

New poly(*N*- δ -acryloyl ornithine) gels cross-linked with *N,N'*-methylenebisacrylamide. Sorption properties

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ABSTRACT

To make a polymer from ornithine the acryloyl group was added to δ -amino group of the amino acid and *N*- δ -acryloyl ornithine was polymerized. The presence of α -amino acid groups attached to the polymeric network of the gels enables the complexation of some di- and trivalent metal cations. Copper ions, which can form two complexes of different stoichiometry (1:1 and 1:2) with amino acids, were used to investigate the influence of the complexation process on the swelling behavior and sorption properties of the obtained gels. The swelling ratio decreased as copper ion concentration increased. The poly(*N*- δ -acryloyl ornithine) gel was most sensitive to the copper ions in the concentration range of 1–100 mg/mL. The obtained UV–Vis spectra indicated that the copper ions mainly formed complexes of stoichiometry 1:2 with the α -amino acid group. Copper ion uptake was found to exceed 94% in a wide pH range (4–10). The maximum sorption capacity calculated by applying the Langmuir equation was 18.0 mg/g. Kinetic data showed that the sorption process reached equilibrium within 30 min and indicated the importance of the intraparticle diffusion step.

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1. Introduction

Polymeric hydrogels are cross-linked hydrophilic polymer networks filled with an aqueous solution. The properties of these materials are determined by the chemical composition of the polymeric network. Both the frame and the attached functional groups play an important role here. An interesting feature of the polymeric hydrogels, which is extensively studied by a number of groups, is their ability to undergo a drastic change in volume due to a variation in the environmental conditions. It is known that changes in such environmental factors as the presence of specific ions [1–3], temperature [4–6] and pH [7–9] can induce drastic changes in the state of the swollen polymer network. The networks of pH-, temperature- and ion-sensitive gels contain ionizable groups, hydrophobic groups and groups able to complex specific ions, respectively.

Because of their sensitivity to the presence of specific ions, these polymeric hydrogels have been investigated as possible materials for sensors, swing absorbers and molecular recognizers [10–15]. The ability to complex metal ions makes polymeric hydrogels also very attractive as metal adsorbents.

The need for efficient methods of removing some metal ions from solutions is a matter of concern because of their toxicities in relatively low concentration and their tendency towards bio-accumulation [16]. Among several conventional methods used for this purpose, the most common method involves sorption of heavy metal ions onto various solid supports (ion exchange resins, carbon-based sorbent, zeolites, ion chelating agents immobilized on inorganic supports and appropriately modified polymeric gels) because the employed sorbent can be easily regenerated [17–19]. Moreover, solid sorbents can be easily incorporated into an automated analytical procedure for preconcentration and determination of trace metal ions in natural waters [20]. Thus, increasing research efforts have been seeking to synthesize new effective sorbents.

Polymeric-gel sorbent materials usually incorporate various metal-complexing ligands including carboxyl, sulfonic, amide, pyridine, thiol, crown ether and other groups [21–30]. However, there has been no report on polymeric gels with unmodified α -amino acid groups. It is known that natural amino acids can form sufficiently strong complexes with some metal ions and are therefore important low-molecular-weight ligands in biological systems [31,32]. However, when amino acids form natural polymers (e.g. peptides), the α -amino and carboxylate groups are usually bound directly together and lose their ability to complex metal ions. Similarly, synthetic polymers with added amino acids

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cannot efficiently bind metal ions due to the way those groups are attached to the polymeric chains (α -amino acid groups are directly bound to the string) [33–35].

Recently, we have reported on new copolymer gels based on two monomers: *N*-isopropylacrylamide and appropriately modified amino acids [4,36]. The presence of free amino and carboxylic groups in those polymers yielded a possibility to control the charge sign and the excess of charge in the polymeric network as a function of pH. The gels showed an interesting swelling behavior in response to changes in temperature, pH and concentration of divalent metal ions. In this work we used only ornithine appropriately modified with the acrylic group. The polymeric gels were obtained by free radical polymerization and the cross-linking agent was *N,N'*-methylenebisacrylamide. As a result the free α -amino acid groups were present along the entire polymeric network of the gels. This gave us a possibility to form, with a high efficiency, relatively strong complexes of metal ions with these polymeric chains. The influence of the formed complexes of copper ions within the polymeric network on the sorption properties and the swelling behavior of the new poly(*N*- δ -acryloyl ornithine) gels was investigated.

