

REMOVAL OF THE COPPER IONS FROM WATER SOLUTION BY AMMONIUM SALT OF THE MALEIC ACID-STYRENE- HEPTENE-1 TERPOLYMER

E.O. Akperov¹, E.A. Shirinova¹, O.H. Akperov^{1*}, S.R. Gafarova¹

¹ Department of Polymer Chemistry, Baku State University, Azerbaijan

Abstract. Ammonium salt of the maleic acid-styrene-heptene-1 terpolymer was used for removal of copper (II) ions from aqueous solution. Effects of contact time, sorbent dosage and initial Cu^{2+} concentration on removal degree were tested. The equilibrium sorption data were fitted to Langmuir, Freundlich, and Dubinin-Radushkevich and Temkin isotherms. The calculated value of the maximum experimental sorption capacity from the Langmuir and Freundlich equations is equal to 0.819 and 0.878 g g^{-1} respectively. The found value of the mean sorption energy from Dubinin-Radushkevich equation ($7.634 \text{ kJ mol}^{-1}$) specifies that, sorption of the copper ions by synthesized polymer salt has a chemical character. The heat of sorption process was estimated from Temkin isotherm model to be $2.7 \times 10^{-3} \text{ kJ mol}^{-1}$. The kinetic experimental data correlated well with the pseudo-second order model. Thermodynamic parameters such as ΔG° , ΔH° , and ΔS° have also been evaluated, and it has been found that the adsorption process was spontaneous, exothermic, and randomness in nature.

Keywords: Copper ions, isotherm, kinetics, sorption, thermodynamics.

Corresponding Authors: O.H. Akperov, Department of Polymer Chemistry, Baku State University, AZ1148, Z. Khalilov 23, Baku, Azerbaijan, e-mail: okperov@mail.ru

Manuscript received: 24 November 2017

1. Introduction

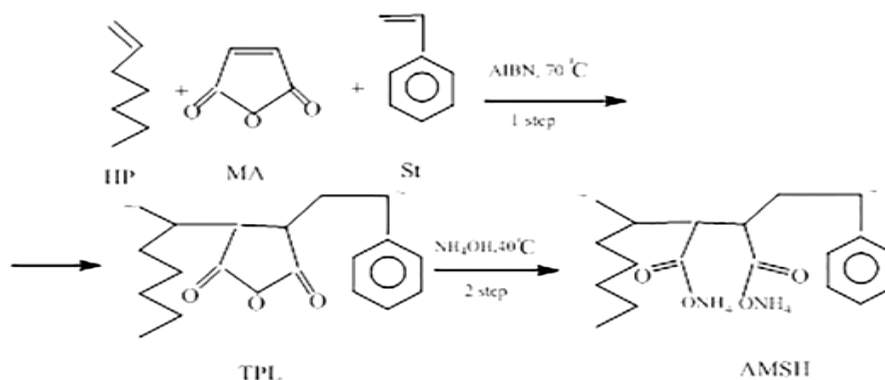
Many industries, such as metal finishing, electroplating, battery manufacturing, electric cable manufacturing, and steel and textile industries, release various concentrations of heavy metals like copper, cadmium, nickel and others into wastewater. Copper is a highly toxic heavy metal and at production and processing sites of copper ores the landscape, underground and surface waters are contaminated with compounds of copper that can do enormous harm to the environment. Among the heavy metals, copper is the major available type of heavy metal in the aquatic environment. Accumulation of copper ions in natural objects does big ecological harm to living organisms, fauna and flora on earth. Recent awareness of toxicity originated from water and wastewater are attending the interest for environmental scientist and researcher. Many types of polymeric adsorbents have been developed and studied for the recovery and removal of toxic heavy metal ions from aqueous solutions (Ngah et al., 2002; Kavaklı & Güven, 2004; Ferrah et al., 2011; Rivas et al., 2003). The complexation of natural or synthetic water-soluble polymers with adequate complexing ions is of great fundamental and practical interest (Oikonomou et al., 2008). These polymers are capable of coordinating to different metal ions through reactive functional groups containing O, N, S, and P as donor atoms to form metal macromolecular complexes. A new chelating polymer sorbent was synthesized through the copolymerization of styrene and maleic anhydride in the

