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CONTENTS

МАЗМҰНЫ

СОДЕРЖАНИЕ

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COPOLYMERS BASED ON ACRYLIC ACID FOR WATER PURIFICATION FROM HEAVY METAL IONS

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Abstract. In this study, stimuli-responsive hydrogels based on acrylic acid (AA) and methyl acrylate (MA) were synthesized via radical copolymerization. The research focused on their swelling behavior, sorption capacity, and interaction with copper (II) ions under different environmental conditions. The influence of temperature on swelling at various pH values was systematically examined. Despite the hydrophobic contribution of methyl groups, the swelling coefficient (V/V_0) increased with temperature, particularly in alkaline media. However, partial shrinkage occurred in acidic and neutral solutions due to suppressed ionization of carboxyl groups and enhanced hydrophobic interactions from MA units. The sorption properties of the hydrogels were studied through complexation with copper (II) ions. Immersing dried AA-MA hydrogels in $CuCl_2$ solutions led to a measurable reduction in Cu^{2+} concentration, which indicated ion-exchange binding. This process was attributed to the substitution of poly(acrylic acid) protons by copper cations, accompanied by redistribution of salts within the medium. To further evaluate metal ion retention and release, hydrogel/copper complexes were prepared using varying copper concentrations. The desorption of Cu^{2+} was investigated under three pH conditions (4, 7, and 9). The results showed that both desorption amplitude and rate were higher in acidic and alkaline solutions compared to neutral ones, which was linked to conformational changes of the hydrogel network and increased ion mobility. Overall, the study demonstrates that AA-MA hydrogels exhibit pH- and temperature-sensitive behavior, which governs their swelling capacity, ion-binding ability, and controlled release of copper ions. These findings highlight their potential application in sorption technologies and controlled release systems.

Key words: acrylic acid (AA), methyl acrylate (MA), groundwater, ionic hydrogels, radical polymerization

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АУЫР МЕТАЛЛ ИОНДАРЫНАН СУ ТАЗАЛАУҒА АРНАЛҒАН АКРИЛ ҚЫШҚЫЛЫ НЕГІЗІНДЕГІ СОПОЛИМЕРЛЕР

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Аннотация. Бұл зерттеуде радикалды сополимерлеу әдісі арқылы акрил қышқылы (АҚ) және метилакрилат (МА) негізіндегі ынталандыруға сезімтал гидрогельдер синтезделді. Сондықтан әртүрлі pH мәндерінде гидрогельдердің ісінуіне температураның әсері зерттеліп, олардың сорбциялық қасиеттері талданып қарастырылды. Бұл АҚ-МА сополимер гидрогельдерінің мыс (II) иондарымен комплексті түзілу ерекшеліктері де қарастырылып зертелді. Гидрогельден мыс иондарының бөлінуін зерттеу үшін әртүрлі мыс концентрациясында [гидрогель/мыс ионы] комплекстері алынды, оның қасиеттері зерттеліп қарастырылды. Осыған байланысты, кешеннен мыс (II) иондарының десорбциясы гидрогельдегі конформациялық өзгерістерді ескере отырып, үш түрлі pH мәндері (pH = 4, 7, 9) толығымен келтірілді. Десорбция жылдамдығы мен амплитудасы қышқыл және сілтілі ортада бейтарап ортамен салыстырғанда жоғары болды, бұл гидрогель көлемінің ұлғаюымен және ерітіндідегі мыс (II) иондарының концентрациясының жоғарылауымен байланысты екені қарастырылып анықталды. Сондықтан әртүрлі pH мәндеріндегі гидрогельдердің ісіну қабілетіне температураның әсері зерттелді. Гидрофобты метил топтарының болуына қарамастан, АҚ-МА сополимерлерінің құрылымы ісіну коэффициентінің (V/V_0) температураның жоғарылауын көрсетті, оның әсіресе сілтілі ортада анықталды. Сонымен қатар қышқылдық және бейтарап ортада карбоксил тобының ионизациясының басылуы мен метилакрилаттан гидрофобты әрекеттесулердің үлесінің жоғарылауына байланысты ішінара шөгу байқалды. Мыс хлоридінің сулы ерітінділеріндегі АҚ-МА негізіндегі гидрогельдердің физика-химиялық әрекеті зерттелді. Сондықтан кептірілген АҚ-МА гидрогельдерін $CuCl_2$ ерітінділеріне орналастыру Cu^{2+} концентрациясының төмендеуіне әкелетіні анықталды, бұл ион алмасу байланысын – поли (акрил қышқылы) протондарды мыс катиондарымен ауыстыруды және ерітіндідегі тұздардың қайта бөлінуін көрсетеді.

