REMOVAL OF Cu^{2+} FROM WATER SOLUTION BY AMMONIUM SALT OF THE MALEIC ACID-ALLYLPROPIONATE-STYRENE TERPOLYMER, CROSSLINKED WITH GLYCERIN

O.H. Akperov*, E.O. Akperov, E.A. Shirinova

Department of Polymer Chemistry, Baku State University, Baku, Azerbaijan

Abstract. The present study investigated the adsorption of Cu^{2+} from water solution using ammonium salt of the maleic acid–allylpropionate–styrene terpolymer, crosslinked with glycerin. Adsorption equilibrium, kinetics and thermodynamics have been investigated as a function of initial Cu^{2+}ions concentration, contact time, sorbent dosage and temperature. Equilibrium data were analyzed using Langmuir, Freundlich, Dubinin-Radushkevich and Temkin isotherm models. Kinetics studies showed that the adsorption is described with pseudo-second order reaction. The negative values of the ΔG^0 and the positive value of the $\Delta H°$ $(11.861 kJ\ mole^{-1})$ indicate that the sorption process is spontaneous and endothermic in nature. The positive value of $\Delta S°$ $(0.04375\ kJ\ mole^{-1}\ K^{-1})$ shows the increasing randomness during adsorption process. The results of this research showed that the adsorption of the Cu^{2+} ions by ammonium salt of the cross-linked maleic acid-allylpropionate-styrene terpolymer occurred through chemical interaction mechanism.

1.   Introduction

One of the water pollutants that become serious problem in aquatic ecosystems are Cu^{2+} ions and accumulation of the copper in natural objects does big ecological harm to living organisms, fauna and flora on earth, including human. Many industries, such as metal finishing, electroplating battery manufacturing, electric cable manufacturing steel and textile industries, release various concentrations of heavy metals like copper, cadmium, nickel and other metals in wastewaters. Unlike organic pollutants, the majority of which are susceptible to biological degradation, metal ions do not degrade into harmless products. Copper toxicity is a much-overlooked cause of many important health conditions, like fatigue, premenstrual syndrome, anorexia, depression, anxiety, migraine headaches, allergies and many others. The conventional methods for removing the copper ions include coagulation, chemical precipitation, ion-exchange, adsorption, membrane separation etc. Among these methods, adsorption of copper ions by polymer sorbents is the most widely used method because it is simple, effective and environmentally friendly method in practice. Many types of polymeric adsorbents and polymeric nanocomposites have been developed and studied for the removal of copper ions from aqueous solutions (Alka & Kathane, 2015; Hui *et al.* 2013; Moussout *et al.*, 2016; Nacer *et al.*, 2011; Barlik & Keskinler 2014; Ramya *et al.*, 2011; Golkhah *et al.,* 2017). Based on the obtained data of sorption parameters, authors of these works consider that many synthetic polymeric sorbents and nanocompositescan be

used as efficient adsorbents for removal of copper and other heavy metal ions from aqueous mediums. These polymers are capable of coordinating to heavy metal ions through functional groups, containing O, N and S as donor atoms.Chelating resins of poly (styrene–alt–maleic anhydride) have been investigated for the remove of Cu^{2+} ions from water solutions (Samadi *et al.*, 2017). The various parameters such as pH, contact time, concentrations of metal ions, mass of resin, and agitation speed were investigated on adsorption effect. The prepared resins showed a good tendency for removing the selected metal ions from aqueous solution and industrial waste water.Polymer adsorbent prepared using acrylic acid and poly(vinylidene fluoride) was used to remove copper ions from water solutions (Song *et al.*, 2008). The sorption data was fit to linearized adsorption isotherms of the Langmuir, Freundlich and Dubinin–Radushkevich models. The sorption kinetics was evaluated using pseudo-first‐order, pseudo-second order reaction models. The adsorption process fits better to the Freundlich isotherm model and the pseudo‐second‐order model. The adsorption mechanism is assumed to be ion exchange between the copper ions and the carboxylic groups of the polymer sorbent. A new chelating polymer sorbent was synthesized by the radical copolymerization of the styrene and maleic anhydride in the presence of the divinylbenzene as crosslinking agent (Roy *et al.*, 2004). The effect of various physicochemical parameters on metal uptake was studied. The sorption capacities of the cross-linked resin for Cu^{2+}, Cr^{3+}, Fe^{3+}, Ni^{2+} and Pb^{2+} were 15.4; 10.2; 14.3; 14.2 and 8.8 mg/g, respectively. The Langmuir and Freundlich adsorption isotherms were used to validate the metal-uptake data. Acrylamide-maleic acid hydrogels having high acid group content prepared with different maleic acid ratios were used for the removal of Cu^{2+} and Pb^{2+} ions from aqueous solutions (Kaşgöz *et al.*, 2006). The effects of pH contact time, and initial metal ion concentration on the metal ion adsorption capacity were investigated. The adsorption isotherm models were applied on experimental data and it is shown that the Freundlich equation was the best model for Cu^{2+} ion, while the Langmuir isotherm model was the best for Pb^{2+}ions. It is stated that these hydrogels can be regenerated efficiently (>95%) and used repeatedly. Terpolymer resin, synthesized from anthranilic acid, 2-aminopyridine and formaldehyde was used to remove some heavy metal ions from water solutions (Raja *et al.*, 2013).The adsorption isotherm was evaluated by Langmuir and Freundlich isotherm models. The order of the kinetics was also determined and the resin follows first order kinetics which shows that physicosorption may be involved in the ion-exchange process. A novel chelating terpolymer resin has been synthesized by terpolymerization of anthranilic acid, salicylic acid and formaldehyde (Ahamed *et al.,* 2010). Batch equilibrium method was employed to explore the selectivity and binding capacity of the terpolymer resin towards some divalent metal ions, such as Pb^{2+}, Zn^{2+}, Cu^{2+}, Mg^{2+} and Ba^{2+} in different electrolyte concentrations and different time intervals. The review of the published works on removal of heavy metal ions from water solutions, shows that many synthetic polymers with functional groups are effective adsorbents for water purification from heavy metal ions. The research results on removal of the Cu^{2+} ions from water solutions by ammonium salt of the maleic acid-allylpropionate-styrene terpolymercrosslinked with glycerin were given in the presented work. The effects of the sorbent dosage, initial copper ions concentration, contact time and temperature were studied and equilibrium isotherm data were analyzed by the Langmuir, Freundlich, Dubinin-Radushkevich, Temkin isotherm models. Pseudo-first and pseudo-second order kinetic models were used to fit experimental data and the adsorption thermodynamic parameters were