2. Experimental section

2.1. Materials

Polymer constituents *N,N'*-methylenebisacrylamide (BIS, 99%) and ammonium persulphate (APS, 99.99%) were purchased from Aldrich, and *N*- δ -acryloyl ornithine was synthesized. The reagents for the synthesis of δ -acryloyl derivative of ornithine: L-ornithine monohydrochloride salt (99%) and acryloyl chloride (96%) were purchased from Aldrich and Fluka, respectively. Thioacetamide ($\geq 99\%$), sodium hydroxide (NaOH, 99%), copper (II) sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 98%), acetic acid (CH_3COOH , $\geq 99.5\%$), sodium hydroxide (NaOH, $\geq 98\%$) and nitric acid (HNO_3 , 65%) were purchased from POCH (Poland). All chemicals were used as received. All solutions were prepared using high-purity water from a Milli-Q Plus/Millipore purification system (conductivity of water: $0.056 \mu\text{S cm}^{-1}$).

2.2. Synthesis of *N*- δ -acryloyl derivative of ornithine (AcOrn)

2.2.1. Synthesis of *N*- δ -acryloyl ornithine copper complex

To a solution of NaOH (2.35 g, 58.7 mmol, in water 55 ml), L-ornithine monohydrochloride (5 g, 29.6 mmol) was added. Next, a solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (3.75 g, 15 mmol, in 55 ml of water) was added and the resulting deep blue solution was cooled to 10°C . Acryloyl chloride (3 ml, 37.5 mmol) and 2 M NaOH (15 ml) were simultaneously added

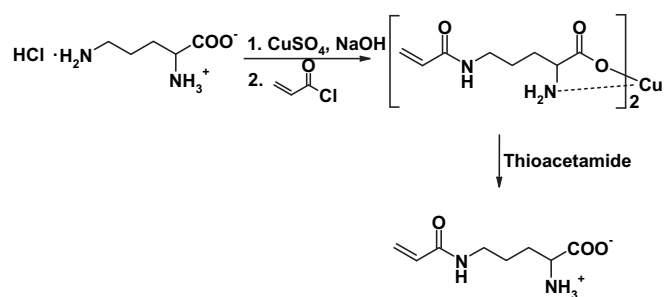


Fig. 1. Scheme of synthesis of *N*- δ -acryloyl ornithine.

dropwise, maintaining the pH at 9–10. The addition was complete after ca. 30 min. The reaction mixture was allowed to reach room temperature and was stirred overnight. The blue precipitate was filtered and washed successively with water (50 ml), ethanol (50 ml \times 2) and diethyl ether (50 ml \times 2). The precipitate was air dried for 24 h. The preparation yield was 4 g of the complex.

The synthesis of *N*- δ -acryloyl ornithine and the way of ensuring its purity were recently reported [36]. To improve upon that procedure and to avoid the chromatographic separation of *N*- δ -acryloyl ornithine from the EDTA–Cu complex, thioacetamide was employed to remove copper from *N*- δ -acryloyl ornithine copper complex.

2.2.2. Synthesis of *N*- δ -acryloyl ornithine

To a stirred suspension of *N*- δ -acryloyl ornithine copper complex (1 g, 2.3 mmol) in water (25 ml), thioacetamide was added (187.5 mg, 2.5 mmol). After stirring the mixture for 20 min, pH was adjusted to 9 and the copper sulfide precipitate was filtered through a celite pad, giving a colorless filtrate. The water was evaporated and the residue was dissolved in a 2% solution of CF_3COOH in MeOH and later precipitated with Et_2O . The crude product was recrystallized from MeOH/ Et_2O to yield 700 mg of white powder. The scheme of *N*- δ -acryloyl ornithine synthesis is shown in Fig. 1.

MS $[\text{M} + \text{H}]^+$ 187.1. $^1\text{H NMR}$ (500 MHz, D_2O): δ 6.19–6.33 (m; 2H; vinyl), 5.79 (dd; $J = 10 \text{ Hz}$, $J = 1.5 \text{ Hz}$; 1H; vinyl), 3.79 (t; $J = 6.25 \text{ Hz}$; 1H), 3.30–3.40 (m; 2H), 1.86–1.98 (m; 2H), 1.59–1.75 (m, 2H). $^{13}\text{C NMR}$ (50 MHz, D_2O): δ 177.20, 171.25, 132.60, 129.86, 57.11, 41.40, 30.53, 26.91.