presence of divinylbenzene as crosslinking agent, followed by hydrolysis (Roy et al., 2004). This newly developed chelating matrix has a high resin capacity for metal ions such as Cr, Fe, Ni, Cu and Pb. A chelating resin based on modified poly (styrene–alt–maleic anhydride) with 3–aminobenzoic acid was synthesized (Hasanzadeh et al., 2013). The adsorption behaviour of Fe(II), Cu(II), Zn(II) and Pb(II) ions was investigated by synthesized chelating resins in various pH and the order of removal percentage changes as follow: Fe(II) > Cu(II) > Zn(II) > Pb(II). In addition, the prepared resins were examined for removal of metal ions from industrial wastewater and were shown to have a very efficient adsorption in the case of Cu (II), Fe (II) and Pb (II). Chelating copolymers bearing carboxylic acid and/or carboxylate moieties based on ethyl methacrylate in the absence and in the presence of divinyl benzene as a cross–linked were prepared via new emulsion copolymerization route (El-Ghaffar et al., 2013). The prepared chelating copolymers have been tested as adsorbents for various toxic heavy metal ions. Chitosan and nanocomposite 5% bentonite/chitosan prepared from the natural biopolymer were tested to remove Cu (II) ions using a batch adsorption experiment at various temperatures (25, 35 and 45°C) (Moussout et al., 2016). The data were confronted to the nonlinear Langmuir, Freundlich and Redlich–Peterson models. The maximum monolayer adsorption capacity for the Cu (II) was 404–422 mg g⁻¹ for chitosan and 282–337 mg g⁻¹ for 5% bentonite/ chitosan at 25–45°C. The thermodynamic study showed that the adsorption process was spontaneous and endothermic. The complexation of Cu (II) with NH₂ and C = O groups as active sites was found to be the main mechanism in the adsorption processes. A blended polymer adsorbent prepared using acrylic acid and polyvinylidene fluoride was used to remove copper from aqueous solutions (Song et al., 2008). The sorption data was fit to linearized adsorption isotherms of the Langmuir, Freundlich, and Dubinin–Radushkevich (D-R) isotherms models. The batch sorption kinetics was evaluated using pseudo-first-order, pseudo-second-order, and intraparticle diffusion kinetic reaction models. The adsorption isotherm fits better to the Freundlich isotherm model and the pseudo–second order kinetics model gives a better fit to the batch sorption kinetics. The adsorption mechanism is assumed to be ion exchange between the copper ion and the carboxylic acid functional group of the blended polymer. This work is focused on the removal of Cu²⁺ ions from aqueous solutions using ammonium salt of the maleic acid-heptene-1-styrene terpolymer as a sorbent. The effects of the sorbent dosage, initial copper ion concentration, contact time and temperature were studied. Equilibrium isotherm data were analyzed by the Langmuir, Freundlich, Dubinin-Radushkevich and Temkin isotherm models. The pseudo-first order and pseudo-second order were used in kinetic study of the removal process. Thermodynamic parameters such as ΔG° , ΔH° and ΔS° have also been evaluated.

2. Experimental

2.1. Preparation of the sorbent

Ammonium salt of maleic acid-heptene-1-styrene terpolymer (AMHS) was prepared in two steps:



In the first step the maleic anhydride–styrene–heptene–1 terpolymer (TPL) was synthesized by reaction of maleic anhydride, styrene and heptene-1 in butyl acetate in the presence of AIBN at 70°C (Akperov et al., 2009). MA (3.92 g), ST (2.08 g, 2.3 mL), HP (1.96 g, 2.8 mL) (molar ratio MA/ ST /HP =2:1:1) and AIBN (0.08 g, 1.0 %) were dissolved in butyl acetate (30 mL), after heating the mixture at 70°C for 1 h, the obtained TPL were precipitated in ethanol or heptane and dried at 40°C in a vacuum oven (72.5 % yields). The monomer contents of TPL were determined by chemical analysis and the ¹H NMR-spectrum. It was established that the molar contents of MA, HP and ST in the terpolymer were 51.5; 29.5 and 19.3 mol %, respectively. The intrinsic viscosity was 0.66 dl⁻¹ (methyl ethyl ketone, 20°C).

In the second step, a mixture of TPL (4.4 g) and ammonium hydroxide (5% solution, 30 mL) was heated at 40-50°C for 1 h. The obtained AMSH was precipitated in acetone, washed repeatedly with acetone and dried at 40°C in the vacuum oven.

