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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

**OBTAINING SODIUM AND AMMONIUM SALTS OF MALEIC
ACID TERPOLYMERS AND STUDY OF THEIR SORPTION
PROPERTIES IN RELATION TO COPPER (II) IONS**

Speciality: 2304.01 – Macromolecular Chemistry

Field of science: Chemistry

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SUMGAYIT – 2022

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INTRODUCTION

Actuality and amazing the subject. Currently, heavy metal ions are the most common pollutants found in water sources, which poses a major challenge to the environment and public health. Emissions by industrial enterprises into the atmosphere and sewage create prerequisites for heavy metals to enter the ground, groundwater and open reservoirs, as well as plants, animal bodies and, consequently, the human body. The problem is also that heavy metal ions are stable and persistent pollutants of the environment, as they do not decompose or degrade under natural conditions. They come into water bodies from natural sources (rocks, surface soil layers and groundwater), with sewage from many industrial enterprises and atmospheric precipitation. One of the most common pollutants of natural waters is copper compounds. The main sources of copper in the environment are enterprises of mining, metalworking and woodworking industries. Copper compounds are part of copper-containing pesticides used to treat crops. At their use there is an accumulation of copper in plant raw materials, and as a consequence, in living organisms. Poisoning a person with copper and its compounds leads to diseases such as tachycardia, anemia, eczema, acute kidney and liver failure.

Today, the problem of water purification from heavy metal ions is quite acute and research aimed at developing modern technologies of water purification from metal compounds is relevant and timely. It is therefore necessary to develop efficient, low cost and environmentally friendly water treatment methods. The sorption method, based on contact sorption of contaminants on the adsorbent surface and traditionally used to extract heavy metals from aqueous solutions, provides a higher degree of purification and is quite effective. In most cases, the best results are achieved by using synthetic sorbents based on polymeric materials, such as ion exchange resins, which are characterized by high sorption properties and reusability. The advantages of this method are high productivity, simplicity of hardware design. Taking into account the above, the theme of the work presented, dedicated to the study of the extraction of copper ions from

aqueous solutions of sodium and ammonium salts terpolymers of maleic acid with styrene and monomers with allyl group is very relevant.

Purpose and object of research. The object of research is polymer-sorbent of sodium and ammonium salts, the purpose of research is based on study sorption properties of polymer salts obtained sorbents.

The goal and position of the investigation. The main goal of this thesis is to develop the production of sodium and ammonium salts terpolymers of maleic acid with styrene and monomers with allyl group and study the process of extraction of copper ions (II) from aqueous solutions of the resulting polymer salts. The following works have been carried out to achieve this objective:

- development of conditions for obtaining sodium and ammonium salts terpolymers maleic acid-styrene-allyl propionate, maleic acid-styrene-hepten-1, maleic acid-styrene-nonen-1, maleic acid-styrene-decen-1 and study of composition and structure of the obtained salts;
- identification of the possibility to use the obtained polymer salts as a sorbent for extraction of copper ions (II) from aqueous solutions;
- study of influence of mass quantity of polymer salts, contact time, pH of solution, initial concentration of copper ions (II) and temperature on the degree of metal ions extraction and equilibrium sorption capacity of polymer-sorbents;
- processing of the obtained experimental data within Langmuir, Freundlich, Dubinin-Radushkevich, Temkin models and determination of the equation parameters of these models;
- determination of kinetic and thermodynamic parameters of copper ions (II) extraction from water solutions;
- investigation of polymer-sorbents before and after sorption by methods of FTIR and UV-spectroscopy, DTA-analysis and revealing of a possible mechanism of the process of extraction of copper ions (II) from aqueous solutions by synthesized polymer-sorbents.

Investigation methods. All syntheses were studied at Baku State University, Department of Macromolecular Chemistry with known methods. The residual concentration was determined by the photometric method on KFK-2 photocolimeter. The presence of

terpolymer units in macromolecules was identified by NMR ^1H and ^{13}C spectra. Spectra for ammonium salts were taken on a UV-visible SPECORD 210 PLUS spectrophotometer (Germany). IR-Fourier spectra were taken in the Department of Chemical Physics of Nanomaterials of the Baku State University on spectrophotometers Varian 3600 FTIR and Nicolet IS 10 FTIR (USA).

Main provisions of thesis defense:

- Synthesis of sodium and ammonium salts of the terpolymers of maleic acid with styrene and monomers with an allylic group, and ammonium salts of triethanolamine and glycerol crosslinked ternary copolymer of maleic acid-styrene-allylpropionate;
- Determination of possibility of using synthesized salts as sorbents for extracting copper ions from water solutions and study of various factors influence on sorption process;
- processing of obtained experimental sorption data in coordinates of the equations of Langmuir, Freundlich, Dubinin - Radushkevich, Temkin isotherms and determination of values of characteristic parameters of these isotherms;
- determination of basic kinetic parameters of copper (II) ions sorption by synthesized sorbents;
- determination of values of thermodynamic parameters of copper ions sorption by synthesized sorbents;
- study of sorbents after sorption using FTIR, UV-spectroscopy and TG-DTA-analysis.
- identification of a possible mechanism of the sorption process.

The novelty of the research. For the first time in research:

- maleic acid-styrene-allylpropionate, maleic acid-styrene-hepten-1, maleic acid-styrene-nonen-1 and maleic acid-styrene-decen-1, as well as ammonium salts cross-linked with triethanolamine and glycerol terpolymer maleic acid-styrene- allylpropionate were identified;
- conditions ensuring effective extraction of copper (II) ions from aqueous solutions by synthesized polymer-sorbents have been identified;
- sorption isotherms were constructed, equilibrium experimental and maximum sorption capacity of polymer salts was determined;

- experimental data were processed in the coordinates of the Langmuir, Freundlich, Dubinin-Radushkevich and Temkin equations and parameters of these equations were determined;
- the values of basic kinetic and thermodynamic parameters of copper ions (II) extraction from aqueous solutions by synthesized polymer-sorbents were determined;
- Assumptions have been made about the nature and possible mechanism of the sorption process of copper ions (II) by polymer sorbents obtained.

Theoretical and practical importance of the research. Sodium and ammonium salts of terpolymers of maleic acid effectively extracting copper (II) ions from aqueous solutions have been synthesized for the first time. The conditions providing a sufficiently high degree of extraction of copper ions from aqueous medium have been revealed. Assumptions about the probable sorption mechanism have been made.

Approbation and publication of the work. The main contents of the works are reported and discussed at the following scientific conferences:

- III Republican Conference "Modern Problems of Monomers and Polymers Chemistry" (Sumgait, 2015);
- IX Republican Scientific Conference "Actual Problems of Chemistry" dedicated to the 92nd anniversary of national leader Heydar Aliyev (Baku, 2015);
- VI Republican Conference dedicated to the 80th anniversary of "Analytical Chemistry" Department (Baku,2015);
- X Republican Scientific Conference "Actual problems of chemistry" on the 93rd anniversary of national leader Heydar Aliyev (Baku,2016);
- XI Republican scientific conference 'Actual problems of chemistry' on the 94th anniversary of national leader Heydar Aliyev (Baku,2017);
- XXXIII International Correspondence Scientific and Practical Conference "Chemistry, Physics, Biology,

Mathematics: Theoretical and Applied Research”
(Moscow,2020);

- International Scientific and Practical Conference
(Warsaw,2020).