2.3. Synthesis of poly(*N*- δ -acryloyl ornithine) (poly(AcOrn)) hydrogels

Appropriate amounts of AcOrn and BIS were dissolved in deionized water. The total residue concentration was fixed at

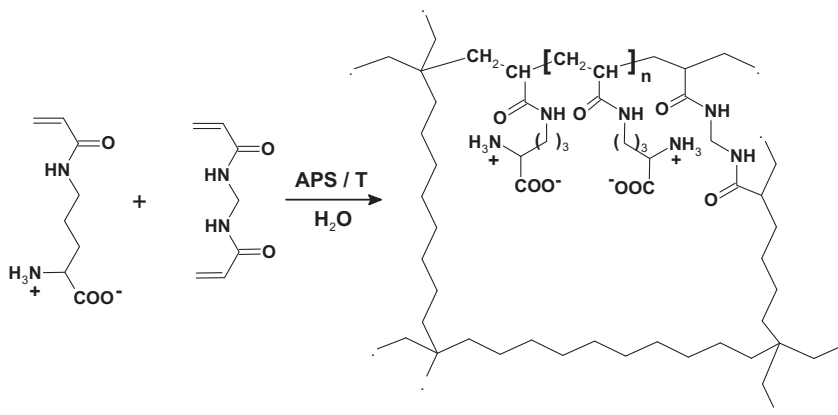


Fig. 2. Scheme of synthesis and structure of gel based on poly(*N*- δ -acryloyl ornithine) lightly cross-linked with *N,N'*-methylenebisacrylamide.

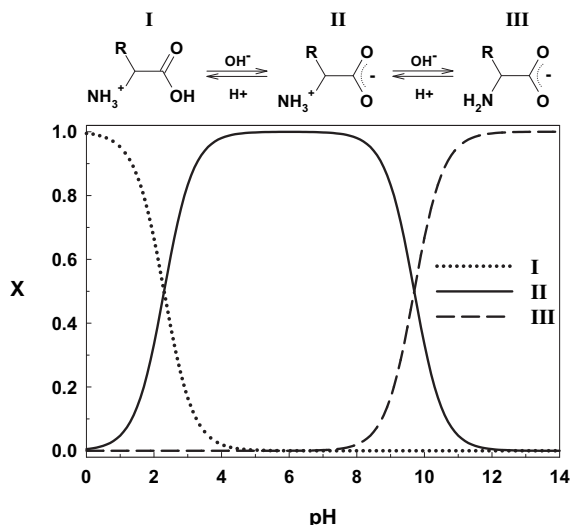


Fig. 3. Calculated distribution of three forms of amino acid group as a function of pH. $pK_{a1} = 2.36$, $pK_{a2} = 9.60$.

700 mM. The polymerization was initiated by ammonium persulfate and carried out at 70 °C for 2 h. The mole ratio of AcOrn and BIS in the pregelation solution equaled 99:1. The gels were synthesized in Teflon pipes of inner diameter 1.10 mm and in bulk. After the polymerization process the gels were immersed into a large amount of deionized water for 1 week to wash away the excess of residual chemicals. During the washing time, the water was exchanged several times. Then the synthesized gels in bulk were dried gently at approximately 60 °C to constant mass and then grounded. Gel rods obtained in Teflon pipes were conditioned in acetate buffer at pH 5. The scheme of synthesis and structure of poly(*N*- δ -acryloyl ornithine) cross-linked with *N,N'*-methylenebisacrylamide is shown in Fig. 2.