2.2. Materials and Methods

All chemicals used were analytical reagent grade. Maleic anhydride (MA) was purified before use by recrystallization from benzene and by sublimation under vacuum. Styrene (ST) and Heptene–1 (HP) were distilled before use and had the following characteristics: ST: b.p. 144–145°C; HP: b.p. 93–94°C. Azobisisobutyronitrile (AIBN) was purified by recrystallization from ethanol. A stock solution of Cu²⁺ ions was prepared by dissolving 25 g of CuSO₄ · 5H₂O in 0.5 L deionized water to obtain a concentration of Cu²⁺ ions of 0.2 mol L⁻¹ (6.4 g L⁻¹). The stock solution was diluted to obtain solutions with concentrations of Cu²⁺ in the range of 0.0025–0.02 mol L⁻¹ (0.16–1.28 g L⁻¹). A 0.001 mol L⁻¹ xylenol-orange solution was prepared by dissolving 0.076 g of the reagent in 100 mL of deionized water. Buffer solutions CH₃COOH/NH₄OH with pH6 were used for formations of a Cu²⁺-xylenol-orange complex. Removal of copper ions on synthesized AMSH was carried out using a batch experiment method. 40 mL of CuSO₄ solution of a certain concentration was placed in a 100 mL Erlenmeyer flask containing sample of sorbent and was agitated in a thermocontrolled water bath to carry out sorption experiment. At the end of the experiment an AMSH complex with copper ions separated from solution and residual copper ions in solution was defined by a photometric method. For this purpose 1 mL of the copper ion solution and 2 mL of the xylenol-orange solution placed into the 25 mL graduated flask, were diluted with the buffer solution and the optical density has been defined. The value of residual of copper ions was determined using a calibration curve.

The sorption degree (%) and sorption capacity ($g\ g^{-1}$) were calculated by the equations (1) and (2), respectively.

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

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

where C_0 and C_e ($g\ L^{-1}$) are initial and equilibrium concentrations of copper ions solutions, respectively, V_{sol} (L) is the volume of the copper ions solution submitted to sorption, and m_{sorb} (g) is the weight of sorbent.

3. Result and Discussion

3.1. Effects of sorbent dosage

Effects of sorbent dosage, contact time and initial Cu^{2+} concentration on removal degree were tested. The result shows that, the removal degree increases with increasing of the sorbent weight. The increase of the sorbent weight from 0.5 up to 2.5 $g\ L^{-1}$ (0.02 up to 0.1 g in 40 mL of the solution taken for sorption) causes the increase in the removal degree from 56.2 up to 75.1% (Table 1).

Table 1. Effect of sorbent dosage on the sorption degree
($C_0=0.32\ g\ L^{-1}$, $V=0.04\ L$, $20^\circ C$, 60 min)

| | | | | | | | |
|------------------------------------|------|------|------|------|------|------|------|
| Sorbent dosage, ($g\ L^{-1}$) | 0.5 | 0.75 | 1.0 | 1.25 | 1.5 | 1.75 | 2.5 |
| Removal degree, R , (%) | 56.2 | 64.6 | 70.1 | 74.3 | 74.9 | 75.3 | 75.1 |

The sorption degree increased with the increasing of the sorbent weight up to 1.25 $g\ L^{-1}$ (0.05 g in 40 mL of the solution), beyond which it attained almost a constant value (74.3 %). Hence, sorbent amount equal to 1.25 $g\ L^{-1}$ is optimum at initial concentration of copper ions equal to 0.32 $g\ L^{-1}$.

3.2. Effects of contact time

The effect of contact time on copper ion sorption by AMSH was investigated at different contact time varying between 5 and 120 min (Table 2).

Table 2. Effect of contact time on sorption degree
($C_0=0.32\ g\ L^{-1}$, $V=0.04\ L$, sorbent dosage 1.25 $g\ L^{-1}$, $20^\circ C$)

| | | | | | | | | |
|------------------------------|------|------|------|------|------|------|------|------|
| Ti Time, min. | 5 | 10 | 15 | 30 | 45 | 60 | 90 | 120 |
| R Removal degree, R , % | 36.4 | 49.3 | 58.1 | 67.2 | 70.5 | 74.3 | 75.1 | 76.7 |

The removal degree increased with the increasing of contact time up to 60–70 min, beyond which it attained almost a constant value (74.3%). Therefore, the contact time equal to 60–70 min was considered to be sufficient for sorption of copper ions onto AMSH and has been used for all experiments.

3.3. Effects of initial copper ions concentrations

Copper ions sorption by AMSH was studied at initial copper ions concentrations ranging from 0.16 up to 1.28 $g L^{-1}$. The results showed that with increasing of initial copper ions concentration, sorption degree is decreasing (Fig.1). It is explained that with increasing metal ion concentration, the specific sites were saturated and exchange sites were filled (Patel et al., 2007). Equilibrium sorption capacity of sorbent was calculated in the initial copper ions concentration range between 0.16 and 1.28 $g L^{-1}$ at 20°C, and 60 min contact time. The experimental results show that the sorption capacity of the sorbent increases with the increasing of equilibrium concentration of copper ions (Fig.2). When the copper ion concentration reached a certain extent, the increase in adsorption capacity became slower and approaching a constant value. It can be concluded that the experimentally maximum sorption capacity (q_{exp}) of the AMSH at the equilibrium conditions is 0.556 $g g^{-1}$.