Түйін сөздер: акрил қышқылы (АҚ), метилакрилат (МА), жер асты сулары, иондық гидрогельдер, радикалды полимерлену

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СОПОЛИМЕРЫ НА ОСНОВЕ АКРИЛОВОЙ КИСЛОТЫ ДЛЯ ОЧИСТКИ ВОДЫ ОТ ИОНОВ ТЯЖЕЛЫХ МЕТАЛЛОВ

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Аннотация. В данном исследовании были синтезированы чувствительные к раздражителям гидрогели на основе акриловой кислоты (АК) и метилакрилата (МА) с использованием метода радикальной сополимеризации. Изучено влияние температуры на набухаемость гидрогелей при различных значениях pH, а также проанализированы их сорбционные свойства. Также рассмотрены особенности комплексообразования гидрогелей АК-МА с ионами меди (II). Для изучения высвобождения ионов меди из гидрогеля были получены комплексы [гидрогель/ион меди] при различных концентрациях меди. Изучали десорбцию ионов меди (II) из комплекса при трех различных значениях pH (pH = 4, 7, 9) с учетом конформационных изменений гидрогеля. Скорость и амплитуда десорбции были выше в кислых и щелочных средах по сравнению с нейтральными средами, что, как было установлено, связано с увеличением объема гидрогеля и повышением концентрации ионов меди (II) в растворе. Изучено влияние температуры на набухаемость гидрогелей при различных значениях pH. Несмотря на наличие гидрофобных метильных групп, структура сополимеров АЦ-МА показала, что коэффициент набухания (V/V_0) увеличивается с ростом температуры, особенно в щелочной среде (pH 9). При этом в кислых и нейтральных средах наблюдается частичная усадка, обусловленная подавлением ионизации карбоксильных групп и увеличением вклада гидрофобных взаимодействий метилакрилата. Исследовано физико-химическое поведение гидрогелей на основе АЦ-МА в водных растворах хлорида меди. Установлено, что помещение высушенных гидрогелей АЦ-МА в растворы $CuCl_2$ приводит к снижению концентрации Cu^+, что свидетельствует об ионообменном связывании -замещении протонов полиакриловой кислоты катионами меди и перераспределении солей в растворе.

Ключевые слова: акриловая кислота (АК), метилакрилат (МА), грунтовые воды, ионные гидрогели, радикальная полимеризация

Introduction. Transition metal ion compounds are common in natural waters. For example, the primary sources of copper ions in natural waters are wastewater from chemical and metallurgical industries, mine water, aldehyde reagents for algae control, etc. The purification of copper ions from water, industrial waters, and solutions contaminated with copper ions, or the separation of copper ions, has been considered for a long time (Safronov et al, 2012; Azhkeyeva et al, 2018; Wang et al, 2012; Azhkeyeva et al, 2012; Yermukhambetova et al, 2011).

The removal of copper (II) and lead (II) ions from aqueous solutions of acrylic acid starch hydrogel /montmorillonite cross-linked nanocomposite (AASH/MMT) was investigated in the work of Gamze Guçle and colleagues (Mohammad et al, 2011). The article considers the influence of various factors on the removal of heavy metal ions, such as solvent treatment time, initial pH of the solvent, initial concentration of metal ions, and the amount of MMT. It was found that pH = 4 is optimal for the removal of metal ions from the solution. In a research work by Farhad Narimani and his colleagues, superabsorbent hydrogels based on acrylic acid tetrasulfonate-co-acryloyl tetrasodium thiocalix-(4) arenes were synthesized by polymerization in a dextrin-seeded solution (Gamze et al, 2010). The synthesized hydrogels were characterized using Fourier transform infrared spectroscopy, TGA, DMTA, and rheometric methods. The removal of metal ions Cd^{2+}, Pb^{2+}, and Hg^{2+} from the gels was studied by atomic adsorption. It was found that the adsorption capacity of metal ions decreases in the series $Pb^{2+}>Cd^{2+}>Hg^{2+}$. It was shown that the hydrogels are restored after being freed from heavy metal ions, and that repeated use for about 5 hours leads to a loss of less than 7% of their adsorption capacity (Azhkeyeva et al, 2018). In this work, to solve the above problem, new hydrogels based on acrylic acid (AA) and methyl acrylate (MA) were synthesized, and their complexes with copper ions were studied.