2.4. Measurement of swelling ratio of gel rods

The purified rod-shaped gel samples were inserted into a water-jacketed cell filled with acetate buffer at pH 5. The changes in the gel volume, caused by changes in concentration of Cu^{2+} , were determined from the changes in sample diameter. The latter were determined using an inverted optical microscope (Olympus, model PME 3) equipped with a calibrated scale. During the experiments, temperature was controlled at 20 °C using a refrigerated circulator (Polysta, Cole Parmer). The swelling ratio for the rod-shaped gels is

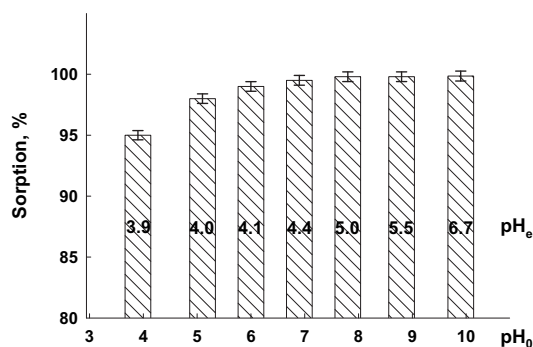


Fig. 4. Influence of initial pH (pH_0) of solution on sorption of Cu^{2+} by p(AcOrn) gel. Final pH (pH_e) of investigated solutions is shown as numbers in bars. Initial metal concentration: 10 mg/L; sorbent dose: 50 mg/10 mL.

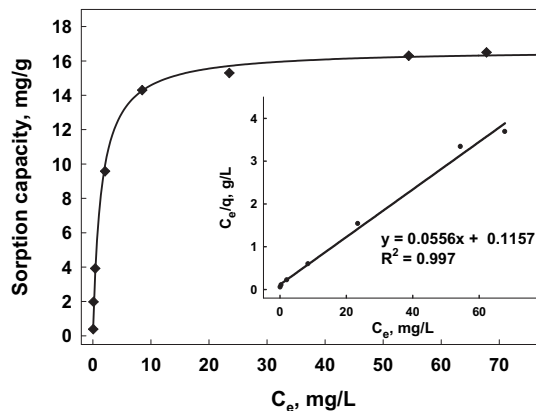


Fig. 5. Sorption isotherm of Cu^{2+} . Experimental conditions: $C_0 = 2 \div 200$ mg/L; $\text{pH} = 5$; sorbent dose: 50 mg/10 mL. Inset: plot of C_e/q_e against C_e .

usually defined as $V/V_0 = (l/l_0)(d/d_0)^2$, where V and V_0 represent the equilibrium volume of the hydrogel and the initial gel volume, d and l are the diameter and the length of the gel rod, and d_0 and l_0 denote the diameter and the length of the capillary in which the gel was synthesized, respectively. Since the determination of l was troublesome (the ends of the gel rods were not well defined), the following approximation for the calculation of the swelling ratio was employed: $V/V_0 = (d/d_0)^3$. The precision of the measurement of the diameter of the gel rods was better than 3%.

2.5. Examination of copper sorption

A sample of Cu^{2+} solution (10 mL, 10 mg/L) was placed in a glass bottle with a stopper and pH was adjusted to one of the prescribed values using either HNO_3 or NaOH . 50 mg of the adsorbing material was added to the bottle and the mixture was gently shaken for 2 h at room temperature. The supernatant was then decanted and the amount of metal ions remaining in the solution was determined by atomic absorption spectrometry. The efficiency of sorption of copper ions was calculated as the difference between the initial and final Cu^{2+} concentrations at equilibrium. The results are based on at least three replicate measurements for each pH value.

To estimate the sorption capacity, 50 mg of dry polymer was mixed with 10 mL of metal ion solution (pH 5.0, concentration range 2 \div 200 mg/L). The mixtures were shaken for 2 h; then the metal concentration in the aqueous solutions was determined by atomic absorption spectrophotometry. The sorption capacity q_e (mg/g) was estimated as follows: $q_e = [(C_0 - C_e)V]/m$; where C_0 and C_e are the initial and equilibrium concentrations (mg/L) of metal ion in the aqueous solution, respectively, V is the volume of the metal ion solution and m is the weight of the sorbent.

Table 1
Comparison of copper sorption capacity of selected sorbents.