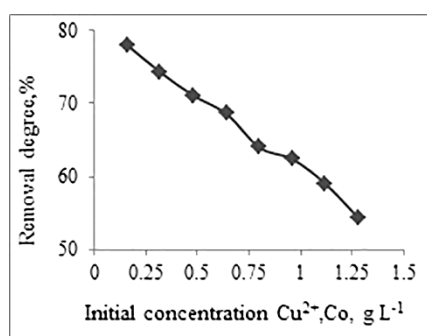


Fig.1. Dependence of removal degree from initial concentration Cu^{2+} (time 60 min, $V=0.04 L$, sorbent dosage $1.25 g L^{-1}$, 20°C).

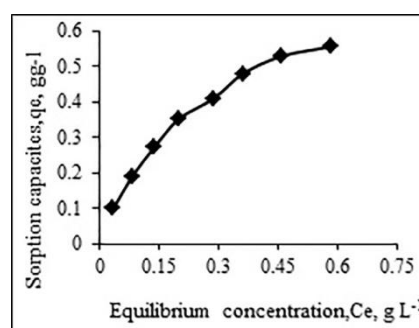


Fig.2. Sorption isotherm

3.4. Sorption isotherms

The equilibrium sorption data were fitted to Langmuir, Freundlich, Dubinin-Radushkevich and Temkin 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 equation (3)

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

where C_e is the equilibrium concentration of copper ions ($g L^{-1}$), q_e is the amount of the copper ions adsorbed at equilibrium ($g g^{-1}$), q_{max} is the monolayer maximum adsorption capacity of the AMHS ($g g^{-1}$) 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)

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

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

The Dubinin–Radushkevich isotherm equation, which is more generally used to distinguish between physical and chemical adsorption, is given by the equation (5)

$$\ln q_e = -K_D \mathcal{E}^2 + \ln B_{DR}, \quad (5)$$

where K_D is the D–R equation constant, B_{DR} theoretical isotherm saturation capacity (mol g^{-1}), q_e is the equilibrium concentration of metal ions (mol L^{-1}) and \mathcal{E} is Polanyi potential, which is defined by equality (6)

$$\mathcal{E} = RT \ln(1 + 1/C_e), \quad (6)$$

where C_e is equilibrium concentration of the copper ions (mol L^{-1}), R is universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$). The Dubinin–Radushkevich constant can give the valuable information regarding the mean energy (E) of adsorption by the equality (7)

$$E = 1 / (2 K_D)^{1/2}. \quad (7)$$

The Temkin isotherm model assumes that the adsorption heat of all molecules decreases linearly with the increase in coverage of the adsorbent surface, and that adsorption is characterized by a uniform distribution of binding energies, up to a maximum binding energy. The Temkin isotherm can be described by equation (8)

$$q_e = B \ln C_e + B \ln A_T \quad (8)$$

$$B = RT / b_T$$

where A_T is the equilibrium binding constant (L mol^{-1}) corresponding to the maximum binding energy, B - is related to the adsorption heat, b_T is the Temkin isotherm constant, R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is the temperature (K). Plotting q_e versus $\ln(C_e)$ results in a straight line of slope B and intercept $\ln A_T$.

The obtained experimental equilibrium data were examined with Langmuir, Freundlich, D–R and Temkin isotherm models (contact time 60 min, $C_0 = 0.16 - 1.28 \text{ g L}^{-1}$, $V = 0.04 \text{ L}$, sorbent dosage 1.25 g L^{-1} , 20°C). The linear curve of specific sorption (C_e / q_e) versus equilibrium concentration of copper ions in solution (C_e) and the curve of the logarithmic equilibrium adsorption capacity ($\log q_e$) versus logarithmic equilibrium concentration ($\log C_e$) are given in Fig.3 and Fig.4, respectively.

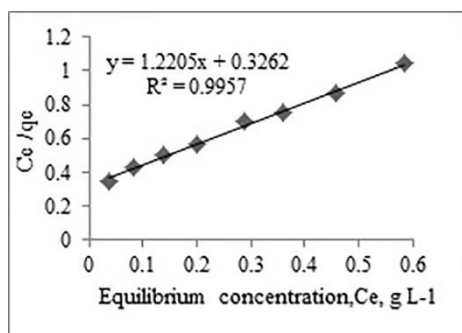


Fig. 3. Langmuir plot for sorption.

