Materials Today: Proceedings xxx (xxxx) xxx

Contents lists available at ScienceDirect

Materials Today: Proceedings

journal homepage: www.elsevier.com/locate/matpr

Complex of hydrogels based on acrylic acid and methyl acrylate with copper ions

R.K. Rakhmetullayeva [a,*], M. Abutalip [f], Zh.R. Urkimbayeva [a], D.K. Kanzhigitova [a,b], R.A. Mangazbayeva [a], A.K. Naushabayev [c], N.B. Sarova [d], Zh.S. Mukatayeva [e], G.N. Zhigerbayeva [b,*]

[a] Department of Chemistry and Chemical Technology, Al-Farabi Kazakh National University, Almaty 050040, Kazakhstan
[b] Department of Chemical and Materials Engineering, School of Engineering and Digital Sciences, Nazarbayev University, Nur-Sultan 010000, Kazakhstan
[c] Department of Agrobiology, Kazakh national agrarian research university, Almaty 050010, Kazakhstan
[d] School of pharmacy, Asfendiyarov Kazakh National Medical University
[e] Department of Educational Programs, Abai Kazakh National Pedagogical University, Almaty 050010, Kazakhstan
[f] National Laboratory Astana, Nazarbayev University, Nur-Sultan 010000, Kazakhstan

ARTICLE INFO

Article history:
Available online xxxx

Keywords:
Acrylic acid
Methyl acrylate
Ionic hydrogels
Radical polymerization

ABSTRACT

At the present time, hydrogels are utilised extensively for the purpose of removing heavy metal ions from water. However, the vast majority of chemical hydrogels are harmful to the surrounding ecosystem, and the swelling behaviours of these materials have not been sufficiently researched. Herein, by radical copolymerization in solution, we synthesized acrylic acid (AA) and methyl acrylate (MA)-based stimuli-responsive hydrogels. We studied the sorption properties of hydrogels based on AA-MA and examined the influence temperature could have on the swelling behaviour of hydrogels in different pH conditions. The structure of the hydrogel was verified using Fourier-transform infrared spectroscopy (FTIR), and the process of heavy metal adsorption was investigated. The complexing characteristics of Cu (II) ions with AA-MA based hydrogels were examined at various concentrations. Before investigating the adsorption of copper ions, the impact of gels on swelling, temperature, and pH in various mediums was investigated. In two hours, the sorption of metal ions at 20% MA was 60%, but at 10% MA, the sorption of metal ions was 80–83%. Having variable thermodynamic parameters and a high absorption efficiency for Cu (II) ions, these AA-MA based hydrogels could be an effective method for removing contamination from aqueous solutions.

Selection and peer-review under responsibility of the scientific committee of the International Symposium on Emerging Materials & Device (ISEMD21).

1. Introduction

Water contamination with heavy metals has been a worldwide issue since antiquity. For instance, the primary sources of copper ions in natural waterways are chemical and metallurgical effluents, mine water, aldehyde chemicals used for algae treatment, etc [1,2].

The hazardous consequences of storage and transportation of contaminated water resources, industrial waters, and solutions with high concentrations of copper ions or extraction of copper ions have been considered in different works [3–8]. {Even at low concentrations, most heavy metal ions are very hazardous. Reverse osmosis, coagulation-flocculation, flotation, electrochemical treatment, and adsorption are currently used to remove heavy metal ions [9–13]. Adsorption remains the most popular method due to its high percentage removal, being relatively inexpensive, and adjustability. Soft-solid materials having three-dimensional network architectures, such as polymeric hydrogels, are typical examples. Recently, a novel approach for the production of efficient, and environmentally friendly, and strong physical hydrogels derived from natural polymers for the absorption of heavy metal ions was discovered [14]. Gamze Gücl et al. examined the removal of copper (II) and lead (II) ions from aqueous solutions using Starch-graft-acrylic acid/montmorillonite (S-g-AA/MMT) nanocomposite hydrogels [15]. Different parameters impacting the removal of heavy metal ions were examined for this goal, such as treatment duration with the solution, initial pH of the solution,

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* Corresponding authors.
E-mail addresses: raikhan.rakhmetullayeva@gmail.com (R.K. Rakhmetullayeva), guldana.zhigerbaeva@nu.edu.kz (G.N. Zhigerbayeva).

https://doi.org/10.1016/j.matpr.2022.07.246
2214-7853/
Selection and peer-review under responsibility of the scientific committee of the International Symposium on Emerging Materials & Device (ISEMD21).

Please cite this article as: R.K. Rakhmetullayeva, M. Abutalip, Zh.R. Urkimbayeva et al., Complex of hydrogels based on acrylic acid and methyl acrylate with copper ions, Materials Today: Proceedings, https://doi.org/10.1016/j.matpr.2022.07.246

starting metal ion concentration, as well as the MMT content. The metal ion removal capabilities of copolymers improved with pH, and pH 4 was determined to be ideal for the highest metal removal capacity. In the study of Farhad Narimani and his colleagues, superabsorbent hydrogels were synthesised using the polymerization process (acrylic acid-so-acryoil tetranatric thiocalyx- (4) arenes tetrasulfonate) in a dextrin-inoculated solution [16]. Numerous adsorbent hydrogels have been created, including N, Ndimethylacrylamide (DMAA)-based hydrogels, which have generated considerable attention owing to their reusability, repeatability of synthesis, and inexpensive price. Hydrogels revert to their original state after being released from heavy-ion metals, and reapplication for 5 h results in a 7% reduction in adsorption capacity [4].