Sorbent	Sorption capacity (mg of Cu^{2+} /g)	pH	Reference
Carbon nanotubes	3.49	9	[40]
Iron-based magnetic nanoparticles with polyacrylic acid	12.7	9	[41]
Imprinted polymethacrylic microbeads with 4-(2-pyridylazo) resorcinol	2.37	7	[42]
Poly(<i>N</i> -vinyl-2-pyrrolidone/acrylic acid) gel	1.28	8	[43]
Poly(2-acrylamido-2-methyl-1-propanesulfonic acid) gel	75.0	6	[23]
Poly(glycidyl methacrylate-glycine) gel	77.5	5	[26]
Poly(acrylamide-co-4-vinylpyridine) gel	20.1	4	[28]
Poly(<i>N</i> - δ -acryloyl ornithine) gel	18.0	5	This work

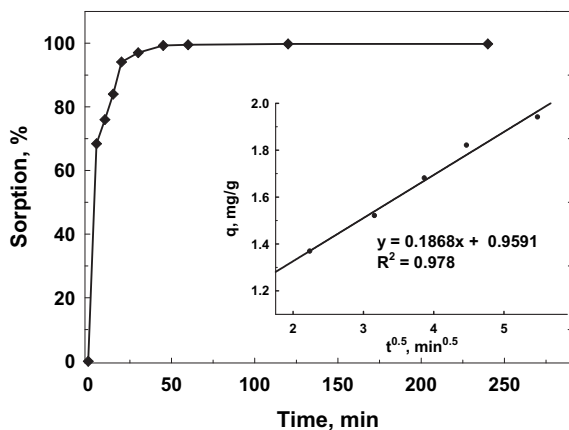


Fig. 6. Dependence of sorption vs. time for Cu^{2+} (initial metal concentration: 10 mg/L, pH = 5). Inset: Weber–Morris plot.

Kinetic studies of the sorption process were conducted with a 50 mg sample of the polymer placed in a 10 mL solution containing the copper ions (10 mg/L) and acetate buffer (0.1 mol/L, pH 5.0). The solution phase was sampled after various time intervals and the metal ion concentration was determined.

3. Results and discussion

3.1. Effect of pH on sorption

The pH of the solution affects the structure of the sorbent as well as the hydrolysis, complexation and precipitation processes of metal ions. The amino acid groups built into the polymeric network of the investigated gel can exist in three forms: as a cation (I), as a neutral form (zwitterions, II) and as an anion (III). The molar fraction of each form (x_I , x_{II} , x_{III}) can be calculated using the following equations:

$$\frac{1}{x_I} = 1 + \frac{K_{a1}}{[H_3O^+]} + \frac{K_{a1}K_{a2}}{[H_3O^+]^2}, \quad \frac{1}{x_{II}} = \frac{[H_3O^+]}{K_{a1}} + 1 + \frac{K_{a2}}{[H_3O^+]},$$

$$\frac{1}{x_{III}} = \frac{[H_3O^+]^2}{K_{a1}K_{a2}} + \frac{[H_3O^+]}{K_{a2}} + 1$$

where dissociation constants K_{a1} and K_{a2} are related to the following equilibria:

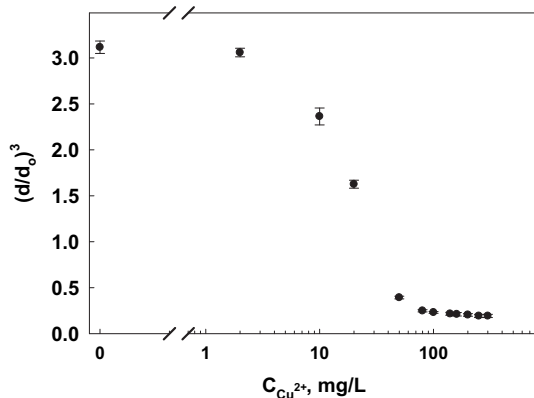


Fig. 7. Influence of concentration of copper ions on swelling ratio of poly(AcOrn) gel.

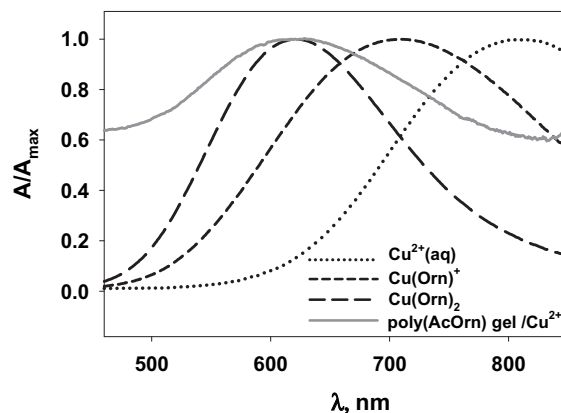
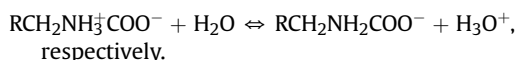
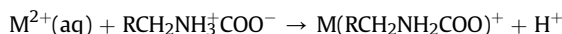


Fig. 8. UV–Vis spectra recorded in aqueous solution: free copper ions (dotted line), copper ions complexed 1:1 by ornithine (short dashed line), copper ions complexed 1:2 (long dashed line), and copper ions complexed by poly(AcOrn) gel (solid grey line).