Materials and methods.

Acrylic acid (AA) with a molecular weight of 72.06266 g/mol (Sigma-Aldrich GmbH, Germany, 98%) was used without further purification.

Methyl acrylate (MA) (Sigma-Aldrich Co, USA, 98%) was used without further purification.

Ammonium persulfate (Affymetrix, China, 99%) was used without further purification.

The product N, N’-methylenebisacrylamide (Sigma-Aldrich Co, USA, 99%) was used without further purification.

Copper chloride (Sigma-Aldrich Co., USA, chemically pure) was used without further purification.

Synthesis of a hydrogel based on acrylic acid and methyl acrylate. Copolymers based on acrylic acid (AA) and methyl acrylate (MA) were obtained by radical polymerization with material initiation. The synthesis was carried out in alcohol-water solutions in molybdenum glass ampoules at a temperature of 60°C. The reaction mixture in the ampoule was purged with argon for 10–15 min to remove oxygen that decomposed over time. Ammonium persulfate was used as an initiator, and N, N’-methylenebisacrylamide as a binding agent. The synthesis was carried out in a water thermostat. The resulting hydrogels were divided into several parts and washed with distilled water for 2 weeks to remove the monomer.

The pH of the solutions was determined using a digital ion meter "781 pH/Ion Meter" ("Metrohm", Switzerland) at a temperature of 20°C. The pH level was adjusted by adding small amounts of 0.1 M hydrochloric acid and sodium hydroxide.

When carrying out complexation reactions with heavy metals under specified conditions, uniformly swollen hydrogels in the form of tablets were placed in the corresponding copper solutions at a constant temperature of 20°C. The complexation process was determined by the change in the volume of hydrogels over time. The complexation process was carried out in a UV spectrophotometer at a wavelength of 220 nm ("Specord 200 Plus", Germany).

The change in the relative volume of hydrogels was estimated using a B-630 catheterometer (Russia), depending on various values of pH of the medium and temperature, using the relative volume $F = V/V_0$, where V_0 is the volume of the sample during the synthesis, and V is the volume of the sample in the state of equilibrium swelling. The equilibrium degree of swelling of polymer hydrogels was determined by the formula:

$$a = (m-m_o)/m_0 \qquad (1)$$

Where: m is the equilibrium swelling mass of the polymer hydrogel, m0 is the mass of the dry sample.

The mass of the dry sample was determined after it was dried in a vacuum oven until a constant weight was achieved.

The degree of swelling was determined by conducting several series of experiments and taking their average value.

To study the effect of changing the pH of the polymer in the environment and the impact of temperature, a hydrogel sample in the form of a tablet with uniform swelling was placed in special cells. When studying thermally induced collapse, uniformly swollen polymers were placed in cylindrical cells with a diameter of 7 mm and a height of 5-6 mm, containing heat-stabilizing water. The hydrogel in each ratio had a different pH (4, 7; 9), and the temperature was changed discretely in 5°C increments. Each temperature was maintained for 30 minutes until a stable degree of swelling was achieved. The degree of swelling of the hydrogel was determined using a B-630 catheterometer and was estimated by the ratio V/V_0, where V is the equilibrium swelling volume of the sample under given conditions, and V_0 is the volume of the hydrogel sample during the synthesis process (Gamze et al, 2010).