The total volume of the dissertation with a sign, including the volume of the structural units of the dissertation separately. The dissertation consists of an Introduction, 4 chapters, a conclusion and a list of references, covering 159 pages in A4 format. The main part of the work (excluding figures, tables, graphs and bibliography) is the sign 168603 (including Introduction – 9457, Chapter I – 48286, Chapter II-24880, Chapter III – 33632, Chapter IV – 43478, Conclusion -2862. The list of used literature includes 165 sources cited in the dissertation. The dissertation contains 19 tables and 52 figures reflecting the results.

The volume of the dissertation and structure. Dissertation organized of introduction, literature review, discussion of the results, experimental part, conclusions, references and extra part and consist of 159 computer pages. The results of performed research were given in 52 figures and 19 tables. References consist of 165 citations.

Personal addition of author. Performing of the dissertation work, contender took part in debate: recent years in this field references have collected, synthesized, ideas and results have collected and articles have written.

The actuality of the work was justified, purpose of the work, scientific novelty, practical importance of the work and important defending parts were described in the **introduction** part.

The first chapter dedicated to the analysis of literature review.

Synthesis and reactions based on polyfunctional compounds terpolymers were given in **the second chapter**.

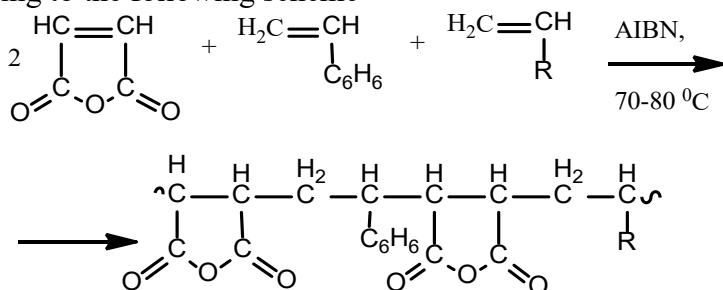
Practical part of the research, also physical-chemical properties of polymer-sorbents are shown **in the third chapter**.

The fourth chapter were determination of analytical, kinetic and thermodynamic parameters of copper ions sorption by synthesized polymer sorbents.

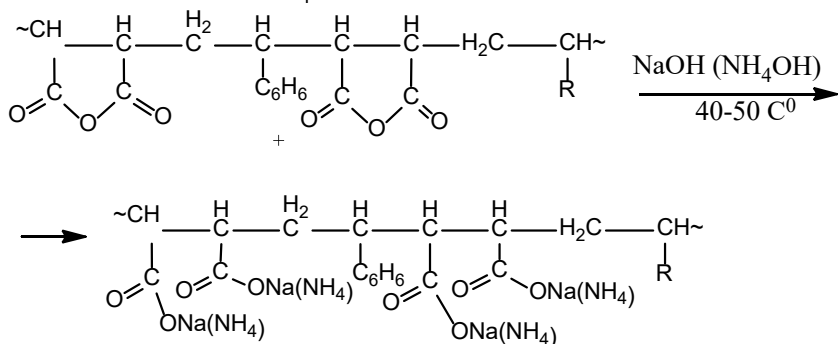
MAIN CONTENT OF THE WORK

1.Synthesis of sodium and ammonium salts terpolymers of maleic acid and styrene with allylpropionate, hepten-1, nonen-1 and decene-1.

The synthesis of sodium and ammonium salts terpolymers of maleic acid (MA) and styrene (St) with allylpropionate (AP), heptene-1(HP), nonen-1(NO) and decene-1(Ds) were prepared in two stages. First, terpolymers of maleic anhydride and styrene with allylpropionate and olefins C₇, C₉ and C₁₀ were obtained by radical terpolymerization of somonomers at 70°C in the presence of AIBN according to the following scheme



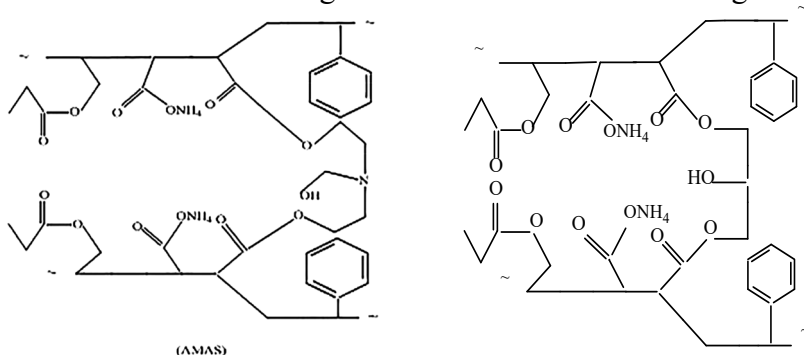
with subsequent treatment of the obtained terpolymers with aqueous solutions of NaOH and NH₄OH:



R: -CH₂OCOCH₂CH₃, -(CH₂)₄CH₃, -(CH)₆CH₃, -(CH₂)₇CH₃

Ammonium salts cross-linked with triethanolamine (TEA) and glycerine (Gl) terpolymer of maleic acid and styrene with allylpropionate were also obtained in two steps: cross-linked

terpolymer of maleic anhydride-styrene-allylpropionate, with subsequent treatment of the cross-linked terpolymer by water solutions of NH_4OH . Fragments of the salts obtained are given below



The yield of polymer salts was 69-78%.

Synthesized sodium and ammonium salts were used as sorbents to extract copper ions (II) from aqueous solutions.

2. Study of sorption conditions of copper ions (II) from aqueous solution with sodium and ammonium salts of maleic acid

Various factors influence the process of sorption (adsorption) of heavy metal ions from aqueous solutions, which is a physical and chemical interaction of metal ions and sorbent. Among a number of other factors, the most characteristic and important are the nature of the environment, the time of contact of the sorbent with the solution of metal ions, the mass of the sorbent, the initial concentration of metal ions in the solution, temperature, etc. Experimental results of studying the influence of these factors on the sorption process are used in the further framework of various models of sorption isotherms, for kinetic and thermodynamic analysis of the process, by the results of which we can judge about the probable mechanism of sorption. When studying the influence of the mentioned factors on the sorption process were used aqueous solution of CuSO_4 of various concentrations, 0.001M xylenol-orange solution as a reagent-complexing agent and buffer solution $\text{NH}_4\text{OH}/\text{CH}_3\text{COOH}$. The residual concentration of copper ions after sorption was determined by photometric method using a

calibration curve.

The degree of sorption R (%) and equilibrium sorption capacity q_e (g^{-1} or $mol\ g^{-1}$) were calculated by the formulas:

$$R = \frac{C_0 - C_e}{C_0} \cdot 100\%$$
$$q_e = \frac{(C_0 - C_e) \times V_{sol}}{m_{sorb}}$$

where C_0 the initial concentration of copper ions (II), $g\ l^{-1}$ or $mol\ l^{-1}$;

V -volume of the solution $CuSO_4$ taken for sorption, L ;

m -mass of sorbent, g .