The distribution of each form, as a function of pH, is presented in Fig. 3. The values of the dissociation constants of the unbound aliphatic amino acid (leucine) were used: $\text{p}K_{a1} = 2.36$, $\text{p}K_{a2} = 9.60$ [37]. The plots shown in Fig. 3 indicate that in a wide pH range, from 4.5 to 7.5, the dominated form of ornithine is the neutral one. For polyelectrolyte p(AcOrn) gel the pH range of domination of zwitter ionic species should be wider due to self stabilization related to the Coulombic attractions between the positive and negative charges along the polymer backbone. The neutral, zwitter ionic species can form relatively stable complexes with some divalent metal ions [31,32]. Two complexes of different stoichiometry (1:1 and 1:2) can be formed:



In a more basic medium the formation of complexes with deprotonated form III should be preferred; however, then the metal ion may precipitate as the hydroxide. On the other hand, in a more acidic pH medium, when the free metal ions exist in the aqueous solution the functional groups of the polymeric network of the gel are protonated (form I) and the complexation process is not possible. Copper ions were used to investigate the sorption properties and influence of the complexation process on the swelling behavior of the obtained gels.

The effects of initial pH on the sorption of Cu^{2+} and variation of pH due to the sorption process were investigated in a pH range of $3.9 \div 9.9$. As it can be seen in Fig. 4 the copper ions were quantitatively sorbed in the studied pH range; even in a slightly acidic medium the retention of copper exceeded 94% of its initial content. Additionally, pH of the solutions decreases significantly due to the release of H^+ during the complexation process. The above conditions are very suitable for the retention and preconcentration of dissolved copper from natural water and wastewater samples at their original pH without any pretreatment. Moreover, this should enable the separation of copper from magnesium and calcium ions, which have much lower affinity towards this type of sorbent [18].

3.2. Sorption capacity

Sorption capacity is an important factor because it determines the amount of sorbent, which is required for the quantitative

