Abstract. Hydrogel copolymers based on N, N-dimethyl acrylamide (DMA) and acrylic acid (AAc) were synthesized with different molar composition ratios ([DMA:AAc] = 30:70, 50:50 and 70:30 mol. %) using ammonium peroxydisulfate as a free radical initiation system in the presence of various amounts of N, N'-methylene bis (acrylamide) as a crosslinker (0.05, 0.1 and 0.3 mol. %) and water as reactant medium. The swelling behavior of the obtained was characterized based on the amount of the by different amounts to added of the crosslinking agent. While the use of a large amount of crosslinking agent in the poly (DMA-co-AAc) hydrogels was reduced the swelling degree in the water medium, a smaller amount in the gel indicated the tendency of the gel to burst. Absorption studies were made using different concentrations of copper sulfate (CuSO₄). Poly(DMA-co-AAc) hydrogels absorption capacity is competitive when there are more N, N-dimethyl acrylamide content in copolymer than others. The swelling ratios of low concentration of Cu (II) ion are higher than those of higher concentration of Cu (II) ion. Hydrogel gave the highest swelling ratio for the solution containing the lowest Cu (II) ion concentration than for the solution containing the highest Cu (II) ion.

Key words: N, N-dimethyl acrylamide; acrylic acid; hydrogel; swelling degree; treating wastewater.

Introduction

Cross-linked polymers with various properties have been applied in industrial applications, including medicine, agriculture, electronics, biotechnology, engineering, food industry, etc. Polymers belong to the class of intelligent polymers because of their sensitivity to temperature [1-5].

N-isopropyl acrylamide hydrogels are widely studied as thermosensitive materials in different applications because of their excellent valuable properties. Phase transition of such polymers occurs at a fixed temperature interval. For poly-N-isopropyl acrylamide, its low critical solution temperature (LCST) is 32°C. It noted that a person’s change in body temperature from normal to elevated during diseases is within 36-41°C. That is why the expansion of the thermal sensitivity range of the above-mentioned linear copolymers is significant. The task can be solved by adjusting the hydrophilic-hydrophobic balance of macro chains by copolymerizing these monomers with other comonomers [6-10].

Many authors studied the swelling kinetics based on DMA hydrogels with different monomers in different nature. Several monomers had been added to copolymer based on DMA to improve its special properties for applications, such as ion loading hydrogels. That the swelling kinetics of hydrogel had different properties depending on copolymer composition (hydrophobic/hydrophilic balance of copolymer), crosslink density, the degree of ionization and their interaction with ions are important [11-15].

The crucial application of hydrogel is a carrier of medicinal substances, such as drug delivery and high antibacterial activity. Poly(DMA-co-AAc) cross-linked copolymers have shown antimicrobial properties against both Grams (positive and negative) bacteria. Hydrogels’ killing bacteria and drug delivery mechanisms have been proposed to improve Poly(DMA-co-AAc) [15].
In the present work, Poly(DMA-co-AAc) hydrogels were prepared using free radical polymerization in water media. The swelling properties of poly(DMA-co-AAc) hydrogel aqueous solution were investigated via the gravimetric method. Kinetics of sorption metal ions of Poly(DMA-co-AAc) hydrogel were studied.

Materials and methods

Material. N, N-dimethyl acrylamide (DMA, 99%), ammonium persulfate (98%, APS, CAS 7727-54-0), N, N’-methylene-bis-acrylamide (99%, BIS, CAS 110-26-9), and Copper (II) salt (CuSO$_4$) (98%, CAS 7758-99-8) were purchased from Sigma Aldrich (Heidelberg, Germany). Oil emulsion was obtained from the Kyzylykiya field (Kazakhstan).