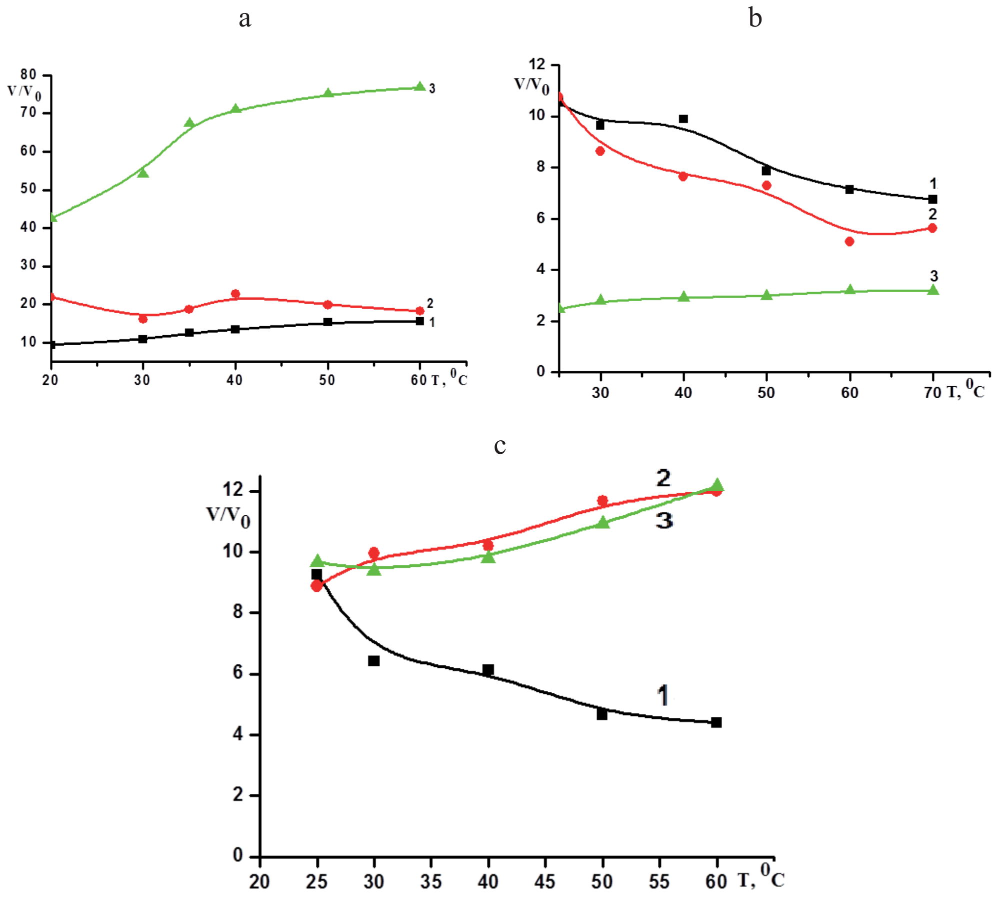
Results and discussion. In the work, water-swellable copolymers based on acrylic acid and methyl acrylate were synthesized by the method of direct radical copolymerization. It was observed that the yield of the copolymer increased with the increase in the content of acrylic acid in the initial monomer mixture (IMB) (Table 1). The increase in the degree of swelling (α value) in water and alcohol for hydrogels based on AA-MA is explained by the rise in the percentage of the ionogenic component AC in the initial monomer mixture and the ionization of the carboxyl groups of AA.

Table 1. Gel-sol fraction of AA-MA copolymers

IMB [AA]:[MA], мол.%	Gel fraction, %	α_{water}, g/g	$\alpha_{alcohol}$, g/g
50:50	58,3	219,75	177,13
80:20	64,2	248,05	180,25
90:10	83,5	280,89	254,30