There are evident limits to the use of hydrogels in wastewater treatment, including the development of various toxic wastes after adsorption and the complexity of removal. To solve this problem, new hydrogels based on acrylic acid (AA) and methyl acrylate (MA) were synthesised and their complex with copper ions was considered.

2. Experimental

2.1. Materials

Acrylic acid (AA) with molecular weight 72.06266 g/mol, which produced by «Sigma-Aldrich Chemie GmbH» (Germany) was used without further purification, Methyl acrylate, 99%, contains $\leq$ 100 ppm monomethyl ether hydroquinone as an inhibitor, manufactured by «Sigma-Aldrich Co.» (US), Dialysis membrane, Medical International Ltd (Liverpool Road, London), Ammonium persulfate, (99,9%, «Affymetrix», China) brand "chemically pure" is used without further purification, N, N′-Methylenebis(acrylamide) ("Sigma-Aldrich Co.," USA) brand "chemically pure" is used without further purification, Copper sulfate ("Sigma-Aldrich Co.," USA) brand "chemically pure" is used without further purification.

2.2. Synthesis of hydrogels

Copolymers based on acrylic acid (AA) and methyl acrylate (MA) were obtained by radical polymerization by substance initiation. The synthesis was carried out in alcohol-aqueous solutions in an ampoule made of molybdenum glass at a temperature of 60° C. Ampules were purged with argon for 10–15 min to release the reaction mixture from oxygen blown over time. Ammonium persulfate was used as an initiator, N, N'-methylene bisacrylamide as a sewing agent. At the end of the synthesis, the hydrogels were divided into several parts and washed with distilled water for 2 weeks to remove the monomer.

2.3. Physicochemical methods of research

The pH of the solutions was determined on a digital ionomer "781 pH / Ion Meter" ("Metrohm", Switzerland) at a temperature of 25 °C. The pH was adjusted by adding a small amount of 0.1 M hydrochloric acid and sodium hydroxide solutions.

In the case of complex reactions with heavy metals, hydrogels in the form of tablets, evenly swollen, were immersed in appropriate copper solutions at a constant temperature of 25 °C. The process of complex formation was determined by changes in the volume of hydrogels over time. The complexing process was carried out on a UV spectrophotometer, at a wavelength of 220 nm (Specord 200 Plus, Germany).

The change in the relative volume of hydrogels was estimated on the catheter B-630 (Russia) with a relative volume $\Phi = V/V_0$ depending on different pH media and temperature, where V_0 is the volume of the sample during synthesis, and V is the volume of the sample under equilibrium swelling.

The degree of equilibrium swelling of polymer hydrogels is determined by the formula:

$$a = (m - m_o)/m_o \tag{1}$$

where

m - is the equilibrium swelling mass of the polymer hydrogel, and m_0 - is the mass of the dry sample.

The mass of the dry sample was determined after drying in a vacuum cabinet until it reached a constant weight.

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

A hydrogel sample in the shape of a swollen tablet was placed in specialized cells to evaluate the effect of changes in the pH of the polymer in the medium and the effect of temperature. To explore thermodynamic collapse, 7 mm in diameter and 5–6 mm in height cylinders containing thermostatic water were filled with equally swollen polymers. Each ratio of hydrogel had a different pH (4; 7; 9) and the temperature was varied discretely every 5 °C. The sample was kept at each temperature for 30 min until a constant degree of swelling was achieved. The degree of swelling of the hydrogel was measured using catheter B-630 and the ratio V/V_0, where V is the volume of equilibrium swelling of the sample and V_0 is the volume of the hydrogel sample during synthesis.

To analyze the surface and cross-section structures of the produced hydrogels, a scanning electron microscope (SEM) was used. The cylindrical gels were freeze-dried for 24 h after reaching equilibrium swelling. The samples were subsequently vacuum-coated with gold–palladium and analyzed by SEM (JEOL JSM-840A).

3. Results and discussion

Hydrogels based on MA with AA were obtained by radical copolymerization in water. Studies have shown that AA is the most active in comparison with MA. Studies have shown that with an increasing content of MA in the initial monomer mixture there is a noticeable reduction of the yield of copolymers, indicating greater activity of AA. It is established that the process of formation of crosslinked copolymers is significantly affected by the difference in reactivity of the comonomers. As shown previously in [17,18], the structure of polymer networks formed by copolymerization of monomers, a significantly different activity is heterogeneous and contains in its composition areas of high and low density of crosslinking, which depends on the speed of three-dimensional polymerization changes of concentration of the more active monomer. In this work, the regularities established for the binary copolymerization of AA-MA are retained in the case of three-dimensional. With the increasing content of active acrylic possible co-monomer (AC) in the original formula, there was a significant increase in the yield of copolymers. Abnormal reduction of quantities for hydrogels based on the AA-MA with the increase of the content of ionogenic component AA in the starting mixture due to the increase in crosslinking with increasing concentration of the more active the possible co-monomer.

