kJ mol}^{-1}$  also indicated that, sorption of Rh 6G by synthesized polymer sorbent has chemical character. The theoretical isotherm saturation capacity of the sorbent ( $B_{DR}$ ) from D-R equation is equal to  $0.1517 \text{ mmol g}^{-1}$  ( $72.66 \text{ mg g}^{-1}$ ). It is found that the pseudo-second-order model was the most appropriate model, describing the sorption kinetics. Conformity between calculated ( $10.76 \text{ mg g}^{-1}$ ) and experimental ( $13.25 \text{ mg g}^{-1}$ ) sorption capacity values, suggesting that chemisorption is a defining stage in the Rh6G adsorption process on a synthesized sorbent. The positive values of the  $\Delta G^0$  ( $5.276 - 3.718 \text{ kJ mol}^{-1}$  at 293-323 K), indicate that the sorption process is nonspontaneous and the positive value of the  $\Delta H^0$  ( $20.388 \text{ kJ mol}^{-1}$ ) indicate that the sorption process is endothermic in nature. The positive value of  $\Delta S^0$  ( $0.052 \text{ kJ mol}^{-1} \text{ K}^{-1}$ ) shows the increasing randomness during adsorption process. The obtained experimental data and UV- spectra of the sorbent before and after sorption show, that the adsorption process of the Rh6G dye with the synthesized sorbent is accompanied by chemical interaction of the dye with the active centers of the sorbent. To summarize, it could be concluded that, *alt*-maleic anhydride-styrene-octene-1 terpolymer, cross-linked with triethanolamine is an efficient adsorbent for removal Rh 6G dye from aqueous solutions.

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