2.1. Effect of pH solution on sorption capacity of sorbents. The influence of pH of the solution on the sorption capacity of sorbents in relation to Cu^{2+} ions was studied in the range of $pH=3.0-9.0$, while keeping all other parameters constant. The required pH value of the solutions was set using acetate buffer systems. The influence of pH on the degree of copper ions sorption from the aqueous solution was studied by the example of MA-AP-St-TEA- NH_4 sorbent. It was found that in a highly acidic environment ($pH\ 3$) sorption of copper ions is very slow. The degree of sorption increases significantly in the pH range from 4 to 6, and the maximum degree of sorption was achieved at $pH\ 6$.

2.2. Influence of sorbent mass on sorption degree. The mass of the sorbent varied in the range of $0.375-3.75\ g\ L^{-1}$ depending on the sorbent used. Under the selected sorption conditions, an increase in sorbent mass results in an increase in the degree of sorption. This continues up to a certain mass of sorbent and further increases in sorbent mass have almost no effect on the degree of copper ion recovery. For sorbents MA-AP-St-Na and MA-AP-St- NH_4 , these mass values are $2.0-2.5\ L^{-1}$, respectively, for sorbents MA-HP-St-Na and MA-HP-St- NH_4 , MA-NO-St-Na and MA-NO-St- NH_4 MA-DS-St-Na and MA-DS-St- NH_4 : $1.25\ g\ L^{-1}$, for sorbents MA-AP-St-TEA- NH_4 and MA-AP-St-GL- NH_4 : $2.5\ g\ L^{-1}$. Constancy of the degree of sorption after a certain mass of sorbent is probably due to saturation of active reaction centers of sorbent at the selected initial concentration of copper ions. It is also possible that this effect is associated with a decrease in the

concentration of copper ions in the solution during sorption.

2.3. Dependence of the degree of sorption on contact time. The degree of copper extraction (II) in the static mode was studied at certain values of the initial concentration of copper ions, sorbent mass, solution volume taken for sorption and temperature. It is established that regardless of other parameters of sorption, the degree of extraction of copper ions increases with increasing contact time reaching 70-80%. However, the time at which a nearly constant degree of sorption is observed is different for individual sorbents. The influence of contact time on equilibrium on sorbents MA-AP-St-Na and MA-AP-St-NH₄ is 180 min (sorption degree 69.7-72.8%), while on sorbents MA-HP-St-Na and MA-HP-St-NH₄ this time is 90 min (sorption degree 76.0-76.9%). For sorbents MA-NO-St-Na and MA-NO-St-NH₄ the equilibrium is set in 110 min with the degree of sorption, 75.0-76.3%. For sorbents MA-DS-St-Na and MA-DS-St-NH₄ and for sorbents MA-AP-St-TEA-NH₄ and MA-AP-St-GI-NH₄, the equilibrium is set in 120 min with the degree of sorption, 71.0-74.3 and 70.1-72.1%, respectively.

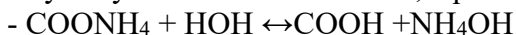
2.4. Dependence of the degree of sorption on temperature. One of the most important parameters affecting the degree of metal ions sorption and sorption capacity of the sorbent is the temperature at which the sorption process is carried out. It is directly related to the kinetic energy of metal ions and, therefore, a rise or fall in temperature should result in a change in the amount of metal ions adsorbed by the sorbent. The results of sorption of copper ions (II) by synthesized polymer-sorbents from aqueous solutions at temperatures 20, 30 and 40°C are illustrated in Table 1. As can be seen from Table 1, an increase in temperature from 20 to 40°C leads to an increase in both the degree of sorption and the sorption capacity for sodium salts of polymeric acids, and for ammonium salts the opposite picture is observed. This is probably due to the difference in strength of O-Na (NH₄) bonds of sodium and ammonium salts. For example, the chemical bond O-Na in carboxylate group -COONa is stronger than O-NH₄ and therefore requires more energy to break it.

Table 1.Dependence of sorption degree (R), and sorption capacity of sorbents (q_e) on temperature

Sorbent	20 ⁰ C		30 ⁰ C		40 ⁰ C	
	$R, \%$	q_e, gg^{-1}	$R, \%$	q_e, gg^{-1}	$R, \%$	q_e, gg^{-1}
MA-AP-St-Na	69.7	0.557	74.6	0.597	78.5	0.627
MA-AP-St-NH ₄	72.8	0.582	69.1	0.553	66.9	0.535
MA-HP-St-Na	72.2	0.186	81.3	0.208	87.6	0.224
MA-HP-St-NH ₄	74.3	0.191	66.2	0.17	58.8	0.15
MT-NO- St-Na	70.4	0.181	75.8	0.194	80.1	0.215
MT-NO-St-NH ₄	72.3	0.188	68.2	0.183	64.5	0.178
MA-DS-St-Na	68.8	0.176	79.3	0.2	90.6	0.23
MA-DS-St-NH ₄	72.3	0.185	66.7	0.171	62.2	0.159
MA-AP-St-TEA-NH ₄	77.7	0.1	79.6	0.102	81.5	0.104
MA-AP-St-GL-NH ₄	78.3	0.1	81.3	0.104	83.5	0.107

2.5. Dependence of the degree of sorption, and the equilibrium sorption capacity of sorbents on the initial concentration of copper ions (II) in an aqueous solution. The initial concentration of metal ions in the solution is one of the main factors determining the distribution of ions between the solution and the solid surface of the sorbent. The essence of metal ion sorption by sorbent is the coordination of ions by free active centers of sorbent, resulting in physical or chemical interaction between metal ions and sorbent. And this largely depends on the concentration of metal ions in the studied initial solution. For establishment of influence of initial concentration of ions of copper (II) on results of sorption we defined equilibrium concentration and equilibrium capacities of sorbents at various initial concentration of ions of copper (II), at identical parameters of conditions of sorption. With the increase of the initial concentration of metal ions a decrease in the degree of sorption and an increase in sorption capacity for all studied sorbents is observed. Decrease of sorption degree with increase of initial concentration of copper ions

(II) can be connected with two reasons: firstly, in process of filling of sorption centers of a sorbent the number of empty sorption positions decreases and the number of sorption ions decreases; secondly, with increase of initial solution concentration the ion force of solution increases and activity of copper ions (II) decreases; that leads to decrease of sorption degree. When comparing the values of sorption degree and sorption capacity obtained for sodium and ammonium salts, relatively high values for ammonium salts can be observed. This effect is probably due to the different degree of hydrolysis of sodium and ammonium salts. The exchange reaction and complex formation between copper ions (II) and groups of $-\text{COONa}$ and $-\text{COONH}_4$ sorbents depend, among other factors, on the degree of hydrolysis of these groups in the aquatic environment. It is known that the degree of hydrolysis of sodium salts of carbon salts is less than that of ammonium salts (for example, constants of hydrolysis of sodium acetates and ammonium have values $5,7 \times 10^{-10}$ and $5,55 \times 10^{-3}$, accordingly). In hydrolysis of ammonium salts, equilibrium



shifted to the right due to the formation of weak electrolytes. And this creates favorable conditions for interaction of copper ions (II) with carboxylic group. It should be noted that the experimental data obtained at different initial concentrations of copper ions (II) were used to construct sorption isotherms to determine the experimental equilibrium sorption capacity of sorbents, as well as to evaluate sorption parameters for the models of Langmuir, Freundlich, Dubinin-Radushkevich (D-R) and Temkin.