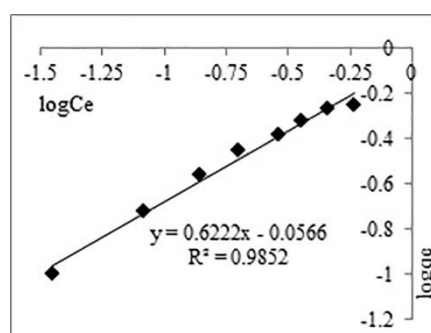


Fig. 4. Freundlich plot for sorption.

The Langmuir and Freundlich isotherm parameters were calculated from the slope intercept of the plots and were given in Table 3. The obtained values of the Langmuir and Freundlich equation parameters specify a high enough sorption activity of the AMSH towards copper ions. High value of K_L (3.745 L g^{-1}) is connected probably with copper ions strong attraction on the sorbent surface owing to chemical interaction of the copper ions with functional groups of AMSH chelate center. 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 equality (9)

$$R_L = 1 / (1 + K_L C_o), \quad (9)$$

where C_o is the initial copper ions concentration (g L^{-1}). The value of R_L lies between 0 and 1 for favorable adsorption, while $R_L > 1$ represent unfavorable adsorption, and $R_L = 1$ represent linear adsorption, while the adsorption process is irreversible if $R_L = 0$ (Rani & Mahajan, 2012). The calculated values of R_L for different initial concentration of the copper ions ($0.16\text{--}1.28 \text{ g L}^{-1}$) were equal to $0.625\text{--}0.1726$, indicates highly favorable adsorption for the copper ions onto AMSH. The calculated value of the maximum experimental sorption capacity from the Langmuir and Freundlich equations is equal to 0.819 and 0.878 g g^{-1} respectively. The value of $(1/n)$ in Freundlich equation is between 0 and 1 (0.6222), which indicated that the sorption process is described by chemisorption's.

Graphics of the D–R and Temkin equations were given in Fig.5 and Fig.6 (contact time 60 min, $C_o = 0.16\text{--}1.28 \text{ g L}^{-1}$, $V = 0.04 \text{ L}$, sorbent dosage 1.25 g L^{-1} , 20°C). The calculated parameters of these equations are illustrated in Table 3. The found value of the mean sorption energy from D–R equation ($7.634 \text{ kJ mol}^{-1}$) also indicated that, sorption of copper ions by synthesized polymer salt has chemical character. The theoretical isotherm saturation capacity of the sorbent (B_{DR}) from D–R equation is equal to $0.0287 \text{ mol g}^{-1}$ (1.837 g g^{-1}). The heat of sorption process was estimated from Temkin isotherm model to be $0.0027 \text{ kJ mol}^{-1}$.

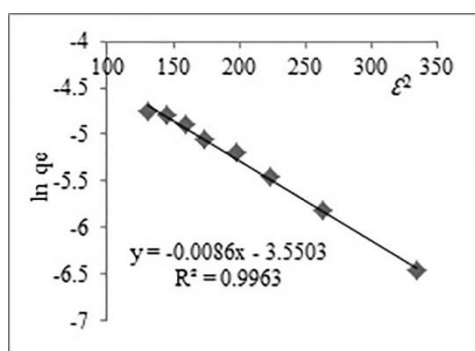


Fig. 5. D–R plot for sorption.

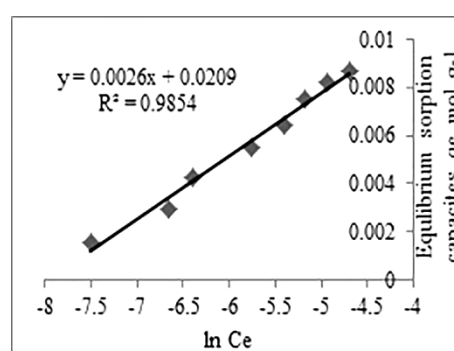


Fig. 6. Temkin plot for sorption

Table 3. Parameters of the Langmuir, Freundlich, D-R and Temkin equations

| Langmuir equation | | | | Freundlich equation | | | |
|-------------------------------|----------------------------|---------------------------------|--------|---------------------------|-----------------------|-------------------------|--------|
| $q_m,$ $g\ g^{-1}$ | $K_L,$ $L\ g^{-1}$ | $R_L,$ $Co=0.16-1.28gL^{-1}$ | R^2 | $K_F,$ $g\ g^{-1}$ | $1/n$ | n | R^2 |
| 0.819 | 3.745 | 0.625-0.1726 | 0.9957 | 0.878 | 0.6222 | 1.607 | 0.9852 |
| D-R equation | | | | Temkin equation | | | |
| $K_{DR},$ $mol^2\ kJ^{-2}$ | $B_{DR},$ $mol\ g^{-1}$ | $E_{DR},$ $kJ\ mol^{-1}$ | R^2 | $A_T,$ $(L\ mol^{-1})$ | $B,$ $J\ mol^{-1}$ | $b_T,$ $J\ mol^{-1}$ | R^2 |
| 0.0086 | 0.0287 | 7.634 | 0.9963 | 3090 | 0.0026 | 9.37×10^6 | 0.9854 |