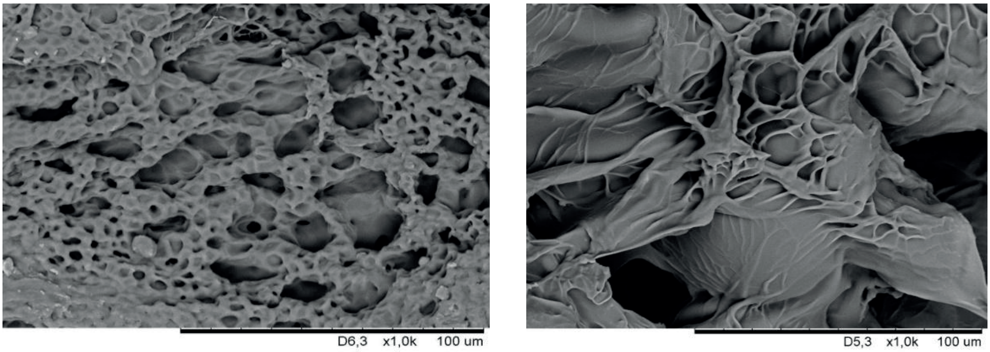
Figure 1 shows the effect of temperature on the swelling capacity of the hydrogel. As can be seen from Figure 1a, despite the presence of hydrophobic groups in the structural network of the AA-MA copolymers (50 mol.% in the initial monomer mixture), the relative volume swelling capacity V/V_0– increases with increasing temperature. This is more pronounced in an alkaline medium than in other media. This leads to additional swelling due to the ionization of carboxyl groups in the copolymer. The results obtained can be interpreted in terms of the Frenkel diffusion method. In this case, the swelling capacity of the hydrogel is determined by the thermal motion of opposite ions in the surface layer of the hydrogel at the hydrogel-solution interface of the double electric layer. After all, such a layer, on the one hand, affects the mobile ions, preventing them from leaving the volume, and on the other hand, involves the uncompensated group in the surface layer of the lattice, stretching it. The force arising here makes its "ionic" contribution to the swelling pressure. From this point of view, it is clear that an increase in the solution temperature leads to an increase in the volume of the polyelectrolyte gel, which we observed in practice (Figure 1a). When studying the effect of temperature on the swelling of the hydrogel, we observe a partial narrowing of curves 2 and 3 in Figure 1a in acidic and neutral media. This is explained by the suppression of the ionization of carboxyl groups and an increase in the hydrophobicity of the methyl groups of methyl acrylate.

With increasing MA content in the initial monomer mixture (MA, 20 mol.%), the hydrogel shrinks in acidic and neutral media (Fig. 1b, curves 1-2). In the case of transparent shielding of the double electric layer, the presence of a specific concentration of salt, the thermally induced effect associated with an increase in the hydrophobic ratio and an increase in the layer thickness compensate each other. The gel does not change its volume in a wide range of temperatures (Fig. 1b). With an increase in the molar ratio of acrylic acid in the initial monomer mixture (AA, 90 mol.%), the hydrogel swells with increasing temperature in alkaline and neutral media, despite the partial suppression of ionic effects at pH = 7 (Fig. 1b, curves 2-3), which indicates sensitivity to pH. Hydrophobic interactions that promote gel shrinkage are enhanced with increasing temperature. In the case of pronounced shielding of the double electrical layer, due to an increase in the hydrophobic coefficient in an acidic environment and an increase in the thickness of this layer, the gel shrinks significantly (Fig. 1b, curve 1).



IMB [AA-MA] = 50-50 (a); 80-20 (b);90-10 (c) mol.%; pH = 4(1); 7(2); 9(3).
Figure 1 - Dependence of swelling of copolymer hydrogels on temperature in environments with different pH.

a b



IMB [AA-MA] = 80-20 (a); 90-10 (b) mol.%.
Figure 2 - Scanning electron micrograph of the hydrogel.

To characterize the surface and cross-sectional structure of the synthesized hydrogels, the surface morphology of the network was examined by scanning electron microscope (SEM) (Fig. 2). As can be seen from the figures, it was found that with the increase of MA percentage in the copolymer, the connectivity of the network increased. The former has a uniform layered structure (Fig. 2a), and the latter has interconnected layers (Fig. 2b), that is, it contains many interlinked voids. The capillary channels, which facilitate the entry of water molecules into the hydrogel network, are clearly visible in the figures. In BMC, we can see that the network with 90 mol% MA percentage has a large number of medium-sized voids compared with the hydrogels with 80 mol% MA percentage. The hydrogel with high MA content shows a small number of interconnected voids, and the folded structure is blocked in many places (Gamze et al, 2010).