determined. Synthesis and researches of the sorption properties of the studied polymer–sorbent toward copper ions are executed for the first time and it defines the novelty of this work.

2.   Experimental

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. Allylpropionate (AP), styrene (St) were distilled before use and had the following characteristics: AP: b.p. 122–123°C; St: b.p. 144–145°C. Azobisisobutyronitrile (AIBN) was purified by recrystallization from ethanol. The stock solution with concentration of Cu^{2+}ions $0.2mole$ L^{-1} (12.8 gL^{-1}) was diluted to obtain solutions with various concentrations of Cu^{2+}. A 0.001 $mole$ L^{-1} xylenole orange $(3,3^1$-Bis [N, N-bis (carboxymethyl) aminomethyl]-o-cresolsulfonphthalein) solution in deionized water and buffer solution CH_3COOH/NH_4OH with pH6 was used for formation of a Cu^{+2}–xylenole orange complex on determining residual concentration of the copper ions by a photometric method. FT–IR spectra of the sorbent before and after sorption were recorded in the range 4000–500 cm^{-1} using a Varian 3600 FT–IR and Nicolet IS 10 FT–IR spectrometers. Photometer (model KFK–3M, Russia) was used to determine concentration of Cu^{2+} after sorption at 490 nm. UV–vis spectra were measured on a UV-vis SPECORD 210 PLUS (Germany) in the range 190–1100 nm. A pH–meter (model pH–600–AQ, Romania) was used for pH measurements.

Preparation and characterization of sorbent

Ammonium salt of cross–linked maleic acid–allylpropionate–styrene terpolymer (ACLT) was prepared by the following consecutive reactions:

(ACLT)   (CLT)
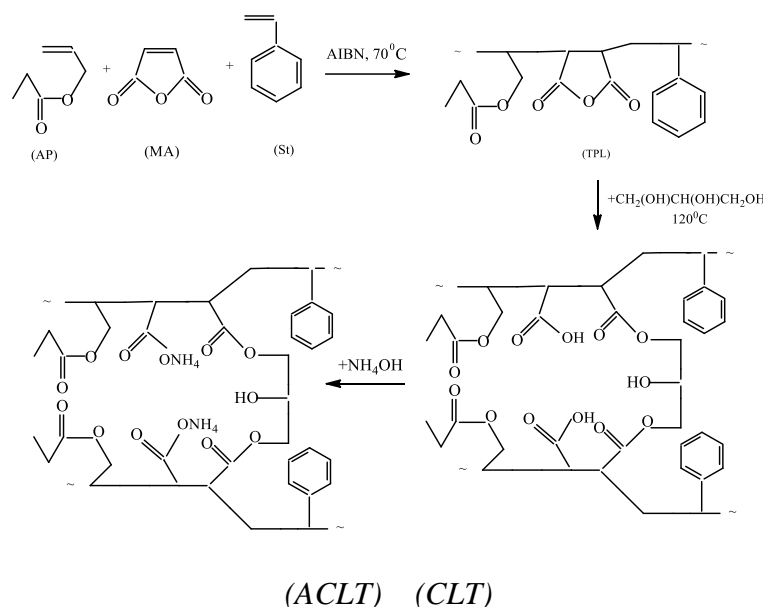
In the first step the maleic anhydride–styrene–allylpropionat terpolymer (TPL) was synthesized by reaction of maleic anhydride, styrene and allylpropionate in butyl acetate in the presence of AIBN at 70°C (Akperov *et al.* 1994; 2009). The molar

contents of MA, AP and St in the terpolymer were 51.5; 17.8 and 30.7 *mole* %, respectively. The intrinsic viscosity was 0.72 *dl* g^{-1} (methyl ethyl ketone, 20°C).In the second step a mixture of TPL (4.14*g*, 0.01 *mole*) and glycerin (0.46 *g*, 0.005 *mole*) as the crosslinking agent was heated at 120°C for 1 h. The obtained crosslinked terpolymer (CLT) was washed repeatedly with deionized water and acetone and was dried at 40°C in the vacuum oven. In the third step 4.0*g* CTL and 50 *ml* 5%–solution of the ammonium hydroxide was heated at 40°C for 1 h. The obtained ACLT was washed repeatedly with acetone and was dried at 40°C in the vacuum oven. The obtained ammonium salt of the maleic acid-allylpropionate-styrene terpolymer crosslinked with glycerin, containing various functional groups was used for removal of the copper ions from aqueous solution.