3.5. Kinetics and Thermodynamics

Kinetic studies were carried out under the optimized conditions from 5 to 120 min. The kinetic data obtained were fitted to linear form of Lagergren pseudo-first order and pseudo-second order kinetic models (Bagherifam et al., 2010). The pseudo-first-order kinetic model known as equation (10)

$$\log(q_e - q_t) = \log q_e - 0.434K_1\tau, \quad (10)$$

where q_t and q_e are the amounts of ion adsorbed at time τ and at equilibrium ($mol\ g^{-1}$), 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 equation (11)

$$\tau/q_t = 1/(K_2 q_e^2) + \tau/q_e, \quad (11)$$

where q_t and q_e are the amounts of copper ions sorbed at time t and at equilibrium ($mol\ g^{-1}$), respectively, K_2 is the pseudo-second-order equilibrium rate constant ($mol\ g^{-1}\ min^{-1}$).

It found that the pseudo-second-order model was the most appropriate model, describing the sorption kinetics (Fig.7). The plot of t/q_t versus t gives a linear relationship with determination coefficient 0.9998 and K_2 ($52.08\ L\ mol^{-1}\ min^{-1}$) and q_e ($0.00322\ mol\ g^{-1}$) have been calculated from the slope and intercept of the line.

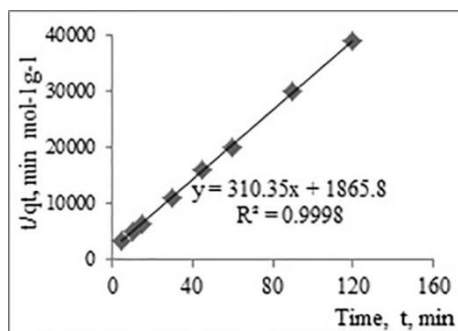


Fig. 7. Pseudo-second-order model ($C_o = 0.32\ g\ L^{-1}$, $V = 0.04\ L$, sorbent dosage $1.25\ g\ L^{-1}$, $20^\circ C$).

Thermodynamic parameters like standard Gibbs free energy (ΔG°), standard enthalpy change (ΔH°), and standard entropy change (ΔS°) were determined in order to explain the effect of temperature on the adsorption of Cu^{2+} ions on AMSH. These parameters can be calculated from the equations (12)-(14)

$$\Delta G^\circ = -2,3 RT \log K_d \quad (12)$$

$$K_d = q_e/C_e \quad (13)$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (14)$$

where R is the gas constant ($8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}$), 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 illustrated in Table 4.

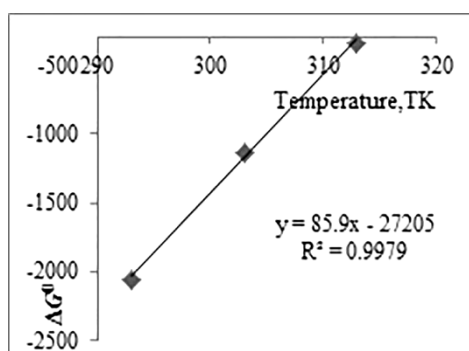


Fig. 8. Plot of ΔG° versus T (time 60 min, $C_0 = 0.32 \text{ g L}^{-1}$, $V = 0.04 \text{ L}$, sorbent dosage 1.25 g L^{-1} , 20°C)

Table 4. Thermodynamic parameters of Cu^{2+} ions adsorption by AMHS.

| T, K | $\Delta G^\circ, \text{kJ mol}^{-1}$ | $\Delta S^\circ, \text{kJ mol}^{-1}$ | $\Delta H^\circ, \text{kJ mol}^{-1}$ |
|------|--------------------------------------|--------------------------------------|--------------------------------------|
| 293 | -2.059 | -0.0859 | -27.205 |
| 303 | -1.131 | | |
| 313 | -0.341 | | |

The negative values of the ΔG° and ΔH° indicates that the sorption process is spontaneous and exothermic in nature. The negative value of ΔS° indicates a decreased disorder during adsorption process.

3.6. Spectrophotometric investigation of the sorbent after sorption

For identification of the possible mechanism of the copper ions sorption process, the sorbent was characterized by the FT-IR (Fig.9) and UV-vis spectra (Fig.10) after sorption.