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

IMM [AA-MA] mol%	Gel fraction, %	α_{water}, Г/Г	$\alpha_{alcohol}$, Г/Г
	58.3	219.75	177.13
80:20	64.2	248.05	180.25
90:10	83.5	280.89	254.30

The yield of the copolymer increased as the acrylic acid concentration in the initial monomeric mixture (IMM) increased (Table 1). The rise in the degree of swelling (α value) in water and alcohol for hydrogels based on AA-MA is due to an increase in the percentage of ionic component AA in the initial monomer mixture as well as ionization of the carboxyl groups of AA.

Fig. 1) presents data on the effect of temperature on the swelling behavior of hydrogels. As can be seen from Fig. 1, despite the presence of hydrophobic groups in the structure of the meshes copolymers AA-MA, their swelling ratio V/V_0 increases with increasing temperature. This is noticeable in the alkaline medium in comparison with the others. The results can be interpreted from the standpoint of diffusion of the approach of Frankel [19], in which swelling of the hydrogel is determined by the properties of the electric double layer occurring on the edges of the hydrogel–solution interface due to the thermal motion of counterions leaving the surface layer of the hydrogel. The field of this layer serves on the one hand, on the mobile ions and prevents their exit from the volume occupied by a charged mesh, another uncompensated charge in the surface layer of mesh, stretching it [20–22]. The resulting force is a significant "ionic" contribution to the total pressure of swelling. From this point of view, increasing the temperature of the solution should lead to an increase in the amount of polyelectrolyte gel, which is what we observed in the experiment (Fig. 1a). In merchant and neutral environments, despite the partial inhibition of ion effects, the hydrogels of copolymers of AA-MA = 90:10 with increasing temperature also swell (Fig. 1a), indicating pH sensitivity. However, it is known that the hydrophobic interactions contributing to the compression of the gel also increase with increasing temperature. It is obvious that in an acidic environment, there is a significant shielding action of the electric double layer. The termoinduction effects associated with increased thickness of this layer and increased hydrophobic interactions mutually compensate for each other, and the gel shrinks (Fig. 1b).

With an increase in MA in the initial monomeric mixture (MA, 20 mol.%), the hydrogel contracts in an acidic and neutral medium (Fig. 1b, curves 1–2). In the case of clear shielding of the two electric layers, the presence of a certain concentration of salt replaces the effect of thermoinduction, which occurs due to an increase in hydrophobic ratio and an increase in layer thickness, and the gel does not change volume over a wide temperature range. (Fig. 1b).

As the molar ratio of acrylic acid in the initial monomer mixture increases (AA, 90 mol.%) in an alkaline and neutral medium, pH = 7, the hydrogel swells with increasing temperature, despite the partial suppression of ionic effects (Fig. 1c, curves 2–3). The hydrophobic interactions that cause the gel to shrink increase with increasing temperature. In the case of a clear shielding of the two electric layers, they are replaced by an increase in the hydrophobic ratio in an acidic medium and an increase in the thickness of this layer, and the gel significantly shrinks (Fig. 1c, curve 1).

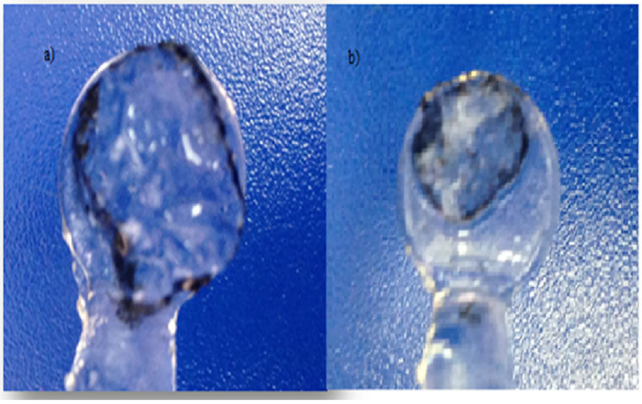


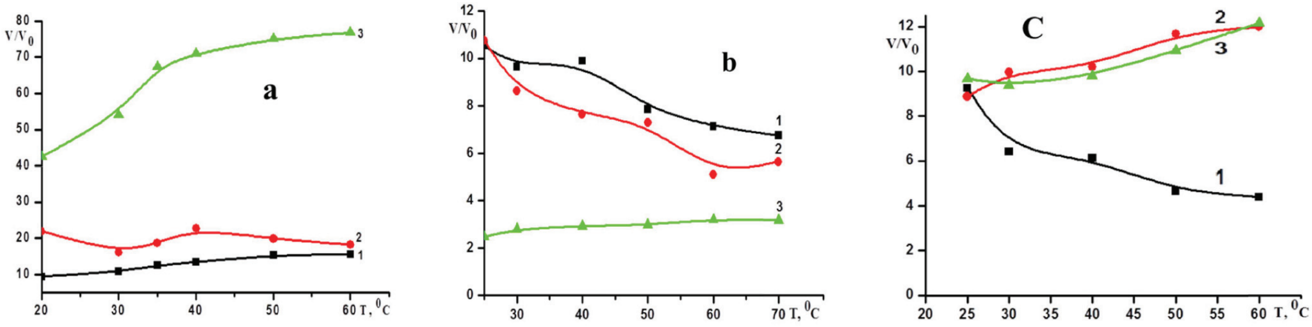
Fig. 2. The visual image of compression hydrogel in an alkaline environment at a temperature of 60 °C a) before b) after the alkali.