Sorption experiments

Batch experiments on sorption of the copper ions with synthesized sorbent from water solution were carried out by the technique described as earlier (Akperov *et al.,* 2016, Akperov *et al.,* 2017). It is known that copper ions form a complex with xylenol orange at pH 5.5-6.0 (Yamada, 1976; Lur'e, 1989, Akperov *et al.*, 2017), therefore we used the buffer solution CH_3COOH/NH_4OH with pH 6 for determining copper ions residual concentration by a photometric method. The residual amount of copper ions was determined using the value of optical density of the copper ions complex with xylenole-orange over the calibration curve. The sorption degree (%) and sorption capacity ($g\,g^{-1}$) of the sorbent have been calculated by the Eq. (1) and (2):

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

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

where C_0 and C_e (gL^{-1}) are initial and equilibrium concentrations of copper ions, 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

Effect of sorbent dosage

The effect of adsorbent dosage on the copper ions sorption process has been investigated at initial copper ions concentration 0.96 gL^{-1}, contact time 60 *min*, 20°C. The result shows that, the removal efficiency increases with increasing of the sorbent dosage. The increase of the sorbent dosage from 0.02*g* (0.5 gL^{-1}) up to 0.15 *g* (3.75 gL^{-1}) causes the increase in the sorption degree of copper ions from 25.3 up to 69.0% (Table 1).

Table 1. Effect of sorbent dosage on sorption degree (copper ions initial concentration 0.96 $g\ L^{-1}$, V=0.04 L, 20°C, 60 *min*)

Sorbent dosage, (gL^{-1})	0.5	1.0	1.5	2.0	2.5	3.0	3.75
Removal degree, *R*, (%)	25.3	40.1	49.5	61.1	67.0	68.1	69.0

The sorption degree rapid increased with the increasing of the sorbent dosage up to 0.1–0.12 g, beyond which it attained almost a constant value (66.2–67.1%). Hence, sorbent amount equal to 0.1 g (2.5 gL^{-1}) is optimum at initial concentration of copper ions equal to 0.96 gL^{-1}. Therefore, in further experiments 0.1 gL^{-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 copper ion sorption by sorbent has been investigated at different contact time varying between 10 and 140 min at 20°C (Table 2).

Table 2. Effect of time on sorption degree (copper ions initial concentration
0.96 g L^{-1}, V=0.04 L, sorbent dosage 2.5gL^{-1}, 20°C)

Time, *min.*	10	20	30	40	60	80	100	120	140
Removal degree, *R*	23.6	40.6	53.3	60.8	67.0	68.6	70.9	72.1	72.2

These results indicated that with the increase of time the removal of copper ions increased to a certain point of equilibrium. During the first 10 min of the sorption 23.6% of the total amount of Cu (II) was immobilized. The state of ion equilibrium in the ACLT structure is reached after 120 min. At that time, 72.1% of Cu (II) ions were removed by sorbent.

Therefore, the contact time equal to 100–120 min was considered to be sufficient for sorption of copper ions onto sorbent and has been used for all experiments.

Effect of initial copper ions concentration and sorption isotherm of sorbent

Copper ions solutions with several initial concentrations in the range of 0.16–1.44 gL^{-1} and at 20°C were equilibrated using 2.5 gL^{-1} adsorbent weight. The results showed that the copper ions sorption onto sorbent were strongly affected by the initial copper ions concentration and with increasing of initial copper ions concentration, sorption degree is decreasing. The Cu^{2+} ions removal degree decreases from 83.1 to 58.2% when its initial concentration increases from 0.16 to 1.44 gL^{-1}. It is explained that with increasing metal ion concentration, the specific sites of a sorbent were saturated and exchange sites were filled. In Fig.1 it is illustrated sorption isotherm, which was constructed on dependence of sorption capacity of a sorbent on equilibrium concentration of the copper ions.

Equilibrium sorption capacity of the sorbent was calculated in the initial copper ions concentration range $(0,16 \div 1.44) gL^{-1}$ at 20°C and for 60 min contact time. It is shown that the sorption capacity of the sorbent increases rapidly with the increasing of equilibrium concentration of copper ions When the copper ion 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 0.336 gg^{-1}.
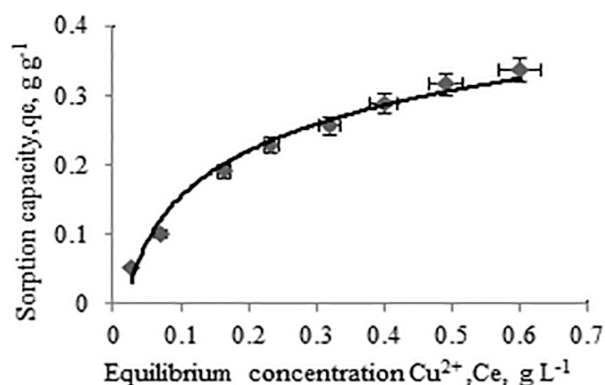
Figure 1. Sorption isotherm of sorbent (pH 6, 60 min,
C_o= 0.16 –1.44 $g\ L^{-1}$, V=0.04 L, sorbent dosage 2.5 $g\ L^{-1}$, 20°C)

Langmuir and Freundlich 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)

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

where C_e is the equilibrium concentration of copper ions (gL^{-1}), q_e is the amount of the copper ions adsorbed at equilibrium (gg^{-1}), q_{max} is the monolayer maximum adsorption capacity of the ACLT ($g\ g^{-1}$) and K_L is the Langmuir equilibrium constant (gL^{-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 Eq. (4)

$$log\ q_e = log\ K_F + \left(\frac{1}{n}\right)log\ C_e \tag{4}$$

where K_F –is the Freundlich constant and *1/n*- is the heterogeneity factor.

The obtained experimental equilibrium data were examined with Langmuir and Freundlich isotherm models. The linear curve of specific sorption versus equilibrium concentration of copper ions in solution and the curve of the logarithmic equilibrium adsorption capacity versus logarithmic equilibrium concentration are given in Fig. 2a and Fig.2b, respectively.

The Langmuir and Freundlich isotherm parameters were calculated from the slope intercept of the plots and were given in Table 3.