The absorption bands at 1540 and 1560 cm^{-1} were assigned to the asymmetric vibration absorption of the carboxylate (COO^-) groups (Bellamy 1975). The absorption bands at 2918 and 2850 cm^{-1} were assigned to the CH_2 -groups stretching, 1457 cm^{-1} – CH_2 groups deformation of the heptene units. It is possible to believe that copper ions enter into a complex with two carboxylate groups of the maleic acid units of the sorbent. The absorption band 1640 cm^{-1} is attributed to $-\text{OH}$ bending mode of adsorbed

water and broad band centred near 3420 cm^{-1} due to -OH stretching band for connected water, which indicates the presence of water molecules in this complex. About a complexation of Cu^{2+} with carboxyl containing polymers, including copolymers of maleic acid are reported (Rivas et al., 2001, 2002, Oikonomou et al., 2008). It is noted that Cu^{2+} ions can form with maleic acid copolymers mononuclear and binuclear complexes and the absorption of a binuclear complexes are observed in the region $350\text{-}370\text{ nm}^5$.

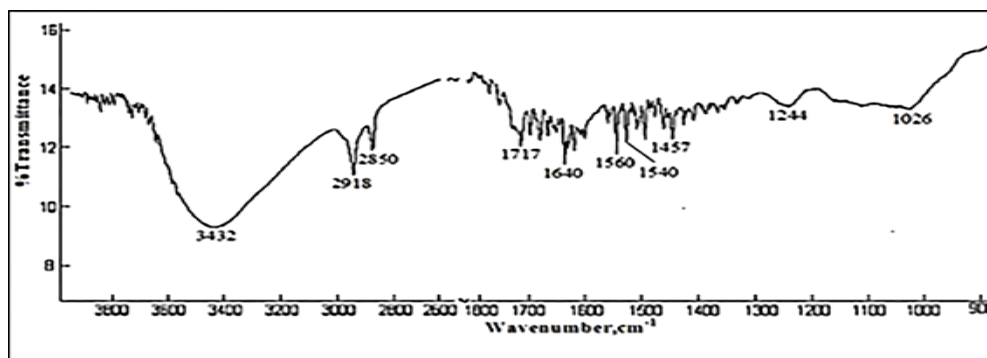


Fig. 9. FTIR- spectra of the Cu^{2+} -AMSH complex

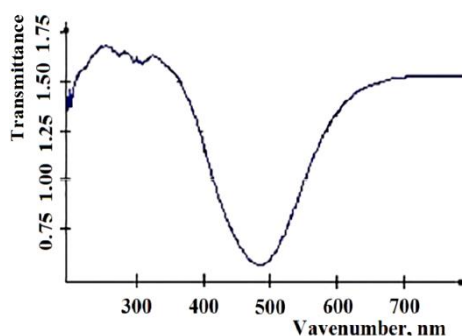
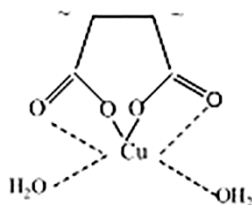


Fig. 10. UV- spectra of the Cu^{2+} -AMSH complex

In our case absorption is observed in form single peak in the range $480\text{-}490\text{ nm}$, that specifies on formation of a mononuclear complex of the Cu^{2+} ions with two carboxylate groups of the maleic acid units and water molecules:



Considering the obtained kinetic data, FT-IR and UV-vis spectra of the sorbent after the sorption, it is possible to come to conclusion that during the sorption process Cu^{2+} ions enters a complex with the carboxylate groups of the maleic acid units of the sorbent.

4. Conclusions

The ammonium salt of the maleic acid-styrene-heptene-1 terpolymer has been used for the removal of Cu^{2+} from aqueous solution. Effects of contact time, sorbent dosage and copper ions initial concentration on removal degree were tested and optimum conditions were evaluated. The calculated value of the maximum sorption capacity from the Langmuir and Freundlich equations is equal to 0.819 and 0.878 g g^{-1} respectively. Separation factor R_L values at different initial concentration of the Cu^{2+} were less than 1 and greater than zero, indicating favorable adsorption. The value of $(1/n)$ in Freundlich equation is between 0 and 1 (0.6222), which indicated that the process of sorption is described by chemisorption's. The found value of the mean sorption energy from D-R equation ($7.634 \text{ kJ mol}^{-1}$) also indicated that, sorption of copper ions by synthesized polymer salt has chemical character. It found that the pseudo-second-order model was the most appropriate model, describing the sorption kinetics. The negative values of the ΔG^0 and ΔH^0 indicate that the sorption process is spontaneous and exothermic in nature. The negative value of the ΔS^0 indicates a decreased disorder during adsorption process. Considering the FT-IR and UV-vis spectra of the sorbent after sorption, it is concluded that Cu^{2+} enters a complex with two carboxylate groups of the maleic acid units of the ammonium salt maleic acid-styrene-heptene-1 terpolymer.