Synthesis of Poly(DMA-co-AAc) hydrogels. Hydrogels based on DMA and AAc were synthesized with different molar composition ratios (M1 (30:70), M2 (50:50), and M3 (70:30)), by free radical polymerization in water in presence of ammonium persulfate (2 × 10$^{-2}$ M) as the radical initiator and N,N’-methylene bis (acrylamide) (0.05, 0.1 and 0.3 mol. %) as the cross-linking agent. Monomer mixture accounts 30% of the total volume, and the rest belongs to the solvent. The whole volume of reagents and solvent mixture was retained at 10 mL for all the compositions.

After degassing with argon for about 10 min to remove oxygen, the glass ampoule containing the reaction mixture was hermetically sealed and placed in the water bath at 60$^\circ$C for various times (10, 20 and 40 minutes).

The obtained hydrogels were washed with distilled water for 10 days to purify the samples from unreacted monomers. Then, the hydrogel samples were dehydrated at room temperature and in a vacuum oven until the weight was kept constant [14].

Swelling study. Hydrogels were taken out after a reaction was cleaned by using distilled water for several days from unreacted monomers. The cleaned hydrogels were cut into small pieces of about 0.5 cm in height and dehydrated. The drying sample was in a vacuum oven at 25$^\circ$C until the weight was constant.

The swelling degree (g/g) was calculated from the formula:

$$\alpha = \frac{m-m_0}{m_0}$$

Where m is the mass of the swollen hydrogel (g); $m_0$ is the gel specimens’ weight in dried (g); and $\alpha$ is the – degree of swelling.

Gel (G) and sol (S) fractions yield were calculated according to the formulas:

$$G = \frac{m}{m_0} \times 100\%$$

$$S = 100-G$$

where S is the sol fraction.

$m_0$ is the weight of the dry sample, g;

$m_0$ is the weight of the synthesized sample, g.

The cross-linking density (J) calculated from formula:

$$J = \frac{1}{(S+S^{1/2})}$$

Results and discussion

The application of hydrogels in many fields is dependent on their swelling behavior in aqueous media. Therefore, studying the swelling kinetics of hydrogels are very important. The swelling ability of Poly(DMA-co-AAc) hydrogels aqueous solution were investigated via the gravimetric method. Figure 1 depicts the degree of swelling and time for the hydrogels based on different ratio monomers DMA and AAc. Water absorbability of Poly(DMA-co-AAc) hydrogels was determined. After two days, water absorption of the gel slows downed and further saturated and striving for balance. The swelling ability of Poly(DMA-co-AAc) was dependent on the copolymer composition. Thus, this process increases with decreasing the ratio of DMA in the hydrogel. The hydrogel showed the highest degree of swelling when more acrylic acid content was in copolymer than others. The work of many researchers reported swelling properties of hydrogels to depend on many factors, such as network density, monomer and solvent nature, polymer-solvent interaction parameter and more [16,17]. The swelling of these Poly(DMA-co-AAc) hydrogels relies on monomers’ nature and parameters of synthesis. Although these hydrogels were synthesized under the same conditions, they showed different degrees of swelling, depending on the monomers nature. Comparing samples M1 and M3, the swelling degree decreased due to increasing the AAc ratio in the copolymer, suggesting.

Synthesis-time and crosslinking content are essential parameters in the preparation of three-dimensional copolymers. If the crosslinking agent in hydrogel synthesis is large, it can be crosslinking tightly and retain only a small amount of solvent. This is inefficient for polymers used as carriers of
our solution. The low content of binders leads to the fact that the hydrogel is rarely meshed, absorbs a considerable amount of solvents, and has difficulties in application. Therefore, it is essential to choose the optimal amount of sewing agent.