Table 3. Parameters of the Langmuir and Freundlich equations(copper ions initial concentration $0.16 – 1.44\ gL^{-1}$, *V*=0.04 *L*, sorbent dosage $2.5 gL^{-1}$, 60 min, 20°C)

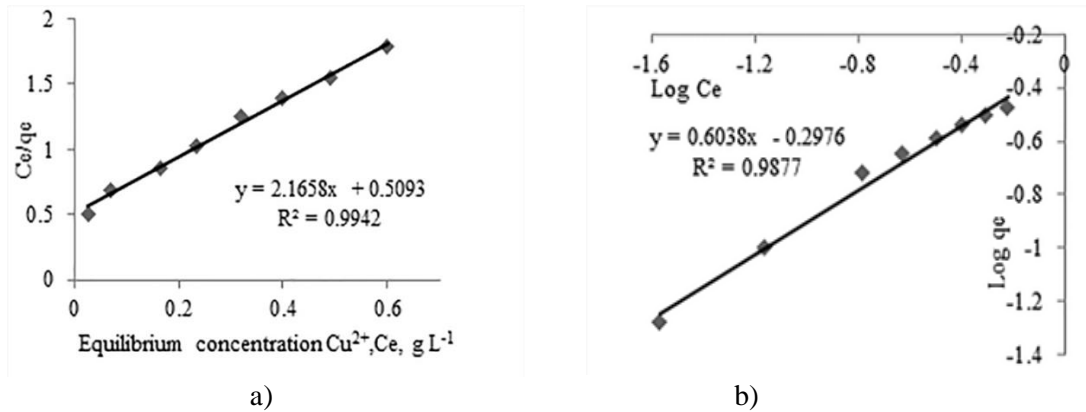| Langmuir equation				Freundlich equation			
q_{max}, gg^{-1}	K_L, Lg^{-1}	R_L	R^2	*1/n*	n	K_F	R^2
0.462	4.255	0.595-0.155	0.9942	0.6038	1.656	0.504	0.9854

Figure 2. Langmuir (a) and Freundlich (b) plots for sorption (pH 6, 60 min, Co= 0.16 – 1.44 gL^{-1}, V=0.04 L, sorbent dosage 2.5gL^{-1}, 20°C)

The obtained values of the Langmuir and Freundlich equation parameters specify a high enough sorption activity of the ACLT towards copper ions. High value of K_L (4.255 Lg^{-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 ACLT chelate center. The value of (*1/ n*) in Freundlich equation is between 0 and 1 (0.6038), which indicated that the sorption process is described by chemisorption's. 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 Eq. (5)

$$R_L = 1/ (1 + C_0) \qquad (5)$$

where C_o is the initial copper ions concentration (gL^{-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 copper ions (0.16–1.28 gL^{-1}) were equal to 0.595– 0.155, indicates highly favorable adsorption for the copper ions onto ACLT. The calculated value of the maximum experimental sorption capacity from the Langmuir and Freundlich equations is equal to 0.462 and 0.504gg^{-1}, respectively, which are close to experimentally obtained value of equilibrium sorption capacity from sorption isotherm (0.336gg^{-1}).

Dubinin–Radushkevich and Temkin isotherms
The Dubinin–Radushkevich (D–R) isotherm equation, which is more generally used to distinguish between physical and chemical adsorption, is given by the Eq. (6)

$$ln\, q_e = - K_D \varepsilon^2 + lnB_{DR} \qquad (6)$$

where K_D is the D-R equation constant, B_{DR} - theoretical isotherm saturation capacity (*mole g^{-1}*), q_e is the equilibrium concentration of metal ions (*mole L^{-1}*) and ε is Polanyi potential, which is defined by Eq. (7)

$$\varepsilon = RT\, ln \left(1 + \frac{1}{C_e}\right) \qquad (7)$$

where C_e is equilibrium concentration of the copper ions (*mole^{-1}*), R is universal gas constant (8.314*J mole^{-1}*). The D-R constant can give the valuable information regarding the mean energy (*E*) of adsorption by the Eq. (8)

$$E = 1 / (2\,KD)^{½} \qquad (8)$$

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 Eq. (9)

$$q_e = B\,ln\,C_e + B\,lnA_T \qquad (9)$$

$$B = RT/b_T$$

where A_T is the equilibrium binding constant ($Lmole^{-1}$) 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 $J\,mole^{-1}\,K^{-1}$) and T is the temperature (K). Plotting q_e versus $ln(C_e)$ results in a straight line of slope B and intercept lnA_T. Graphics of the D-R and Temkin equations were given in Fig.3a and Fig.3b, respectively.
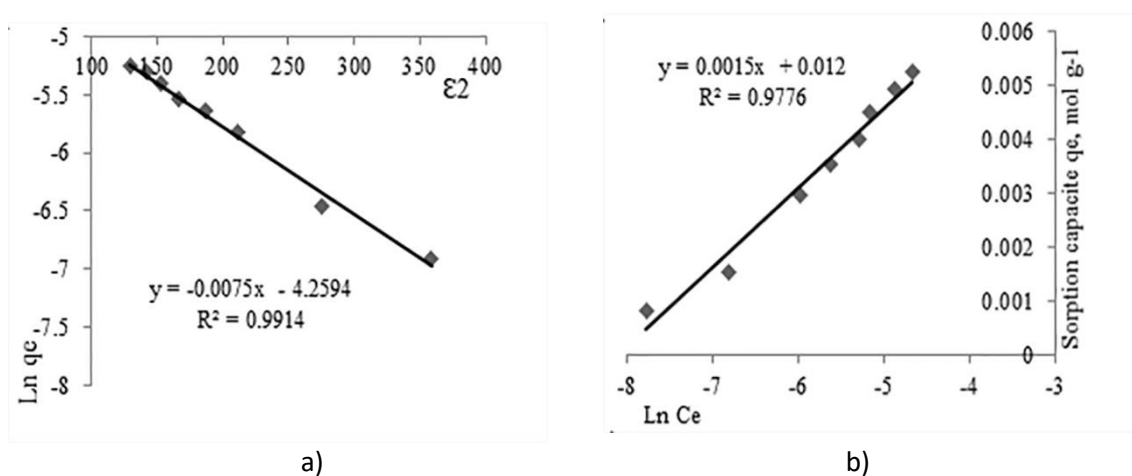

a)   b)