To understand the results of swelling of the polymer under the influence of temperature, the work was made images of changes in the volume of the hydrogel from the alkaline medium at an initial temperature of 60 °C (Fig. 2).

In this study, the temperature dependence of hydrogels on the pH of the medium with a 50% increase in the methylacrylate concentration in IMM (initial monomer mixture) was investigated (Fig. 3). Increasing the molar ratio of methyl methacrylate in the initial monomer mixture (MA, 70 mol.%) (Fig. 3a, curve 2). It is shown that the temperature dependence of the lattice structure obtained by conducting the pH of the medium in an acidic medium, the ie thermocouple, is observed with increasing temperature (Fig. 3a, curve 1).

It was discovered that when the percentage of methyl acrylate in the copolymer is reduced by 10%, i.e. MA, 60 mol.% (Fig. 3b), the temperature dependence of the relative volume of hydrogels, i.e., thermosensitivity, is an alkaline and neutral medium (Fig. 3b, curves 2–3). In an acidic environment, it is shown that the volume of the lattice increases with increasing temperature (Fig. 3b, curve 1).

The synthesized hydrogels were investigated using a scanning electron microscope (SEM) to characterize the surface and cross-section structures. The cylindrical gels reached equilibrium swelling and then were freeze-dried for 24 h. The samples were then

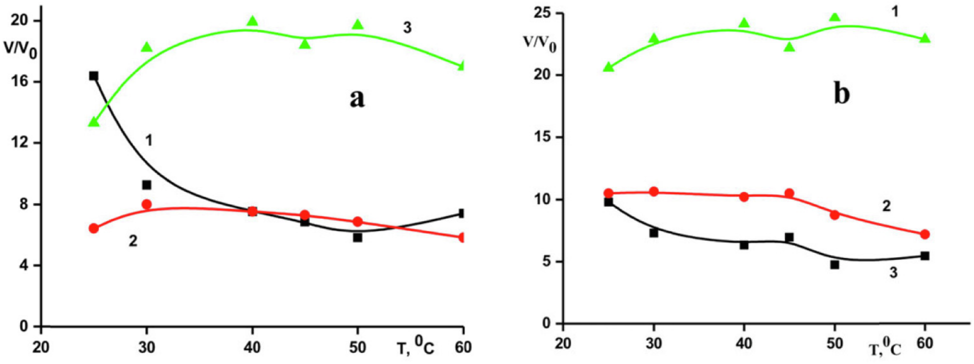


(a)IMM [AA-MA] = 50-50 mol.%.
pH = 4 (1); 7 (2); 9 (3).

(b)IMM [AA-MA] = 80-20mol.%.
pH = 4 (1); 7(2); 9(3).

(c)IMM [AA-MA] = 90-10 mol.%.
pH = 4 (1); 7 (2); 9 (3).

Fig. 1. Dependence of Temperature on swelling ratio of hydrogels at different pH environments.



(a)IMM [AA-MA] = 30-70 mol.%; pH = 4 (1); 7 (2); 9 (3).

(b)IMM [AA-MA] = 40-60 mol.%; pH = 4 (1); 7 (2); 9 (3).

Fig. 3. Dependence of Temperature on swelling ratio of hydrogels at different pH environments.