The paper presents a study of the chemical structure of the hydrogel using FTIR spectroscopy. The peak at 1734 cm^{-1} in the obtained spectra indicates the presence of a carboxyl group and proves that the hydrogel based on AA-MA = 90-10 mol.% contains AA. Chemical binding of metal complexes with polymers enables the formation of insoluble analog structures, increasing activity and selectivity due to the peculiarities of the oxidation process's mechanism and action. [8; 9] - the relationship of copolymers based on linear transition metals copper and nickel with hydroxyethyl acrylate (HEA), butyl methacrylate (BMA) and acrylic acid (AA) (HEA-BMA-AA) and BMA-AA) was studied. It was proven that complexation with water-soluble (co)polymers containing acidic functional groups in their structure with copper ions can be used to regulate thermosensitive properties effectively.

The complexing properties of AA-MA copolymer hydrogels with copper ions (Cu^{2+}) in various concentrations were investigated in the work. Complexation of AA-MA stimulus-sensitive hydrogels with copper ions was studied under conditions of changing the external environment (pH, temperature, and initial concentration of physiological solution). The change in metal ion concentration in the solution is shown in Figure 3. As shown in Figure 3, it takes 10-14 hours to achieve the equilibrium volume of the gel, and the sorption of Cu^{2+} ions in the solution ceases to change 2 hours after the start.

The inconsistency in the change in the kinetics of Cu^{2+} is explained by the peculiarities of the complexation mechanism in the stimulus-sensitive hydrogel–transition metal salt solution system. Initially, a thin layer of a metal-polymer complex with a high concentration of metal ions forms on the surface of the hydrogel, which gradually thickens. In contrast, the inner layer is now free of metal ions. Over time, metal ions enter the sample, resulting in the uniform distribution of metal ions throughout the polymer hydrogel's volume. Comparing the kinetic curves of metal ion sorption by stimuli-sensitive hydrogels and the change in sample volume, we can conclude that there are two stages in this process. The first stage corresponds to the initial section of the kinetic curve, where the concentration of metal ions decreases rapidly over time. At the second stage, the concentration of metal ions in the solution changes insignificantly.

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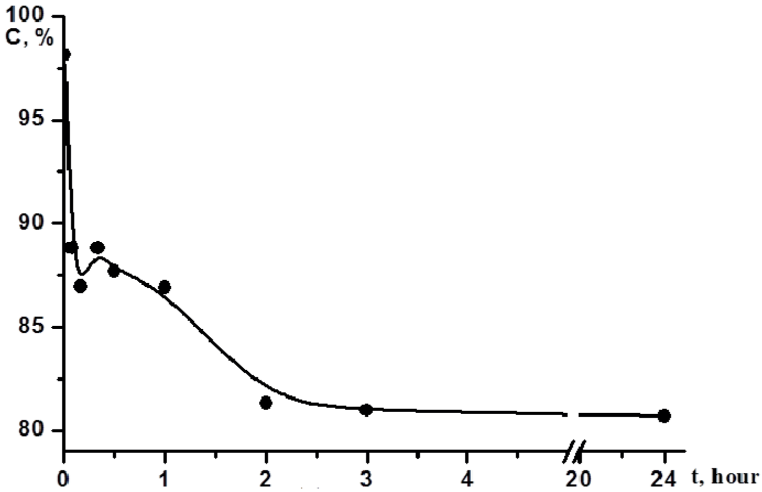
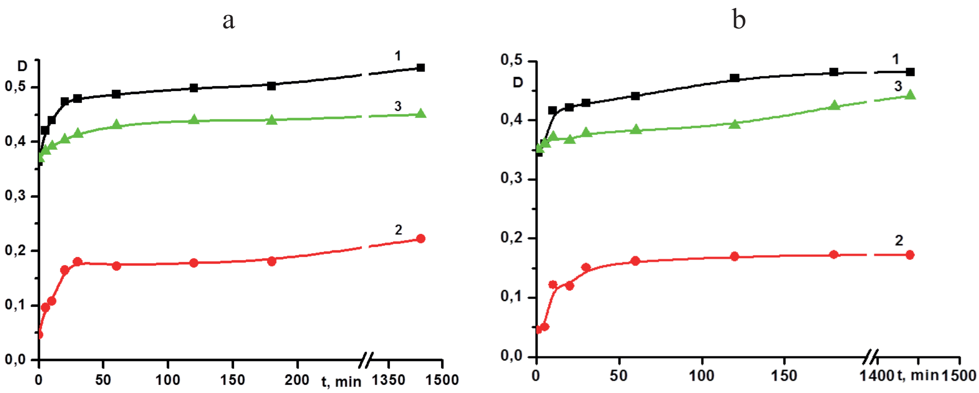
To release copper ions from the hydrogel, a [hydrogel/copper ion] complex was prepared at different copper concentrations in the polymer. Taking into account the desorption of copper (II) ions in the complex structure, the conformational movement of the stimulus-sensitive hydrogel based on AA-MA was carried out in three different pH environments (pH = 4.7.9). The rate and amplitude of desorption in acidic and alkaline environments are higher than in neutral ones, which is due to the increase in the hydrogel volume and the growth of the concentration of copper (II) ions in the solution (Figure 4a, curves 1, 2). The change in the kinetic curve during desorption is exponential. The dependence of $[Cu^{2+}]$ on time has an inverse exponential form, taking into account the logarithmic value of the ordinate. A smooth change in $[Cu^{2+}]$ and V/V_0 over time indicates a relationship between the swelling process and the release of metal ions from the sample volume. An increase in the desorption rate in an acidic environment is explained by the suppression of carboxyl group ionization and the disruption of the resulting polycomplex due to electrostatic interactions. Figure 4b shows the results of desorption in environments with different pH. As can be seen from the figure, the release of copper ions in a neutral environment is slower than in other environments.