Figure 3. D-R (a) and Temkin (b) plots for copper ions sorption (pH 6, contact time 60 min, Co= 0.0025 – 0.0225 mole L^{-1}, V = 0.04 L, sorbent dosage 2.5 gL^{-1}, 20°C)

The calculated parameters of these equations are illustrated in Table 4.

The found value of the mean sorption energyfrom D–R equation $E_D > 8.0\ kJ\,mole^{-1}$) indicated that, sorption of copper ions by synthesized polymer salt has chemical character (Monika *et al.,*2009). The theoretical isotherm saturation capacity of the sorbent (B_{DR}) from D–R equation is equal to 0.01413 $mole\ g^{-1}$(0.904 $gg^{-1}g$). The heat of sorption process was estimated from Temkin isotherm model to be 0.0015 $kJ\,mole^{-1}$.

Table 4. Parameters of the D-R and Temkin equetions (copper ions initial concentration 0.0025-0.225 $mole\ L^{-1}$, V=0.04 L, sorbent dosage 2.5 gL^{-1}, 60 min, 20°C)

D-R equation				Temkin equation			
K_D, $kJ^{2}\,mole^{-1}$	B_{DR}, $Moleg^{-1}$	E_D, $kJ\,mole^{-1}$	R^2	A_T, $L\,mole^{-1}$	B, $kJ\,mole^{-1}$	b_T, $J\,mole^{-1}$	R^2
0.0075	0.01413	8.17	0.9914	2979	0.0015	1.62×10^6	0.9776

Sorption kinetics and thermodynamics

Kinetic studies were carried out under the optimized conditions from 10 to 120 *min*. The kinetic data obtained were fitted to linear form of Lagergren pseudo–first order and pseudo–second order kinetic models (Sunday *et al.,* 2015). The pseudo–first order kinetic model known as Eq. (10)

$$log\ (q_e - q_\tau)\ =\ logq_e - 0.434K_1\tau \qquad (10)$$

where q_τ and q_e are the amounts of ion adsorbed at time τ and at equilibrium (*mole* 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. (11)

$$\tau/q_\tau = 1/(\ K_2\ q_e{}^2) + \tau/q_e \qquad (11)$$

where q_τ and q_e are the amounts of copper ions sorbed at time τ and at equilibrium (*mole* g^{-1}), respectively, K_2–is the pseudo–second order equilibrium rate constant (*mole^{-1} min^{-1}*). Schedules of the equations of the pseudo–first and pseudo–second model are illustrated in Fig.4a and Fig.4b, respectively and the obtained values of kinetic parameters are placed in Table 5.
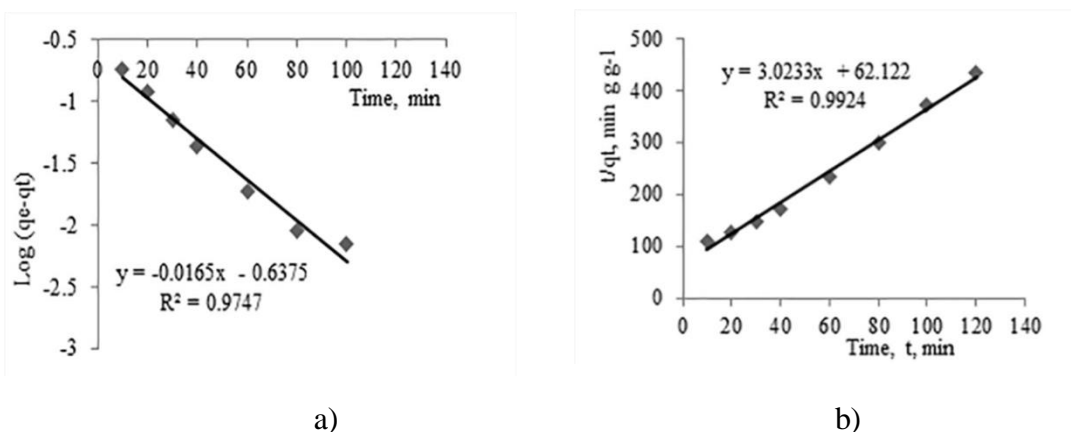

a)   b)

Figure 4. Plots of pseudo–first(a) and pseudo–second(b) order models
(Co = 0.96 g L^{-1}, pH=6, sorbent dosage 2.5 g L^{-1}, V= 0.04 *L*, 20°C)

Table 5. Regression parameters for the kinetics models (copper ions initial concentration 0.96 *g L*$^{-1}$, *V*=0.04 *L*, sorbent dosage 2.5 *g L*$^{-1}$, 20°C)

Kinetic model	$q_e, g\ g^{-1}$	K_1, min^{-1}	$K_2, L\ g^{-1}min^{-1}$	R^2
Pseudo-first order	0.235	0.038	-	0.9747
Pseudo-second order	0.331	-	0.147	0.9924
q_{eks}	0.336	-	-	-

Comparison of the obtained data shows that the sorption process of the copper ions from aqueous solutions with ACLT is better described by the pseudo–second kinetic model with determination coefficient 0.9924. Conformity between calculated (0.331 gg^{-1}) and experimental (0.336 gg^{-1}) q_e values, suggesting that chemisorption is a defining stage in the copper ions adsorption process on a synthesized sorbent.