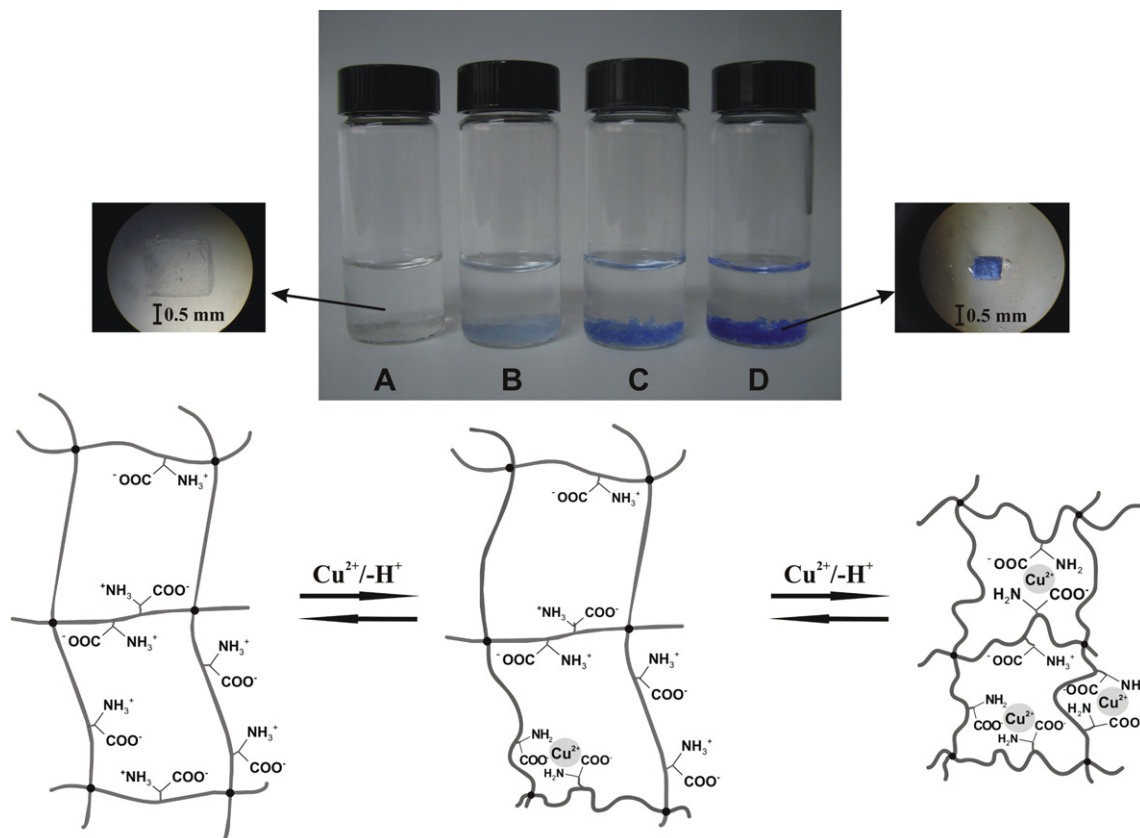


Fig. 9. Picture of vials with p(AcOrn) gel (dry mass of polymer: 50 mg) placed in 10 ml of acetate buffer (pH = 5). Concentration of copper ions: 0 (A), 20 (B), 80 (C) and 200 mg/ml (D). Scheme of formation of complexes between the gel and copper ions and the shrinking process is shown below the vials picture. The real scale of shrinking is shown by two pictures of the gel samples located left and right of vials.

enrichment of trace analyte from the examined solution. In the study of sorption capacity it is assumed that the Langmuir isotherm describes the adsorption equilibrium (the polymer chains can be covered by only a monolayer of adsorbate and there is no subsequent interaction between the adsorbed and dissolved molecules) [33,38,39]. The expression for the Langmuir isotherm is:

$$q = q_m \frac{K_L C_e}{1 + K_L C_e}$$

where q is the amount of Cu^{2+} adsorbed per gram of adsorbent (mg/g); C_e denotes the equilibrium concentration of the metal ions in the solution (mg/L); q_m is the theoretical saturation capacity of the monolayer (mg/g) and K_L represents the Langmuir constant (L/mg) that is related to the affinity of the binding sites. The values of q_m and K_L could be calculated from the intercept and slope of the linear plot of C_e/q vs. C_e . Fig. 5 shows the dependence between the metal ion equilibrium concentration and the amount of the adsorbed Cu^{2+} onto the employed gel. The sorption capacity of the used polymeric gel increases gradually with Cu^{2+} concentration and reaches a plateau which represents the maximum sorption capacity. Our experimental data are in accordance with the Langmuir isotherm model, as the R^2 value for the plot in the inset of Fig. 5 was better than 0.997. The theoretical saturation capacity (q_m) determined from this model is 18.0 mg/g. The sorption capacity of some recently reported sorbents such as carbon nanotubes and various chelate functionalized materials are presented in Table 1.

The advantage of the proposed sorbent is also its ability for regeneration. The sorbed metal cations can be easily leached with

an acid solution and the polymer can be reused many times without considerable loss of its sorption capacity. It should also be noted that the maximum sorption capacity determined from our experimental data was found to be 18.4 mg/g.

3.3. Sorption kinetics

Kinetic examination of the sorption process at the prepared polymeric gels was also carried out. The shape of the curve representing copper ion uptake versus time is presented in Fig. 6. It suggests that two steps were involved in the process. The first step was rapid, lasted circa 20 min, and after it equilibrium was achieved slowly during the next 20 min. The time of 50% sorption ($t_{1/2}$) was circa 3 min. The sorption of copper ions onto the obtained polymer chains should involve three consecutive steps of external diffusion, intraparticle diffusion and finally sorption reaction. Due to the fact that the sorption occurs rapidly, the first two steps determine the kinetics of the entire process. Therefore, the progress of the sorption process can be described by the Weber–Morris model [44]:

$$q_i = k_d t^{0.5}$$

where k_d is the rate constant of the intraparticle transport. The results are shown in the inset of Fig. 6. Plots of q_i versus square root of time were found to be linear ($R^2 = 0.978$) and k_d value was found to be equal to 0.19 mg/g min^{0.5}. The obtained results indicated the importance of intraparticle diffusion. However, as the determined line does not pass through the origin, external diffusion, in addition to intraparticle diffusion, has some influence.