3. Determination of analytical, kinetic and thermodynamic parameters of copper ion (II) sorption from aqueous solutions by synthesized polymer sorbents

3.1. Sorption isotherms. Experimental sorption isotherms are the most common way to describe sorption phenomena. Sorption isotherms characterize the dependence of sorption capacity or sorption capacity on the concentration of the sorbable component in the solution at a constant temperature.

Sorption isotherms of copper ions (II) from aqueous solutions by synthesized polymer sorbents were constructed as a dependence of equilibrium sorption capacity (q_e) on equilibrium concentration of copper ions in solution (C_e) at different initial concentrations of copper ions (II) in solution (C_0). The value q_e corresponding to a straight line section of the curve was taken as an experimental sorption capacity of the sorbent. The experimental capacities of sodium and ammonium salts terpolymers of maleic acid, styrene and monomers with ally group synthesized in this way are determined below:

MA-AP-St-Na.....	0.71 g^{-1}
MA-AP-St-NH ₄	1.05 g^{-1}
MA-HP-St-Na	0.518 g^{-1}
MA-HP-St-NH ₄	0.556 g^{-1}
MT-NO-St- Na	0,45 gq^{-1}
MT-NO-St-NH ₄	0,66 gq^{-1}
MA-DS-St-Na	0.512 g^{-1}
MA-DS-St-NH ₄	0.54 g^{-1}
MA-AP-St-TEA- NH ₄	0.322 g^{-1}
MA-AP-St-GL-NH ₄	0.336 g^{-1}

As it is visible from the resulted data, the experimental sorption capacity of ammonium salts terpolymers is higher in comparison with sodium salts that is connected, probably, with greater degree of hydrolysis of ammonium salts. In addition, the experimental capacity of ammonium salts of polymer-sorbents with a mesh structure is less than the corresponding salts of a linear structure. This may be associated, in our opinion, with a smaller number of carboxylate groups in sorbents of the mesh structure (one carboxylic group of maleic acid is associated with molecules of cross-linking agents TEA and GL).

Taking into account the obtained experimental data on sorption capacities of sorbents, it can be concluded that all synthesized polymeric sorbent salts show rather high sorption capacity in relation to copper ions (II).

3.2.Processing of experimental data in coordinates of the

Langmuir, Freundlich, Dubinin-Radushkevich and Temkin equations

3.2.1. The Langmuir model. The basic idea of Langmuir's adsorption theory is to use the concept of adsorption as a quasi-chemical reaction between adsorbate and adsorption centers on the adsorbent surface. The Langmuir equation is used as the following linear form:

$$\frac{C_e}{q_c} = \frac{1}{K_L q_{\max}} + \frac{1}{q_{\max}} C_e$$

C_e is the equilibrium concentration of copper ions (g L^{-1}),

q_c is the amount of the copper ions adsorbed at equilibrium (g g^{-1}),

q_{\max} is the monolayer maximum adsorption capacity of the AMAS (g g^{-1}),

K_L is the Langmuir equilibrium constant (L g^{-1}).

The affinity between adsorbate and adsorbate or the sorption capacity of a certain sorbate in relation to a certain sorbate is characterized by a dimensionless equilibrium parameter R_L which is defined by equality

$$R_L = 1 / (1 + K_L C_0)$$

K_L -constant of Langmuir equation,

C_0 - initial concentration of sorbate in solution ($\text{mol}\cdot\text{L}^{-1}$, or $\text{g}\cdot\text{L}^{-1}$ or $\text{mg}\cdot\text{L}^{-1}$).

The adsorption process depending on the R_L factor, can be estimated as follows: if $0 < R_L < 1$, then the conditions for sorption are favorable, if $R_L > 1$, then the conditions for sorption are unfavorable, if $R_L = 1$, then the sorption is linear, if $R_L = 0$, then the sorption process is irreversible. The obtained experimental data on the sorption of copper ions (II) from aqueous solutions of sodium and ammonium salts terpolymers of maleic acid with styrene and monomers with allyl group were processed in the coordinates of the Langmuir equation with the construction of graphs of dependence $C_e/q_c = f(C_e)$. The maximum sorption capacity of sorbents was calculated from the graph equations q_{\max} as well as the values of the dimensionless equilibrium parameter R_L using values q_{\max} and initial concentrations of copper ions (II) at which the sorption process is carried out. The results are presented in

Table 2. As can be seen from the table, experimental data obtained on sorption of copper ions (II) from aqueous solutions with all synthesized sorbents are well described by Langmuir model with high correlation coefficients (0.9891-0.9996). The data also show that the maximum sorption capacity of ammonium salts is higher compared to sodium salts.

For all sorbents the condition $0 < R_L < 1$ is observed, which indicates the favorable process of sorption of copper ions (II) from aqueous solutions of sodium and ammonium salts of polymers of maleic acid with styrene and monomers with ally group.

Table 2. Parameters of Langmuir equation for sorption of copper ions (II) from water solutions with synthesized sorbents

Sorbent	q_{max}		K_L		R_L	R^2
	gg^{-1}	$molg^{-1}$	Lg^{-1}	$Lmol^{-1}$		
MA-AP-St-Na	0,75	0,0117	2,05	0,032	0,433- 0,07	0,999 6
MA-AP-St-NH ₄	1,258	0,0197	2,02	0,0316	0,456- 0,072	0,999
MA-HP-St-Na	0,735	0,0115	3,659	0,057	0,631- 0,176	0,997
MA-HP-St-NH ₄	0,819	0,0128	3,745	0,059	0,625- 0,173	0,995 7
MT-NO-St-Na	0,545	0,0085	5,0	0,078	0,555- 0,03	0,991 7
MA-DS-St-Na	0,722	0,0113	3,175	0,0496	0,663- 0,177	0,992 1
MA-DS-St-NH ₄	0,754	0,0118	4,136	0,0646	0,602- 0,161	0,989 1
MA-AP-St-TEA-NH ₄	0,433	0,0068	4,545	0,071	0,579- 0,149	0,995 6
MA-AP-St-GL-NH ₄	0,462	0,0072	4,255	0,067	0,595- 0,155	0,994 2

3.2.2. The Freundlich model. The Langmuir model is valid for monomolecular adsorption running on an adsorbent with energy equivalent adsorption centers. In the case of sorbents with

heterogeneous surfaces, the Freundlich empirical equation is used for processing the data:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

K_F - constant of the Freundlich equation showing the relative sorption capacity (g^{-1} or $mol g^{-1}$)

n - parameter corresponding to the binding energy between the metal atom and the adsorbent, which shows the intensity of sorbent-sorbate interaction.

If $n < 1$, the bond energy increases, at $n > 1$, the sorbent-sorbate bond energy decreases as the surface fills up; in case $n = 1$, all sorbent-sorbate centers are equivalent. If $0 < (1/n) < 1$, then sorption is chemisorption.