Thermodynamic parameters, like standard Gibbs free energy ($\Delta G°$), standart enthalpy change ($\Delta H°$) and standart entropy change ($\Delta S°$) were determined in order to explain the effect of temperature on the adsorption of Cu^{2+} ions on ACLT. These parameters can be calculated from the Eq (12) -(14)

$$\Delta G^o = - 2,3 \, RT \, logK_d \quad (12)$$
$$K_d = q_e/C_e \quad (13)$$
$$\Delta G^o = \Delta H^o - T\Delta S^o \quad (14)$$

where R is the gas constant (8.314 $J \, mole^{-1} \, K^{-1}$), T–is absolute temperature, K_d– is equilibrium constant at the temperature T. The values of $\Delta H°$ and $\Delta S°$ were obtained from the slope and intercept of the plots of ΔG^o versus T (Fig.5) and are placed in Table 6.
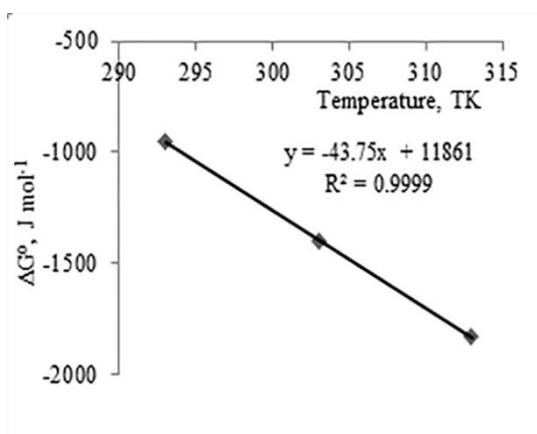
Figure 5. Plot of $\Delta G°$ versus T (pH 6, 60 *min*, Co= 0.005 *mole L^{-1}*, V=0.04 *L*, sorbent dosage 2.5 *g L^{-1}*)

Table 6. Sorption thermodynamic parameters

Temp.,K	ΔG^o,k $J \, mole^{-1}$	ΔH^o,k $J \, mole^{-1}$	ΔS^o, k $J \, mole^{-1}K^{-1}$
293	− 0.955	11.861	0.0438
303	− 1.40		
313	− 1.83		

The negative values of $\Delta G°$ confirm the spontaneity of adsorption process, and the positive value of $\Delta H°$ (11.861 *kJ mole^{-1}*) suggested that the adsorption is endothermic in nature. The positive value of $\Delta S°$ (0.04375 *kJ mole^{-1} K^{-1}*) shows the increasing randomness during adsorption process.

Spectrophotometric investigation of the sorbent before and after sorption

For identification of the possible mechanism of the copper ions sorption process onto ACLT, FT-IR spectra of the ACLT before and after sorption (Fig.6 *a, b*), also UV–vis spectra before and after sorption (Fig.7 *a, b*) of the sorbent have been compared.

Comparison shows that asymmetric bands 1542 and 1558 *cm^{-1}* of the COO$^-$ (carboxylate) structure of the ACLT before sorption (Fig. 6 *a*) disappear and two absorption bands at 1404 *cm^{-1}* and 1576 *cm^{-1}* appear in FT–IR spectra of the ACLT after sorption (Fig.6*b*), which assigned to symmetric vibration absorption ($v_{s \, COO-}$) and asymmetric vibration absorption ($v_{as \, COO-}$) of the carboxylate groups in the complex fragment Cu^{2+}–ACLT (Bellamy, 1975, QI Xin–Hua et al. 2010).The absorption band at

1724 cm^{-1} in FTIR spectra ACLT after sorption is attributed to $\nu C = O$ of the uncoordinated carboxylic and ester groups. The band at 1166 cm^{-1} is characterized by the C–O stretching in the ester groups. The absorption broad band centred near 3431 cm^{-1} due to –OH stretching band for glycerin fragment and –OH groups of the carboxylic fragments, which can be formed as a result of hydrolysis of the –COONH₄ groups. The two absorption bands at 701 and 764 cm^{-1} corresponds to the monosubstituted aromatic rings of the styrene units of the sorbent. It is possible to believe that copper ions enter into a complex with carboxylate groups of the maleic acid units of the sorbent.
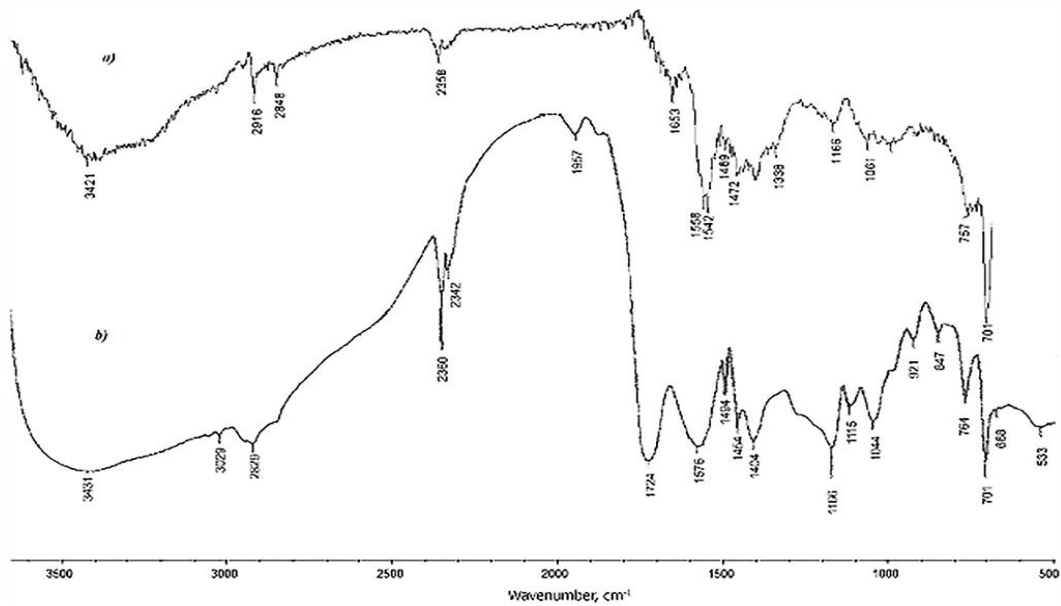