3.4. Swelling behavior

The next investigation was related to the influence of copper concentration on the swelling ratio of the poly(AcOrn) gels. The experimental data presented in Fig. 7 form a sigmoidal dependence. The swelling ratio decreases with an increase in concentration of Cu^{2+} ; the gel is most sensitive to the Cu^{2+} concentration in the range 1–100 mg/mL. Both complexes, with stoichiometry 1:1 and 1:2, should influence the gel swelling ratio. In order to examine which of these complexes dominate in the gels, UV–Vis spectra of the complexes of ornithine and Cu^{2+} with stoichiometry 1:1 ($\text{Cu}(\text{Orn})^+$) and 1:2 ($\text{Cu}(\text{Orn})_2$) in an aqueous solution were obtained and compared with the spectra of the poly(AcOrn) gel swollen with a solution of Cu^{2+} . The mass of dry polymer was 50 mg, the volume of solution was 10 mL and the concentration of Cu^{2+} equaled 20, 80, 160 and 200 mg/L. The bands in the spectra of the gels are only somewhat wider than those obtained for the solution. More importantly, the wavelength corresponding to the maximum absorbance is very close to the maximum wavelength corresponding to the $\text{Cu}(\text{Orn})_2$ complex in the aqueous solution. The spectra obtained in the solutions and in the gel conditioned in a solution containing 80 mg/L of Cu^{2+} are presented in Fig. 8. The presence of each complex in the gel should influence the gel swelling ratio. The presence of the 1:1 complex should cause the expansion of the polymer network by introducing excessive positive charge to the polymeric chains, which should lead to an increase in the osmotic pressure between the solution and the gel. The presence of the 1:2 complex increases the overall cross-link density of the gels and leads to the shrinking of the polymer network (see Fig. 9). The obtained results suggest that the copper ions are mainly involved in the complex stoichiometry of 1:2, which is in good agreement with the investigation of the influence of Cu^{2+} concentration on the swelling ratio. Since α -amino acid groups are attached to flexible polymeric chains of the gel network using sufficiently long and flexible spacers. Such construction allows to form stable 1:2 complexes and this is probably the main reason for a relatively high copper ion sorption capacity.

Assuming that all α -amino acid groups are involved in 1:2 complexes with the copper ions and the relative content of the amino acid incorporated into the polymeric network of the gels is equal to its mole ratio in the pregelation solution, the calculated maximum sorption capacity is 169.3 mg/g. The experimental value of maximum sorption capacity is nine times smaller than this calculated value. This difference may be explained in terms of steric reasons that make many amino acid groups inaccessible for the metal ions. In other words, the formation of the complexes with copper ions increases the cross-link density and makes the polymeric gels collapse. The internal structure of the gel becomes denser, which makes the penetration of the gel by subsequent ions more difficult.

4. Conclusions

A new gel based on modified L-ornithine cross-linked with N,N'-methylenebisacrylamide was synthesized by simple free radical polymerization. Due to the way the polymeric chains are built, the α -amino acids groups do not lose their typical properties, e.g. an ability to complex some metal ions. Based on the obtained UV–Vis spectra it could be concluded that the copper ions are mainly involved in complexes of 1:2 stoichiometry with the α -amino acid group attached to the polymeric network. An increase in the amount of absorbed copper ions leads to the shrinking of the polymeric network, which makes the removal of the gel from the solution easier and is useful, for instance, for further regeneration. However, the shrinking process due to steric reasons is probably

responsible for the fact that the obtained maximum sorption capacity achieved only ca. 11% of that calculated. Nevertheless, the obtained results show that the equilibrium adsorption capacities are relatively high compared with those corresponding to other materials presented in the literature. Both the high uptake capacity (>94% of the maximum experimental value) in a wide range of pH and the fast time of reaching equilibrium (ca. 30 min) suggest that the p(AcOrn) hydrogels may be a potential novel metal ion absorbent and have great potential application in environmental protection.

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