The dependency graphs were drawn $\log q_e = f(\log C_e)$ using the experimental data obtained and calculated from these graphs the values of K_F , n and correlation coefficients, which are given in table 3. The table shows that the experimental data correlate well in the coordinates of the Freundlich equation and the correlation coefficients have sufficiently high values (0.9132-0.9968). The K_F values given in Table 3, characterizing the relative sorption capacity of sorbents, are high enough and correspond to the values of sorption capacity of sorbents obtained by processing the experimental data in the coordinates of the Langmuir equation (Table 2).

Table 3. Parameters of the Freundlich equation

SORBENT	PARAMETRS				
	K_F		$1/n$	n	R^2
	gg^{-1}	$Mol g^{-1}$			
MA-AP-St-Na	0,662	0,0103	0,4034	2,48	0.9132
MA-AP-St-NH ₄	0,73	0,0114	0,4241	2,353	0.9242
MA-HP-St-Na	0,742	0,0116	0,6018	1,659	0.9827
MA-HP-St-NH ₄	0,878	0,0137	0,6222	1,607	0.9852
MA-NO-St-Na	0,603	0,0094	0,4012	2,492	0.9842
MA-DS-St-Na	0,725	0,0113	0,6169	1,62	0.9908
MA-DS-St-NH ₄	0,809	0,0126	0,6148	1,6265	0.9867
MA-AP-St-TEA-	0,4736	0,0074	0,588	1,70	0.9854

NH ₄					
MA-AP-ST-GL-NH ₄	0,504	0,0079	0,6038	1,656	0.9877

We can see that the parameter $1/n$ for all sorbents is less than one, which indicates the chemical nature of the sorption process. For all sorbents $n > 1$, which also indicates intensive interaction between sorbents and copper ions (II).

3.2.3. Model Dubinin-Radushkevich (D-R). Although the Langmuir and Freundlich models are widely used in the study of adsorption processes, they do not provide any information on the adsorption mechanism. The model of the D-R isotherm is more general than that of Langmuir and allows to determine the constants of the model equation, the values of which can be used to judge the physical or chemical nature of sorption. In general, it is used to distinguish between physical and chemical adsorption. The D-R model equation has the form

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

K_D - constant associated with adsorption energy ($mol^2 kJ^2$),

q_e - sorption capacity of sorbate at different initial concentrations of sorbate ($mol g^{-1}$, $mmol g^{-1}$, or g^{-1} or $mg g^{-1}$).

B_{DR} -maximum capacity of sorbent at full saturation of active reaction centers ($mole g^{-1}$, $mmol g^{-1}$, or g^{-1} or $mg g^{-1}$),

ε -Polanyi potential ($kJ mol^{-1}$), reflecting the isothermal work of the transfer of one molecule of metal ions from the volume of the equilibrium solution to the sorbent surface and determined from the expression

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

R - gas constant ($8,314 J mol^{-1} K^{-1}$),

C_e -equilibrium concentration of sorbate ($molL^{-1}$ or $mmolL^{-1}$, or gL^{-1} or mgL^{-1}).

In the equation of D-R model of K_D constant is associated with free energy of sorption (E) as follows

$$E \frac{1}{\sqrt{2K_D}}$$

It is believed that if $E < 16 \text{ kJ mol}^{-1}$, then adsorption is of chemical nature, and if $E < 8 \text{ kJ mol}^{-1}$, then adsorption is of physical nature.

In order to reveal the mechanism of the sorption process of copper ions(II) from the aqueous solution by synthesized polymer sorbents, the equilibrium data were processed using the D-R isotherm model.

By plotting the dependence $\ln q_e = f(\varepsilon^2)$ it is possible to determine the K_D and B_{DR} values from the mathematical equation of the straight line expressing this dependence.

Using the q_e , C_e and ε , calculated from the experimentally obtained data, plots of dependence $\ln q_e = f(\varepsilon^2)$ for each polymer-sorbent and the values of B_{DR} , K_D and E have been determined. The values of the parameters of equation D-R are placed in Table 4. According to the data presented in the table, the following conclusions can be drawn about the process of sorption of copper ions (II) from aqueous solutions by synthesized polymer- sorbents:

1.The sorption capacity of sorbents at full saturation of all sorption centers (B_{DR}) is high enough ($0.8915\text{-}1.837 \text{ g}^{-1}$ or $0.01393\text{-}0.0287 \text{ mol g}^{-1}$).

2.Calculated values of free energy of sorption of E_D are closer or more than $8,0 \text{ kJ mol}^{-1}$, that testifies to ion-exchange (chemical) character of interaction of ions of copper (II) and sorbents.

Thus, the synthesized sodium and ammonium salts terpolymers are effective sorbents for the extraction of copper ions (II) from aqueous solutions.

Table 4. Parameters of the Dubinin-Radushkevich equation

SORBENT	PARAMETERS				
	K_D	B_{DR}		$E, \text{ kJ mol}^{-1}$	R^2
		Mol g^{-1}	g g^{-1}		
MA-AP-St-Na	0,0025 7	0,257	1,645	7,813	0,9686
MA-AP-St-NH ₄	0,0081	0,0285	1,824	7,874	0,9728

MA-HP-St-Na	0,0086	0,0252	1,613	7,634	0,9958
MA-HP-St-NH ₄	0,0086	0,0287	1,837	7,634	0,9963
MA-DS-St-Na	0,0088	0,025	1,6	7,838	0,9978
MA-DS-St-NH ₄	0,0086	0,027	1,728	7,634	0,9975
MA-AP-St-TEA-NH ₄	0,0077	0,1393	0,891 5	8,066	0,9962
MA-AP-St-GI-NH ₄	0,0075	0,0141 3	0,904	8,17	0,9914

3.2.4. Temkin model. The Temkin model takes into account indirect interaction between adsorbate and adsorbent with the condition that due to these interactions the adsorption heat of all molecules in the layer decreases linearly as the layer is filled. The equation of Temkin's isotherm determines that as the degree of saturation of active sorption centers of adsorbent increases, the sorption heat decreases linearly. The Temkin isotherm equation can be presented in the following form:

$$q_e = B \ln A_T + B \ln C_e$$

$$B = RT/b_T$$

B -parameter that determines the sorption heat associated with chemical bond energy (kJ mol^{-1}),

A_T -equilibrium constant of the Temkin isotherm (L mol^{-1}), which takes into account the interaction between adsorption centers and metal ions, R -universal gas constant,

b_T -constant of the isotherm, T -temperature (K).