Figure 6. FT–IR spectra of the ACLT a) before and b) after sorption
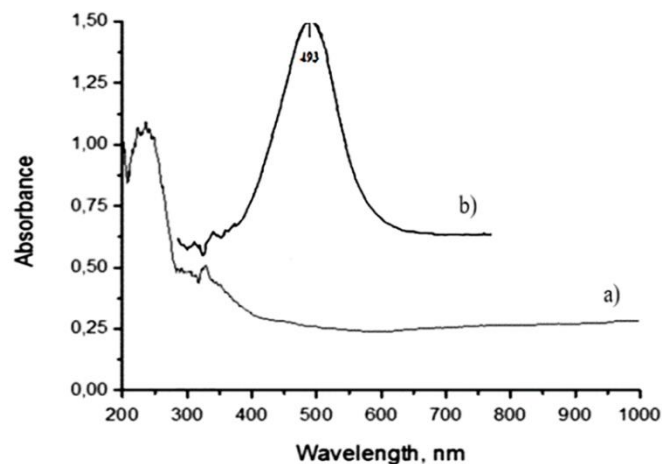

Figure 7. UV–vis spectra of the ACLT a) before and b) after sorption

About a complexation of Cu^{2+} with carboxyl containing polymers, including copolymers of maleic acid are reported (Oikonomou *et al.,* 2008; Rivas *et al.,* 2001). 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 350–370 *nm*. In our case absorption is observed in form single peak at 493 *nm* (Fig. 7 b), that specifies on formation of a mononuclear complex of the Cu^{2+} ions with carboxylate groups of the maleic acid units.

Apparently from Fig.7 a, in the UV-vis spectra of the sorbent before sorption the peak specifying presence of any complex of copper ions with a sorbent isn't observed. The peak in the area of 250-260 *nm* probably is connected with excitement of the π-electronic system of a benzene ring. Considering the FT–IR and UV–vis spectra of the sorbent before and after the sorption, it is possible to come to conclusion that during the sorption process Cu^{2+} ions enter a complex with the carboxylate groups of the maleic acid units of the sorbent. The possible mechanism of a sorption copper ions by sorbent was offered on the basis of the data obtained at interpretation of the D-R- isotherm ($E>8.0$ *kJ mole^{-1}* indicated that, sorption of copper ions by synthesized polymer salt has chemical character) and the pseudo-second order character of a sorption process, which showed that interaction between copper ions and a sorbent has chemical character, with formation of donor-acceptor complexes. Formation of a donor-acceptor complex is confirmed with FTIR- and UV spectra. Options of a possible complexing between copper ions and polymer sorbent are given below, but other options are not excluded.
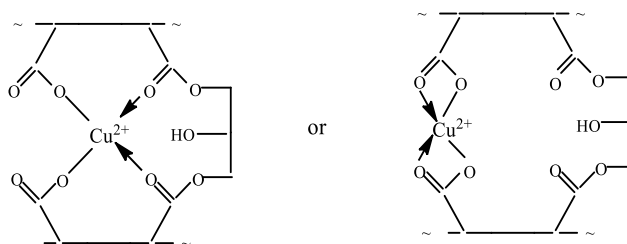
4.   Conclusions

The ammonium salt of the cross–linked maleic acid–allylpropionate–styrene terpolymer has been used for the removal of Cu^{2+} 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 and Freundlich equations is equal to 0.462 and 0.504 gg^{-1}respectively. Separation factor R_L values at different initial concentration of the Cu^{2+} were less than 1 and greater than zero, $(1>R_L>0)$ indicating favorable adsorption. The value of $(1/n)$ in Freundlich equation is between 0 and 1(0.6038), which indicated that the process of sorption is described by chemisorption's'. The found value of the mean sorption energy from D–R equation (8.17 *kJ mole^{-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 the positive value of the $\Delta H°$ (11.861 *kJ mole^{-1}*) indicate that the sorption process is spontaneous and endothermic in nature. The positive value of $\Delta S°$ (0.0438 *kJ mole^{-1} K^{-1}*) shows the increasing randomness during adsorption process. Considering the FT–IR and UV–vis spectra of the sorbent before and after sorption, it is concluded that Cu^{2+} enters a complex with carboxylate groups of the maleic acid units of the ammonium salt of the cross-linked maleic acid–allylpropionate–styrene terpolymer.

References

Ahamed, M.A.R., Azarudeen, R.S., Karunakaran, M. & Burkanudeen, A.R. (2010). Synthesis, characterization, metal ion binding capacities and applications of a terpolymer resin of anthranilic acid/salicylic acid/formaldehyde. *Iranian Polymer Journal*, *19*(8), 635-646.

Akolo, S.A. & Kovo, A.S. (2015).Comparative study of adsorption of copper ion onto locally developed and commercial chitosan. *Journal of Encapsulation and Adsorption Sciences*, *5*(01), 21-37.