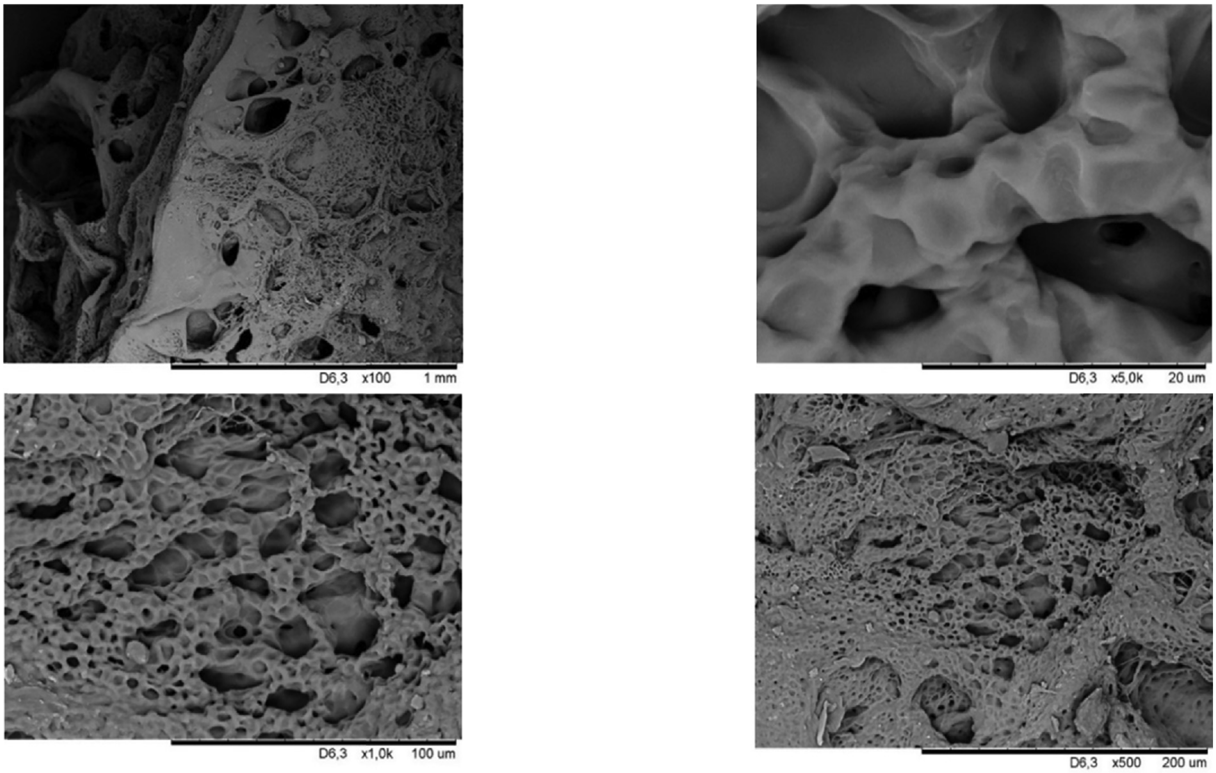


Fig. 4. SEM images of hydrogels IMM [AA-MA] = 80–20 % mol.

coated with gold–palladium under vacuum and examined in an SEM.

As seen in the figures, the compatibility of the lattice improves as the percentage of AA in the copolymer increases. The first has a consistent layered structure (Fig. 4), the second is layered and interconnected (Fig. 5), and the third has several interconnected voids. Images depict capillary tubes that permit water molecules to enter the hydrogel lattice. We discovered that the IMM contains a substantial number of medium-sized voids at a percentage of 90 mol. %, hydrogels at 80 mol. %, and the IMM at a percentage of 70 mol. %. Hydrogels with a high MA concentration have a small number of interconnected holes and a layered structure that is blocked in various places.

The chemical structure of the hydrogel was studied by the method of the IR Fourier spectrum. The obtained spectra are shown in Fig. 6 and Table 2. The peak of 1734 cm^{-1} indicates the presence of a carboxyl group and proves the presence of a hydrogel based on AA-MA = 90–10 mol.%.

The chemical bonding of metal complexes with polymers makes it possible to obtain an insoluble analog structure and increase