The obtained experimental data on sorption of copper ions (II) from aqueous solutions by synthesized polymer-salts were processed in the coordinates of the Temkin equation and the results are presented in Table 5. The presented data in Table 5 show rather high maximum binding energy of copper ions (II) with sorption centers of sorbents ($A_T=1324-3436, \text{L mol}^{-1}$)

Table 5. The parameters of the Temkin equation

SORBENT	PARAMETRS			
	$A_T, \text{L mol}^{-1}$	B, kJ	$b_T, \text{kJ mol}^{-1} \times 10^{-6}$	R^2

		mol^{-1}		
MA-AP-St-Na	1324	3,7	6,58	0,9792
MA-AP-St-NH ₄	1800	4,1	5,94	0,9804
MA-HP-St-Na	2844	2,4	1,05	0,9872
MA-HP-St-NH ₄	3090	2,6	0,937	0,9854
MA-DS-St-Na	2123	2,4	1,015	0,9783
MA-DS-St-NH ₄	2355	2,6	0,937	0,9812
MA-AP-St-TEA- NH ₄	3436	1,4	1,74	0,9833
MA-AP-St-Gl-NH ₄	2979	1,5	1,62	0,9776

Parameter B , which characterizes the heat of sorption, has values 0.0014- 0.0041 $kJ mol^{-1}$. This difference may be due to the different degree of hydrolysis of sodium and ammonium salts, as the sorption process involves mainly carboxylic groups released by hydrolysis of -COONa and -COONH₄ groups.

3.3.Sorption kinetics of copper ions (II) from aqueous solution by synthesized sorbents

The study of kinetic parameters is important in the description of adsorption processes, because the kinetic data can be used to judge the process, and they also provide information about the factors controlling the adsorption rate. Various kinetic models are used to describe the adsorption process. Pseudo-first and pseudo-sorption kinetic models are most commonly used in the study of sorption kinetics.

The equations of pseudo-first order and pseudo second order Lagergren models, which are most widely used to study the sorption kinetics of heavy metal ions from water solutions, have the following linear expressions:

$$\log(q_e - q_t) = \log q_e - 0,434k_1t$$

$$t/q_t = \frac{1}{k_2q_e^2} + \frac{t}{q_e}$$

Parameters k_1 ($L min^{-1}$) and k_2 ($g^{-1}min^{-1}$) are the equilibrium

constant of the reaction rate of pseudo-first order and pseudo-second order, respectively, q_e (g^{-1})-quantity of adsorbed metal by one gram of sorbent in equilibrium state. Plotting the dependency graphs $\log(q_e - q_t) - t$ and $t/q_t - t$, you can define the values k_1 and k_2 . For graphic determination of kinetic parameters of copper ions sorption (II), experimental data obtained at different sorption times were used. The obtained kinetic indices of pseudo-first and pseudo-second orders are given in Table 6. According to Table 6, the correlation coefficients R^2 are higher for the pseudo order model than for the pseudo order model. This shows that adsorption of copper ions (II) on synthesized sorbents is better described by the pseudo-first order model than by the pseudo-first order model. We can see that the values of sorption capacity calculated from the graphs of the pseudo-first order equation are higher than the values obtained for the pseudo-first order. In addition, the values of the sorption capacity calculated from the graphs of the pseudo- order equation practically coincide with their experimental values.

3.4. Thermodynamics of copper (II) ion sorption from aqueous solutions with synthesized sorbents

Temperature is one of the most important parameters of the process of metal ions sorption by functional sorbents, affecting its thermodynamics. Changes in temperature cause changes in thermodynamic parameters such as ΔG° , ΔH° and ΔS° , which explain the sorption process mechanism. Experimental data reflecting the influence of temperature on the sorption process of heavy metal ions are used to determine these parameters by the formulary

$$\Delta G^\circ = -2.3 RT \log K_d$$

$$K_d = q_e / C_e$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

ΔG° - change of standard free energy ($kJ\ mol^{-1}$), R - universal gas constant ($8.314 \times 10^{-3}\ kJ\ mol^{-1}$), ΔS° - change of entropy ($kJ\ mol^{-1}$), T - temperature in degrees Kelvin, K_d - equilibrium constant at temperature T .

Table 6: Kinetic parameters of sorption of copper ions (II) from aqueous solutions with synthesized sorbents

Sorbent	Kinetic model	Sorb.cap , $q_e, g\ g^{-1}$	$k_1,$ min^{-1}	$k_2,$ Lg^{-1} min^{-1}	R^2
MA-AP-St-Na	I order	0,682	0,0186 6	-	0.9597
	II order	0,833	-	0,012 7	0,9829
MA-AP-St-NH ₄	I order	0.9786	0,0216 6	-	0.966
	II order	0,807	-	0,017 5	0,9953
MA-HP-St-Na	I order	0,131	0,0456	-	0,9298
	II order	0,224	-	0,342	0,9984
MA-HP-St-NH ₄	I order	0,171	0,038	-	0,9375
	II order	0,261	-	0,435	0,9994
MA -DS-St- Na	I order	0,116	0,0652	-	0,9848
	II order	0,191	-	0,923	0,9996
MA-DS-St-NH ₄	I order	0,109	0,0454	-	0,9848
	II order	0,202	-	0,769	0,9998
MA-AP-St-TEA-NH ₄	I order	0,277	0,047	-	0,9835
	II order	0,328	-	0,15	0,9895
MA-AP-St-Gl-NH ₄	I order	0,235	0,038	-	0,9747
	II order	0,331	-	0,147	0,9924

The dependence in $\Delta G^\circ - T$ is a straight line, which allows to determine the values of ΔH° and ΔS° . The parameters ΔG° , ΔH° and ΔS° provide valuable information on the sorption process. ΔG° indicates the possibility of a sorption process and a negative value of ΔG° indicates a spontaneous (random) process.

To determine the thermodynamic parameters of sorption of copper ions (II) from aqueous solutions by synthesized sorbents, the values of equilibrium concentrations (C_e) and sorption capacity (q_e) at

different temperatures were determined experimentally. The values of C_e and q_e were used to calculate the values of K_D and ΔG° and to determine ΔH° and ΔS° sorption from the dependence graph of ΔG° -T. Table 7 illustrates the values of thermodynamic parameters of ion sorption from aqueous solutions by synthesized sorbents.

Table 7. Thermodynamic parameters of sorption of copper ions (II) from aqueous solutions with synthesized sorbents

SORBENT	ΔG° $\kappa J mol^{-1}$	ΔH° , $\kappa J mol^{-1}$	$\Delta S^\circ, \kappa J$ mol^{-1}	R^2
MA-AP-St-Na	(-1,55)-(-3,37)	17,46	0,061	0,9994
MA-AP-St-NH ₄	(-0,713)-(-0,028)	-10,7	-0,0342	0,9684
MA-HP-St-Na	(-4,505)-(-1,8)	37,8	0,136	0,9999
MA-HP-St-NH ₄	(-2,059)-(-0,341)	-27,2	-0,0859	0,9979
MA-DS-St-Na	(-5,14)-(-1,38)	53,38	0,188	0,9864
MA-DS-St-NH ₄	(-1,8)-(-0,717)	-7,66	-0,054	0,9942
MA-AP-St-TEA-NH ₄	(-1,423)-(-0,852)	7,517	0,02855	0,9994
MA-AP-St-Gl-NH ₄	(-1,830)-(-0,955)	11,86	0,04375	0,9999