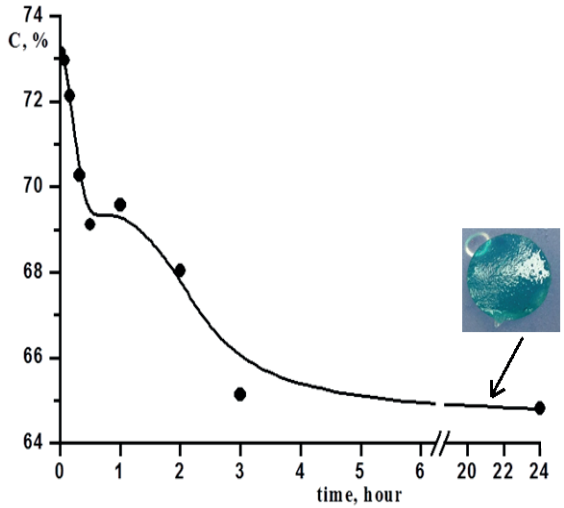


IMB [AA-MA] = 90-10 mol. %; $[Cu^{2+}] = 2.68*10^{-2}$ mol/l.
Figure 3 - Adsorption of copper ions by hydrogels based on AA-MA

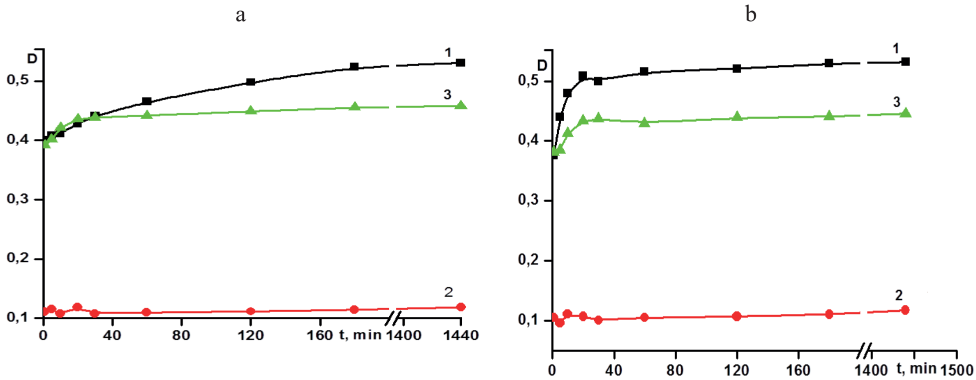


IMB [AA-MA] = 90-10 mol. %; $[Cu^{2+}] = 2.68*10^{-2}$ (a); $1.34*10^{-2}$ (b) mol/l; pH = 4(1); 7(2); 9 (3).
Figure 4 - Desorption of Cu^{2+} ions based on AA-MA