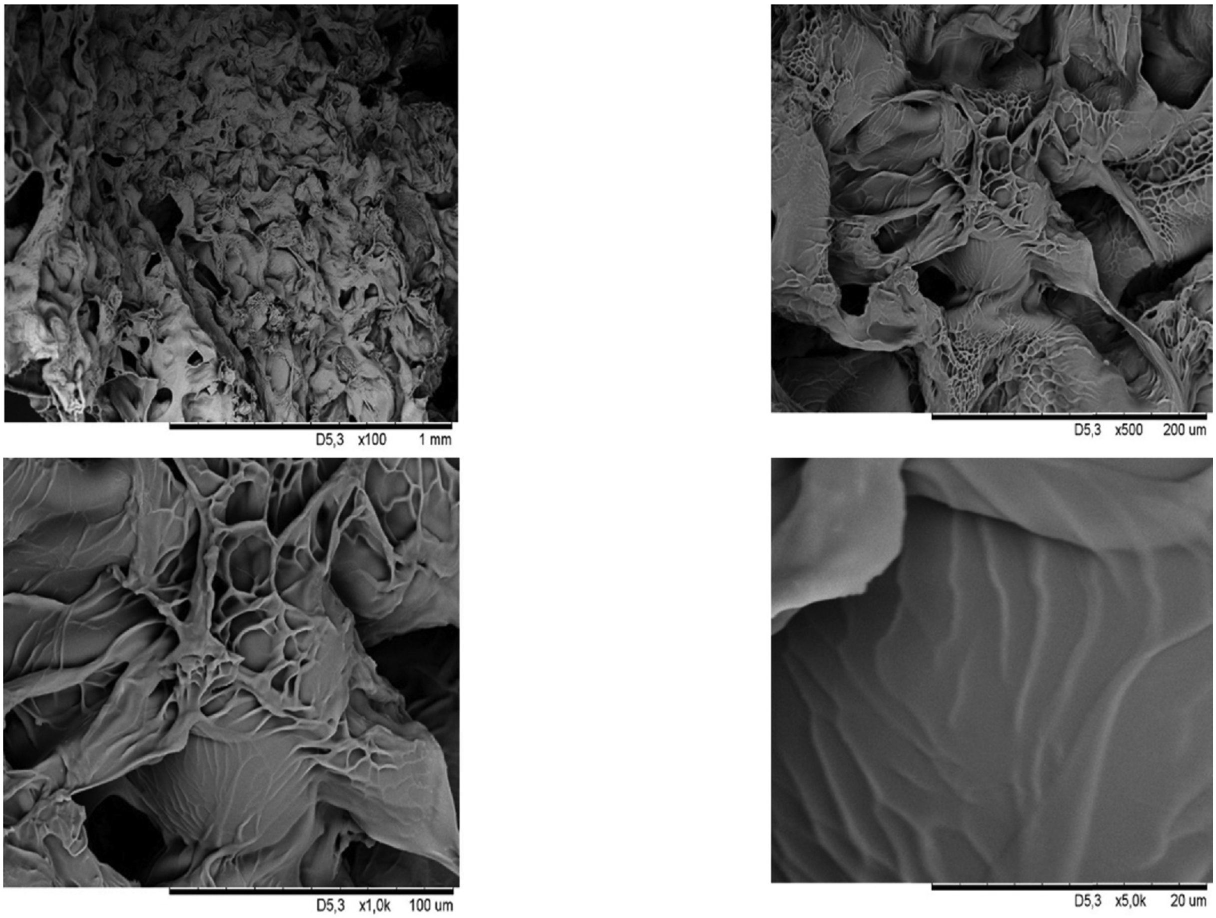


Fig. 5. SEM images of hydrogels IMM [AA-MA] = 90–10 mol.%.

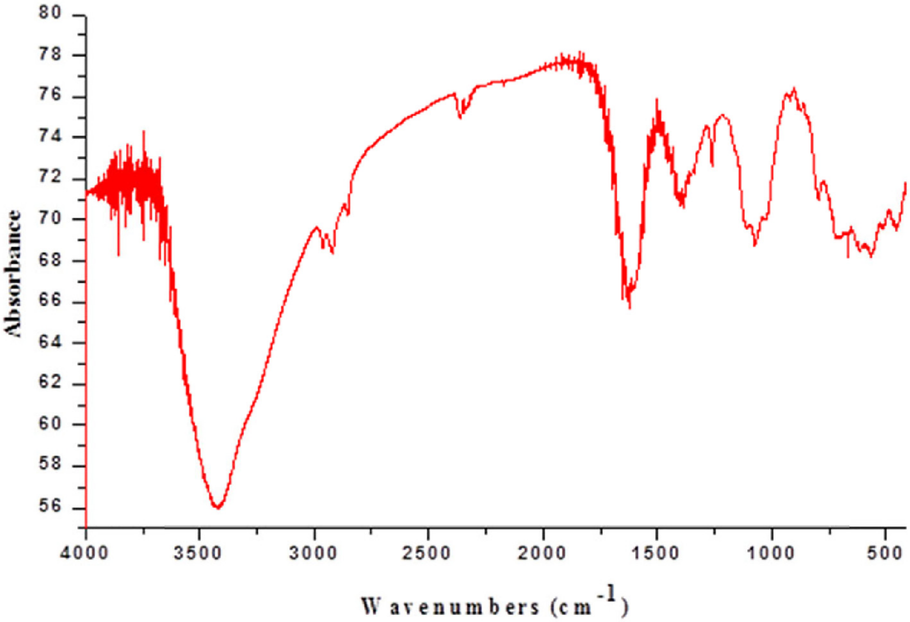


Fig. 6. FTIR spectrum of hydrogels based on AA MA = 90–10 mol.%.

activity and selectivity from the features of the mechanism and action of the oxidative process.

The interaction of polyampholyte hydrogels AA-MA in the processes of complexation with Cu^{2+} ions was studied with a change in the characteristics of the external environment (pH, tempera-

Table 2
Values of the FTIR spectrum of the hydrogel based on the AA-MA.

Functional groups	Wavelength, cm^{-1}
–COOH	1725–1700
–C = O	1633
–OH	3450–3300
$–CH_2$-	2919, 1450–1300

ture, initial concentration of the salt solution). The change in the concentration of metal ions in solution is shown in Fig. 7a.

As you can see in Fig. 7a, it takes 10–14 h for the gel to reach equilibrium, and the change in Cu^{2+} ion stopped 2 h after the start of sorption in solution. Such incompatibility with changes in the kinetics of Cu^{2+} is explained by the peculiarities of the mechanism of complex formation in the system of stimulus-sensitive hydrogel-transition metal saline solution. Initially, a thin layer of high-concentration metal-polymer complex of metal ions is formed and gradually thickens on the surface of the hydrogel, while the inner layer is free of metal ions. Over time, metal ions penetrate the sample, because of which the metal ions are evenly distributed throughout the polymer hydrogel. When comparing the kinetic curves of the sorption of metal ions with stimulus-sensitive hydrogels and changes in the volume of the sample, it can be concluded that there are two stages in the process.

The first stage corresponds to the initial section of the kinetic curve, where the concentration of metal ions in the solution rapidly decreases with time (almost linearly). In the second stage, the concentration of metal ions in the solution changes insignificantly, but the swelling of the hydrogel continues.