Some conclusions can be drawn on the nature of the sorption process from the data in table 7. As can be seen, free energy of Gibbs for sorption of copper ions (II) by all sorbents is of negative value. This indicates that the sorption process is spontaneous (arbitrary). As for ΔH° and ΔS° values obtained for sorption of copper ions on different sorbents, the following distinctive features can be observed. The table shows that ΔH° , in the process of sorption on sodium salts of linear and ammonium sorbents has a positive sign, which indicates the endothermic nature of the process, and in the process of sorption on ammonium salts of linear sorbents the sign ΔH° is negative, i.e., the sorption process has an exothermic nature. This nature of sorption for different polymers of salts is apparently related to the different degree

of dissociation of sodium and ammonium salts. The tabular data also show that the absolute values of ΔH° differ significantly from each other. As mentioned above, the sorption of heavy metal ions is a complex process including chemisorption, complex formation, surface adsorption, ion exchange, chelating, adsorption by physical forces, etc. Obviously, the sign and value of the resulting thermal effect (change of enthalpy) of the sorption process will be determined by superimposing the thermal effects of all processes occurring in this case. Therefore, sorption of copper ions (II) from aqueous solutions by synthesized polymer salts can be qualified as a physical and chemical sorption process rather than a pure physical or chemical process. Typically, when adsorbed on solid sorbents, the change in entropy ΔS° has negative values, which is associated with the ordering of sorbate ions on the sorbent surface. In our case, ΔS° values for ammonium salts of linear terpolymers have a negative sign, which indicates the order of copper ions (II) in the sorbent.

4. Thermal and spectroscopic examination of sorbents before and after sorption

To confirm the presence of copper ions (II) in sorbents after sorption and to establish a possible mechanism of the process of sorption of copper ions (II) from aqueous solutions with sodium and ammonium salts of maleic acid terpolymers, thermo gravimetric and spectroscopic studies of sorbents before and after sorption were carried out. As an example, here are the results of research carried out only with ammonium salts of triple copolymer of maleic acid with allylpropionate and styrene of linear and mesh structure. According to TG and DTG curves of sorbent MA-AP-St-NH₄ after sorption it was found that in the temperature range 66.7- 930°C the weight loss of the canopy is 12.42%. This seems to be due to the evaporation of water included in the sorbent copper complex (II). Intensive degradation was observed at 233.8°C and continued up to 525°C, and the degradation was a step process. At 842 °C, the weight loss of the canopy was about 60% and the balance 40%, which corresponds to the amount of copper adsorbed by the sorbent. This is proof that the synthesized

sorbent effectively adsorbs copper ions (II) from the aqueous solution.

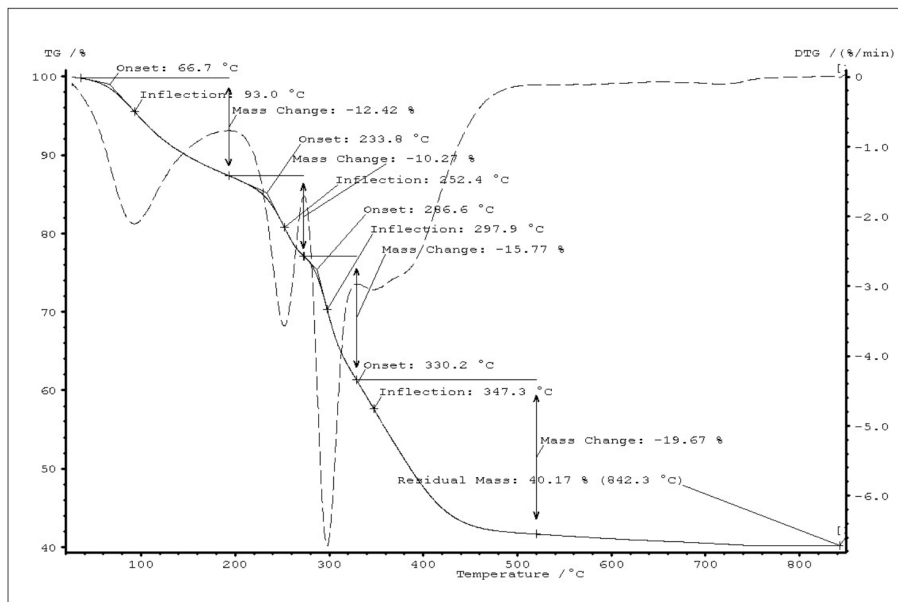


Figure 1. TG-DTG after sorption for MA-AP-St-NH₄

IR- and UV-spectroscopic examination of sorbents before and after the sorption process is one of the possibilities to reveal the mechanism of metal ions sorption from aqueous solutions. That is why we have shot infrared Fourier and UV spectra of ammonium salts of terpolymer maleic acid- allylpropionate styrene linear and cross-linked structures before and after their sorption of copper ions (II) from aqueous solutions. Fig. 1 shows the MA-AP-St-NH₄ spectra removed in 4000-1000 cm⁻¹ Fourier-IR regions after sorption of Cu²⁺ from aqueous solution. Absorption bands 1642, 1583, 1566 cm⁻¹ and 1409,1307 cm⁻¹ belong to asymmetrical and symmetrical carboxylate ion oscillations (COO⁻), respectively. The absorption band 1642 cm⁻¹ characterizes the ester group in sorbent. The absorption bands in the area of 3468 cm⁻¹ can be referred to the valence oscillations of hydroxyl groups of bound water molecules. Fig. 2 shows the Fourier infrared spectra of MA-AP-St-GI-NH₄ sorbent before and after

sorption.

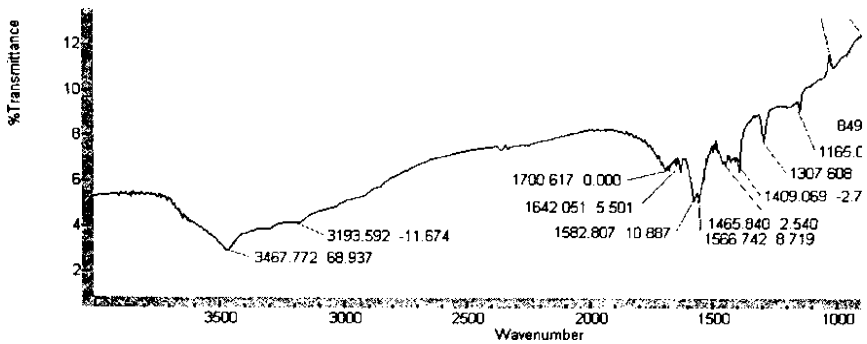


Figure 2. Fourier-IR spectrum MA-AP-St-NH₄ after sorption

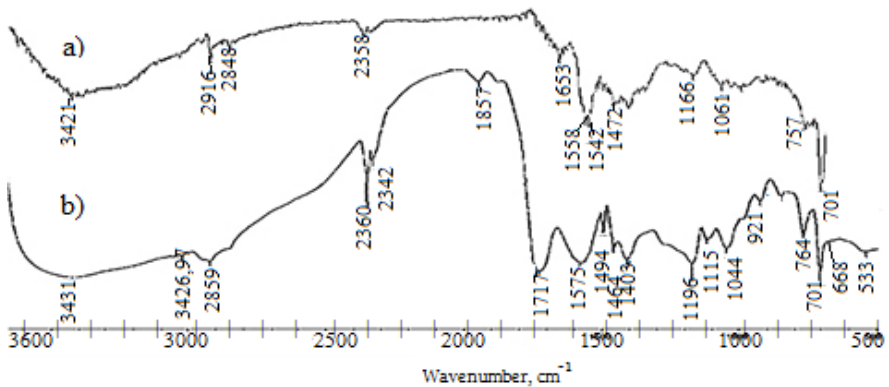


Figure 3. Fourier-IR spectrum MA-AP-St-GL-NH₄ before (a) and after (b) sorption.