The work also shows that the sorption of copper ions in the initial monomer mixture has an AA content of 80 mol. % were studied for copolymers containing. As can be seen from Figure 5, the change in Cu^{2+} ions ($[Cu^{2+}]=1/34*10^{-2}$mol/l) in the solution ceased to change after 3 hours. In fact, it would take 10–14 hours to achieve the equilibrium volume of the gel, which we explain by the discrepancy in the change in the Cu^{2+} kinetics and the features of the complexation mechanism in the stimulus-sensitive hydrogel–transition metal salt solution system. Initially, a thin layer of metal complex-polymer with a high concentration of metal ions is formed on the surface of the hydrogel, which leads to a gradual shrinkage of the hydrogel surface, which in turn ensures free penetration of metal ions into the gel (Abdykalykova et al, 2012; Yakiyayeva et al, 2013; Zhang et al, 2021; Dong et al, 2021).



IMB [AA-MA] = 80-20 mol. %; [Cu^{2+}] = 1.34*10^{-2} mol/l.
Figure 5 - Adsorption of Cu^{2+} ions based on AA-MA



IMB [AA-MA] = 80-20 mol. %; [Cu^{2+}] = 2.68*10^{-2} (a); 1.34*10^{-2} (b) mol/l; pH = 4(1); 7(2); 9 (3).
Figure 6 - Desorption of Cu^{2+} ions based on AA-MA

Over time, the reaction spreads inside the sample, resulting in a uniform distribution of metal ions throughout the volume of the polymer hydrogel. Comparing the kinetic curves of metal ion sorption by stimuli-sensitive hydrogels and the change in sample volume, we can conclude that this process has two stages. The first stage corresponds to the initial section of the kinetic curve, where the concentration of metal ions rapidly decreases with time. In the second stage, the concentration of metal ions in the solution changes insignificantly. This is clearly seen in Figure 5. To release copper ions from the hydrogel, a [hydrogel/copper ion] complex was prepared at different copper concentrations in the polymer. Desorption of copper (II) ions from the complex structure and conformational movement of the stimulus-sensitive hydrogel based on AA-MA were carried out in three different pH environments (pH = 4.7.9). The desorption rate and amplitude were higher in acidic and alkaline media than in neutral ones, which was accompanied by an increase in the hydrogel volume and an increase in the concentration of copper(II) ions in the solution (Figure 6). The change in the kinetic curve during desorption is exponential. The dependence of [Cu^{2+}] on time has an inverse exponential form, taking into account the logarithmic value of the ordinate. The smooth change in [Cu^{2+}] and V/V_0 over time indicates a relationship between the swelling process and the release of metal ions from the sample volume. The increase in the desorption rate in an acidic medium is explained by the suppression of the ionization of carboxyl groups and the destruction of the resulting polycomplex based on electrostatics (Gokmen et al, 2021; Zhang et al, 2022; Singh et al, 2024).

Conclusion.

In this work, stimuli-responsive hydrogels based on acrylic acid (AA) and methyl acrylate (MA) were synthesized using the radical copolymerization method. The studies have shown that with an increase in the AA content and a decrease in the MA content in the initial monomer mixture, the yield of the copolymer increased (from 58.3% at 50:50 to 83.5% at 90:10) and the swelling degree became higher. The effect of temperature on the swelling ability of the hydrogels at different pH values was studied. Despite the presence of hydrophobic methyl groups, the structure of the AA-MA copolymers showed that the swelling coefficient (V/V_0) increased with temperature, especially in alkaline medium (pH 9). At the same time, partial shrinkage was observed in acidic and neutral media due to the suppression of carboxyl group ionization and the increased contribution of hydrophobic interactions from methyl acrylate.

The physicochemical behavior of AA-MA-based hydrogels in aqueous copper chloride solutions was investigated. It was found that placing dried AA-MA hydrogels in $CuCl_2$ solutions resulted in a decrease in Cu^{2+} concentration, indicating ion-exchange binding - the replacement of poly (acrylic acid) protons by copper cations and the redistribution of salts in the solution.

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