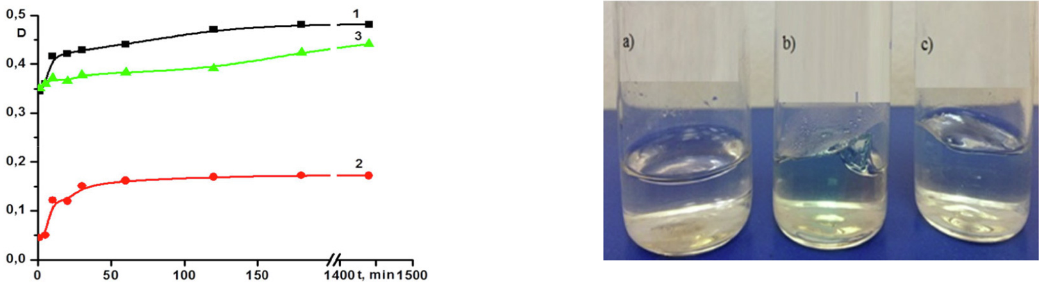
For the release of copper ions from the hydrogel, a complex [hydrogel/copper ion] was obtained at different concentrations of copper in the polymer. The desorption of copper (II) ions in the structure of the complex was carried out in three different pH media (pH = 4,7, and 9), considering the conformational motion of the stimulus-sensitive hydrogel based on AA-MA. The rate and amplitude of desorption were observed to be faster in acidic and alkaline media than in neutral media, which was determined by an increase in the volume of hydrogel and an increase in the concentration of copper (II) ions in solution (Fig. 7b, 7c, curves 1, 2). Changes in the kinetic curve during desorption show exponential properties. The time dependence $[Cu^{2+}]$ indicates the inverse of the exponent, considering the logarithmic value of the ordinate. The uniform change in time $[Cu^{2+}]$ and V/V_0 indicates the ratio of the swelling process and the release of metal ions from the sample volume.

The increase in the rate of desorption in acidic media is explained by the suppression of ionization of carboxyl groups and the destruction of the polycomplex formed based on electrostatics. In addition, the research demonstrates that the sorption of copper ions in the initial monomeric mixture contains 80 mol.% of AA. As depicted in Fig. 8a. the change in the concentration of Cu^{2+} ions in the solution ($[Cu^{2+}]$ = 1.34 · 10^{-2}mol/l) ceased after three hours. Due to the peculiarities of the mechanism of complex formation in the system of stimulus-sensitive hydrogel-transition metal saline solution, it would really take 10 to 14 h for the gel to achieve equilibrium volume. This is explained by the disparity in the change in the kinetics of Cu^{2+}. Initially, a high concentration of metal ions on the surface of the hydrogel generates a thin layer of metal complex-polymer, which leads to a progressive contraction of the hydrogel surface, thereby allowing metal ions to freely penetrate the gel.

Over time, the reaction spreads throughout the sample, resulting in an equitable distribution of metal ions throughout the whole volume of the polymer hydrogel. Comparing the kinetic curves of metal ion sorption with stimulus-sensitive hydrogels and sample volume changes leads to the conclusion that the process consists of two steps. In the first stage, the concentration of metal ions corresponds to the initial portion of the kinetic curve, which declines extremely rapidly over time. The concentration of metal ions in

(a)IMM [AA-MA] = 90–10 mol.%; C(Cu^{2+}) = 2.68·10^{-2} mol/L

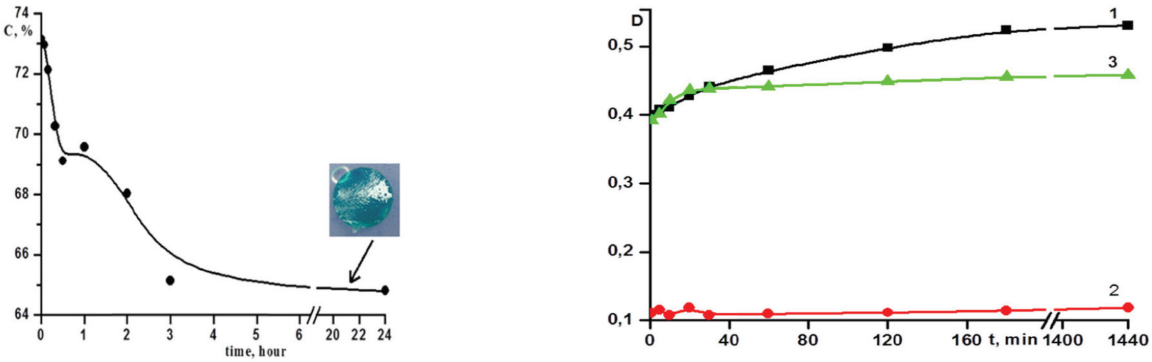
(b)IMM [AA-MA] = 90-10 mol.%; C(Cu^{2+}) = 2.68·10^{-2} mol/L
pH = 4 (1); 7 (2); 9 (3).



(c)IMM [AA-MA] = 90–10 mol. %; $[Cu^{2+}]$ = 1.34·10^{-2} mol / L; pH = 4(1); 7(2); 9 (3).