If we compare these spectra, we can see that the absorption bands 1542 and 1558 cm^{-1} , characteristic for asymmetric fluctuations of COO-groups (Fig.2 a) in the unused sorbent, disappear and new bands 1403 and 1575 cm^{-1} appear on the sorbent spectrum after sorption (Fig.2 b). These bands are characterized by asymmetric vibrations of carboxylate groups in a complex of copper ions with sorbent. A wide strip of 3431 cm^{-1} can be attributed to -OH groups of glycerin and -OH groups of unresponsive carboxylic groups. As for the absorption bands 701 and 764 cm^{-1} , they can be referred to mono-substituted benzene rings of styrene links. To reveal the possibility of formation

of copper ions (II) complexes with the studied sorbents, we took UV spectrum of MA-AP-St-NH₄ (1) and MA-AP-St-GI- NH₄ (2) before and after sorption (Fig. 3).

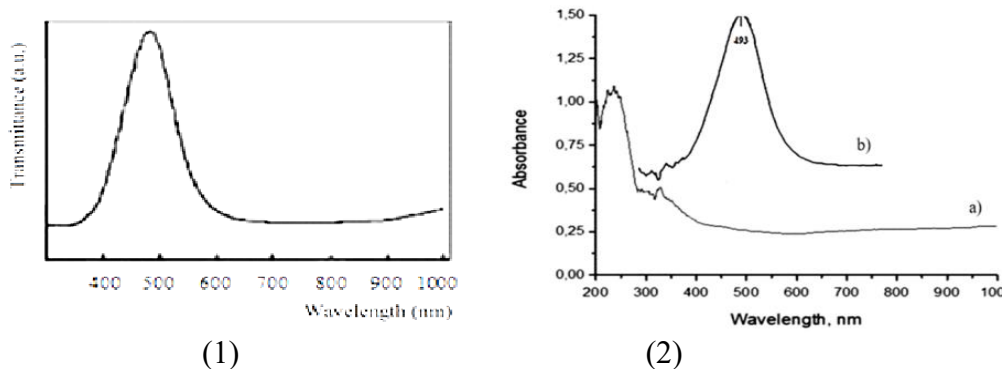
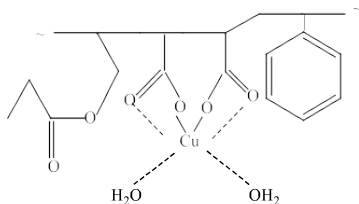
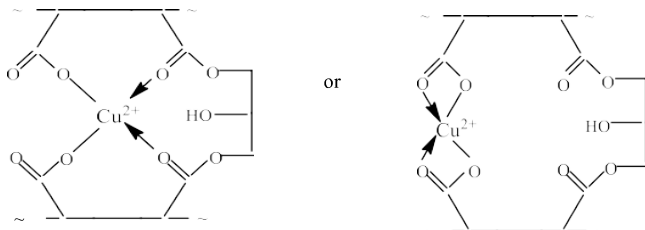


Figure 4. UV spectrum of sorbent MA-AP-St-NH₄ after sorption and MA-AP-St-GI-NH₄ UV spectrum before (a) and after (b) sorption.

The observed maximums of 490 nm (Fig. 3) on the MA-AP-St-NH₄ spectrum and 493 nm (Fig. 3b) on the MA-AP-St-GI-NH₄ spectrum prove the proposal to form the MA-AP-St-NH₄ complex, to which the following structure can be attributed:



and MA-AP-St-GI- NH₄ complexes to which the following structure can be attributed:



Other variants of complexation of copper ions (II) with synthesized

polymer-sorbents are also not excluded.

Conclusions

1. Synthesized and characterized sodium and ammonium salts terpolymers: maleic acid-allylpropionate-styrene, maleic acid-hepten-1-styrene, maleic acid-nonen-1-styrene, maleic acid-decen-1-styrene, as well as ammonium salts of crosslinked triethanolamine and glycerine terpolymer: maleic acid-allylpropionate-styrene.

2. Synthesized sodium and ammonium salts were used as sorbents to extract copper ions (II) from aqueous solutions. The influence of contact time, pH of solutions, sorbent mass, temperature and concentration of copper ions (II) on the degree of metal ions sorption and sorption capacity of sorbents were studied. It is established that under the same conditions of sorption, ammonium salts show a greater sorption capacity compared to sodium salts, which is explained by a comparatively greater degree of dissociation of ammonium salts with the formation of free carboxylate ions.

3. The experimental data obtained were processed in the coordinates of the Langmuir, Freundlich, Dubinin-Radushkevich and Temkin isotherm equations. The values of parameters of these equations are determined. The maximum sorption capacities from the graph of the Langmuir equation, sorption capacities at saturation of sorption centers from the graph of the Dubinin-Radushkevich equation have been determined. Calculated by the Dubinin-Radushkevich isotherm equation, the sorption energy values are 7,634-8,17, which indicates the chemical nature of sorption.

4. The kinetics of sorption of copper ions (II) by synthesized sorbents was studied. Experimental data obtained at different sorption times were processed in the coordinates of the Lagergren equations of pseudo-first and pseudo-second order. It was found that for all sorbents the data are well described by the pseudo-variant order equation with a high correlation coefficient. The values of sorption rate constants and sorption capacity of sorbents are calculated.

5. Thermodynamic values of sorption parameters (ΔG° , ΔH° and ΔS°)

were determined and it was found that for all sorbents the values of ΔG° were negative, which indicates spontaneity (randomness) of the sorption process. It was also found that sorption with ammonium salts is exothermic, and with sodium salts is endothermic.

6. For ammonium salts of the linear terpolymer maleic acid-allylpropionate styrene and triethanolamine cross-linked triple copolymer maleic acid-allylpropionate styrene was removed TG-DTG curves, Fourier infrared and UV spectra after sorption. The TG-curve taken in the temperature range of 20-850°C shows that the amount of copper in the sorbent after sorption is 40.17% at 842°C, and the Fourier infrared and UV spectra fix complexation between copper ions (II) and sorbent sorption centers.

7. Taking into account the results of experimental data processing in the models of adsorption isotherms, kinetic and thermodynamic, as well as IR- Fourier and UV-spectroscopic studies, it can be concluded that the mechanism of sorption of copper ions (II) with synthesized triple copolymer salts of maleic acid is connected with chemical interaction accompanying complex formation between sorption centers of sorbents and copper ions (II).

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The defense will be held on 16th March 2022 at 11⁰⁰ a.m at the meeting of the Dissertation council ED 1.28 of Supreme Attestation Commission under the President of the Republic of Azerbaijan operating at the Institute of Polymer Materials of ANAS.

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Abstract was sent to the required addresses on 08 February 2022.

Signed for print: 30.01.2022
Paper format: 60x90 1/16
Volume: 37 530 characters
Number of hard copies: 20