References

1. Akperov, E.O., Maharramov, A.M., Akperov, O.G. (2009). Uranyl ion adsorption using novel cross-linked maleic anhydride-allyl propionate-styrene terpolymer. *Hydrometallurgy*, 100(1), 76-81.
2. Bagherifam, S., Lakzian, A., Ahmadi, S. J., Rahimi, M. F., Halajnia, A. (2010). Uranium removal from aqueous solutions by wood powder and wheat straw. *Journal of radioanalytical and nuclear chemistry*, 283(2), 289-296.
3. Bellamy, L.J. (1975). *The Infrared Spectra of Complex Molecules*, Chapman and Hill, London.
4. El-Ghaffar, M.A., Elhalawany, N., Ahmed, E., Sabaa, M. (2013). Synthesis and characterization of some chelating polymers bearing maleic acid and/or sodium maleate moieties for removal of some toxic heavy metal ions. *Clean Technologies and Environmental Policy*, 15(6), 1013-1021.
5. Ferrah, N., Abderrahim, O., Didi, M. A., Villemin, D. (2011). Removal of copper ions from aqueous solutions by a new sorbent: polyethyleneiminemethylene phosphonic acid. *Desalination*, 269(1), 17-24.
6. Hasanzadeh, R., Najafi Moghadam, P., Samadi, N. (2013). Synthesis and application of modified poly (styrene-alt-maleic anhydride) networks as a nano chelating resin for uptake of heavy metal ions. *Polymers for Advanced Technologies*, 24(1), 34-41.
7. Kavaklı, P.A., Güven, O. (2004). Removal of concentrated heavy metal ions from aqueous solutions using polymers with enriched amidoxime groups. *Journal of Applied Polymer Science*, 93(4), 1705-1710.
8. Moussout, H., Ahlafi, H., Aazza, M., Zegaoui, O., El Akili, C. (2016). Adsorption studies of Cu (II) onto biopolymer chitosan and its nanocomposite 5% bentonite/chitosan. *Water Science and Technology*, 73(9), 2199-2210. DOI 10.2166/wst.2016.075
9. Ngah, W.W., Endud, C.S., Mayanar, R. (2002). Removal of copper (II) ions from aqueous solution onto chitosan and cross-linked chitosan beads. *Reactive and Functional Polymers*, 50(2), 181-190.
10. Oikonomou, E.K., Bokias, G., Kallitsis, J.K. (2008). Comparative study of electrostatic binding vs. complexation of Cu^{2+} ions with water-soluble polymers containing styrene

- sulphonic acid and/or maleic acid units or their sodium salt forms. *Journal of Polymer Science Part B: Polymer Physics*, 46(12), 1149-1158.
11. Patel, M., Karadia, M., Patel G., Joshi J. (2007). Synthesis, characterization, ion exchange and antimicrobial study of poly (2-hydroxy-4-methoxybenzophenone ethylene resin and its polychelates with lanthanides (III). *J. React. Funct. Polym.*, 67(8), 746-757.
 12. Rani, S., Mahajan, R.K. (2012). 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*, 28(3-4), 133-147.
 13. Rivas, B.L., Pereira, E.D., Moreno-Villoslada, I. (2003). Water-soluble polymer-metal ion interactions. *Progress in Polymer Science*, 28(2), 173-208.
 14. Rivas, B.L., Seguel, G.V., Geckeler, K.E. (2001). Poly (styrene-alt-maleic acid)-metal complexes with divalent metal ions. synthesis, characterization, and physical properties. *Journal of Applied Polymer Science*, 81(6), 1310-1315.
 15. Rivas, B.L., Seguel, G.V., Geckeler, K.E. (2002). Synthesis, characterization, and properties of polychelates of poly (styrene sulfonic acid-co-maleic acid) with Co (II), Cu (II), Ni (II), and Zn (II). *Journal of Applied Polymer Science*, 85(12), 2546-2551.
 16. Roy, P.K., Rawat, A.S., Choudhary, V., Rai, P.K. (2004). Synthesis and analytical application of a chelating resin based on a crosslinked styrene/maleic acid copolymer for the extraction of trace-metal ions. *Journal of Applied Polymer Science*, 94(4), 1771-1779.
 17. Song, L., Wang, J., Zheng, Q., Zhang, Z. (2008). Characterization of Cu (II) ion adsorption behavior of the polyacrylic acid-polyvinylidene fluoride blended polymer. *Tsinghua Science & Technology*, 13(2), 249-256.