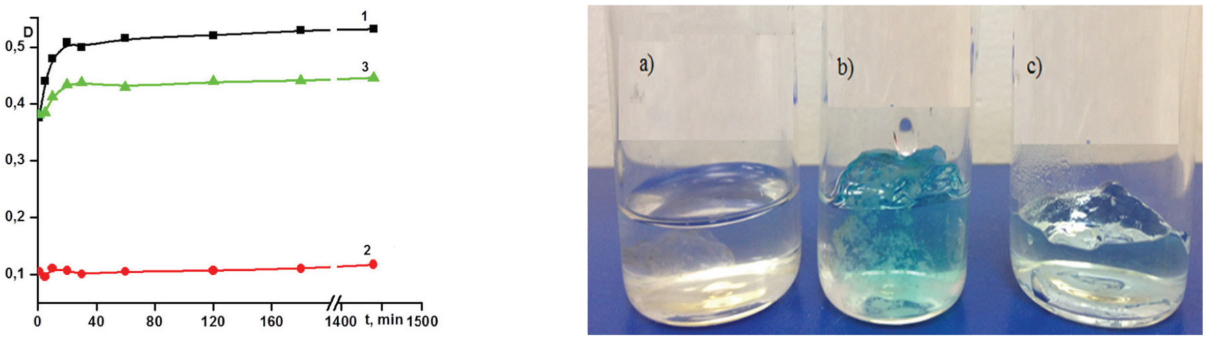
(d)Visual desorption of hydrogel IMM [AA-MA] = 90-10. pH = 4 (a); 7 (b); 9 (c).

Fig. 7. Adsorption (a), Desorption (b) and (c) Desorption of Cu^{2+} ions from solution by hydrogel and (d) experimental picture of hydrogel.



(a)IMM [AA-MA] = 80-20 mol.%; C(Cu^{2+}) = $1.34\cdot10^{-2}$ mol/L

(b)IMM [AA-MA] = 80-20 mol.%; C(Cu^{2+}) = $2.68\cdot10^{-2}$ mol/L
pH = 4 (1); 7 (2); 9 (3).



(c)IMM [AA-MA] = 80-20 mol.%.
C(Cu^{2+}) = $1,34\cdot10^{-2}$ mol/L
pH = 4 (1); 7 (2); 9 (3)

(d)Visual desorption of hydrogel IMM [AA-MA] = 80-20 mol.%.
pH = 4 (a); 7 (b); 9 (c).

Fig. 8. Adsorption (a) and Desorption (b, c) of Cu^{2+} ions from solution by hydrogel and (d) experimental picture of hydrogel.

the solution varies minimally throughout the second stage and Fig. 8a. illustrates this clearly.

At different copper concentrations in the polymer, a complex [hydrogel/copper ion] was produced for the release of copper ions from the hydrogel. Copper (II) ions were desorbed from the structure of the complex in three different pH media (pH = 4,7, and 9), considering the conformational motion of the stimulus-sensitive hydrogel based on AA-MA. It was discovered that the rate and amplitude of desorption are faster in acidic and alkaline media than in neutral media, which is accompanied by an increase in hydrogel volume and an increase in the concentration of copper (II) ions in solution (Fig. 8b, 8c). The time dependence [Cu^{2+}] represents the inverse of the exponent when the logarithmic value of the ordinate is considered. The ratio of the swelling process and the release of metal ions from the sample volume is indicated by the uniform change in time [Cu^{2+}] and V/V_0. The increase in the rate of desorption in acidic conditions can be explained by the suppression of carboxyl group ionization and the destruction of the electrostatically formed polycomplex. Fig. 8d. displays the outcomes of desorption in various pH media. In a neutral medium, copper ions are released at a slower rate than in any other medium.

4. Conclusion

In conclusion, we have successfully synthesized stimuli-responsive hydrogels based on methyl acrylate (MA) and acrylic acid (AA) by a method using radical copolymerization. The FTIR analyses confirmed the existence of an AA-MA-based hydrogel. Studies have indicated that the yield of copolymer decreases as the amount of MA in the initial monomer combination increases. The influence of temperature on the ability of the hydrogel to swell was tested. Despite the presence of hydrophobic groups, the structure of AA-MA copolymers demonstrates that the swelling coefficient V/V_0 increases as the temperature rises. With the suppression of ionization of carboxyl groups in acidic and neutral media and the increase in the hydrophobic ratio of methyl groups in methyl acrylate, a partial contraction was seen while examining the influence of temperature on the swelling ability of the hydrogel. Physicochemical characteristics of AA-MA-based hydrogels in aqueous copper chloride solutions were discovered. It has been demonstrated that the application of AA-MA copolymer hydrogels in an aqueous solution of copper chloride reduces the concentration of heavy metals. This indicates that the protons of polyacrylic acid are exchanged for copper cations, resulting in a redistribution of the salt concentration in the solution.

CRediT authorship contribution statement

R.K. Rakhmetullayeva: Conceptualization, Methodology, Writing – review & editing, Data curation, Supervision. **M. Abutalip:** Conceptualization, Writing – review & editing, Supervision, Visualization, Investigation. **Zh.R. Urkimbayeva:** Data curation, Visualization, Investigation. **D.K. Kanzhigitova:** Writing – original draft, Visualization, Investigation. **R.A. Mangazbayeva:** Conceptualization, Methodology, Supervision. **A.X. Naushabayev:** Visualization, Investigation, Methodology, Supervision. **N.B. Sarova:** Data curation, Supervision. **Zh.S. Mukatayeva:** Visualization, Investigation. **G.N. Zhigerbayeva:** Visualization, Investigation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The work was carried out with the financial support of the Ministry of Education and Science of the Republic of Kazakhstan (grant no. AP09058420).

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