Akperov, E., Akperov, O., Jafarova, E. & Gafarova, S. (2016). Removal of copper ions from aqueous solution by the sodium salt of the maleic acid-allylpropionate-styrene terpolymer. *Water Science and Technology*, *74*(6), 1484-1491.

Akperov, E.O., Maharramov, A. M., Akperov, O.G. (2009). Uranyl ion adsorption using novel cross-linked maleic anhydride-allylpropionate-styrene terpolymer. *Hydrometallurgy, 100*(1),76-81.

Akperov, E.O., Nasirov, F.M., Khanlarov, T.G. & Akperov, O.G. (1994). Kinetics of Radical terpolymerisationAllyl Propionate with Maleic Anhydride and Styrene. *Polymer Science Part A (translated Vysocomolek. Soed.), 36*(7), 892-896.

Akperov, O.H., Maharramov, A.M., Akperov, E.O. & Shirinova, E.A. (2018). Ammonium salt of the cross-linked maleic acid–allylpropionate–styrene terpolymer as effective sorbent for removal of Cu2+ ions from water solutions (sorption of the copper ions). *Journal of Dispersion Science and Technology*, *39*(9),1244-1251.

Alka, T. & Kathane, P. (2015). Adsorption of Cu2+ ions onto polyvinyl alcohol-alginate bound nano magnetite microspheres: A kinetic and thermodynamic study. *International Research Journal of Environment Sciences*, *4*(4), 12-21.

Azarudeen, R.S., Subha, R., Jeyakumar, D. & Burkanudeen, A.R. (2013). Batch separation studies for the removal of heavy metal ions using a chelating terpolymer: synthesis, characterization and isotherm models. *Separation and Purification Technology*, *116*, 366-377.

Barlik, N. & Keskinler, B. (2014).Sulfonation of crosslinked styrene/divinyl benzene copolymer beads formed from porous foam and ion adsorption of copper by them: column adsorption modeling. *Water Science and Technology*, *69*(2), 286-292.

Bellamy, L. (1975).*The infrared spectra of Complex Molecules;* Chapman and Hall, London.

Golkhah, S., ZavvarMousavi, H., Shirkhanloo, H. & Khaligh, A. (2017).Removal of Pb (II) and Cu (II) Ions from Aqueous Solutions by Cadmium Sulfide Nanoparticles. *International Journal of Nanoscience and Nanotechnology*, *13*(2), 105-117.

Hui, L.I., Xiao, D.L., Hua, H.E., Rui, L.I.N. & Zuo, P.L. (2013). Adsorption behavior and adsorption mechanism of Cu (II) ions on amino-functionalized magnetic nanoparticles. *Transactions of Nonferrous Metals Society of China*, *23*(9), 2657-2665.

Kaşgöz, H., Kaşgöz, A., Şahin, Ü.,Temelli, T. Y. & Bayat, C. (2006). Hydrogels with acid groups for removal of copper (II) and lead (II) ions. *Polymer-Plastics Technology and Engineering*, *45*(1), 117-124.

Lur'e, Y.Y. (1989). Reference Book on Analytical Chemistry, Khimiya, Moscow, *Google Scholar*, 448.

Monika, J., Gard, V. & Kadirvelic, K. (2009). Chromium (YI) removal from aqueous solution, using sunflower stem waste. *J. Hazard. Mater., 162*(1), 365–372.

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.

Nacer, F., Omar, A., Mohamed, A., Didier, V. (2011). Removal of copper ions from aqueous solutions by a new sorbent: Polyethyleneimine methylene phosphonic acid. *Desalination, 269(*1–3), 17–24.

Oikonomou, E., Bokias, G. & Kallitsis, J. (2008). Comparative study of electrostatic binding vs. complexion of Cu^{2+} ions with water–soluble polymers containing styrene sulphonic acid and/or maleic acid unit so their sodium salt forms. *J PolymSci, B Polym Phys., 46*(12), 1149-1158.

Qi, X.H., Jia, X.Q., Ying, Y.A.N.G., Niu, L.E. & Hou, L.P. (2010). Recovery of nickel from mixed solution containing light metals by PSt/MA resin. *Transactions of Nonferrous Metals Society of China*, *20*, 102-106.

Ramya, R., Sankar. P., Anbalagan, S., Sudha, P.N. (2011). Adsorption of Cu (II) and Ni (II) ions from metal solutions using cross–linked chitosan–g–acrylonitrile copolymer. *J.Environ. Sci., 1*(6), 1323–1338.

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. *J. Appl. Polym. Sci., 81*(6), 1310–1315.

Roy, P.K., Rawat, A.S., Choudhary, V. & Rai, P.K. (2004). Synthesis and analytical application of a chelating resin based on a cross–linked styrene/maleic acid copolymer for the extraction of trace–metal ions. *J. Appl. Polym. Sci., 94(*4), 1771–1779.

Samadi, N., Ansari, R. & Khodavirdilo, B. (2017). Removal of Copper ions from aqueous solutions using polymer derivations of poly (styrene-alt-maleic anhydride). *Egyptian Journal of Petroleum*, *26*(2), 375-389.

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 and Technology*, *13*(2), 249-256.

Sumanjit, S.R. & Mahajan, R.K. (2012). Kinetic and Equilibrium Studies of Adsorption of Dye Congo Red from Aqueous Solutions on Bagasse Charcoal and Banana Peels. *J. Surface Sci. Technol., 28* (3–4), 133–147.

Yamada, M. (1976). Diprotonated Bimetallic Complex between Copper (II) with 3, 3′-Bis [N, N-bis (carboxymethyl) aminomethyl]-o-cresolsulfonphthalein. *Bulletin of the Chemical Society of Japan*, *49*(4), 1023-1026.