**Figure 1 – Time-dependent swelling of poly (DMA-co-AAc) hydrogels**

*N,N*-methylene-bis-acylamide was used as a crosslinking agent in the synthesis of Poly(DMA-co-AAc) hydrogel. Hydrogels with DMA monomer content of 50% (M2) at three different concentrations of the crosslinking agent (0.05 (a); 0.1 (b) and 0.3 (c) mol.%) were synthesized, and their swelling ability in aqueous medium was studied by gravimetric method. As shown in Figure 2, the higher crosslinking content in the hydrogel (Figure 5a), the lower the degree of swelling in water compared to other conditions (a = 128 g/g), and the lower the gel fraction yield (G = 17.42). This is because the frequent stitching of Poly(DMA-co-AAc) hydrogel prevents water from entering the gel and expanding the grid. Although Poly(DMA-co-AAc) hydrogel contains a small amount of crosslinking agent (Figure 5b), despite the high gel-sol fraction yield (G = 46.68) and swelling degree in water (a = 387 g/g), the gel absorbs a large amount of water. It retains its stable form tends to collapse easily without saving, which causes inconvenience to use. The most favorable condition for synthesizing poly (DMA-co-AAc) copolymer is 0.1 mol. % of the crosslinking agent in the gel. The swelling degree of the gel was 270 g/g, and the gel yield of the fraction was around G = 34. Furthermore, hardness and softness of this hydrogel are very favorable compared to others, and the gel can retain its stable shape.

**Figure 2 – Effect of the crosslinking agent content on the swelling ratio of poly(DMA-co-AAc) (M2).**

a – 0.05; b – 0.1; c – 0.3 mol. % (crosslinking agent)

The swelling degree of hydrogel, along with crosslinking agents, affects the time of synthesis. During polymer synthesis, the longer the temperature is kept below the optimum temperature (in thermostat), the harder the gels are obtained, and the shorter the time, the opposite is true. Therefore, both the synthesis time and the amount of crosslinking are especially important in describing polymerization. Synthesize hydrogels at different times (10, 20 and 40 minutes) of Poly(DMA-co-AAc) hydrogels of swelling kinetics were studied. The initial monomeric composition of the study was 50-50 mol. % (M2) of hydrogel was obtained. The swelling degree of gel for more than two days, kept for 10 minutes at 60 °C in hydrogel preparation, was 387 g/g. The gel reaches its maximum swelling level, it tends to explode faster without retaining its shape. Such Poly(DMA-co-AAc) hydrogels are useless in terms of use. It was proved that the hydrogel, which has a longer fusion time in the thermostat (Figure 3c), can absorb only a small amount of water. This proved ineffective. We consider the optimal time to be 20 minutes (Figure 3b).

For Poly(DMA-co-AAc), the hydrogel properties for metal ions absorption at various concentrations of metal ion, i.e. copper salts (CuSO₄), were investigated by the gravimetric method related to time. The degree of metal ions absorption of poly (DMA-co-AAc) hydrogel samples (M1 and M2) is lower than another sample hydrogel.

The hydrogel containing the greatest amount of DMA (sample M3) possessed the highest degree of swelling as compared with the other prepared copolymers (Figure 4, M3).
The kinetics of sorption various of Cu (II) ion in presence of copolymer hydrogel (M3) is presented on Figure 5.

The swelling degree of the hydrogel containing 0.001M of Cu (II) ions is higher than solutions containing 0.01 and 0.1M. However, the swelling ratios increase with increasing time from 10 to 90 hours. Oil and water are substances that do not mix and become a heterogeneous mixture where oil is at the top and water at the bottom. This is attributed to their density.

Washing of the obtained hydrogels with distilled water was several days for cleaning the hydrogels from monomers unreacted. It was noted that hydrogels performed a high swelling ratio, and initial volume increased several times while immersed in distilled water. It reaches saturation levels by absorbing water. The necessary part of this swollen hydrogel is placed in a cylinder with a diameter of 30 mm and fixed on a tripod, as presented on Figure 6.
While pouring distilled water from the top, the water was filtered. As shown in Figure 6c, the hydrogel can hold the oil emulsion without letting it go down. The oil emulsion’s viscosity was very close to the water and was obtained from the Kyzyldarya field (Kazakhstan). Due to the hydrophobic nature of the oil, Poly(DMA-co-AAc) hydrogel did not absorb the oil’s emulsion. As shown by our results the water accumulating in the oil underside can be cleaned by passing through hydrogels.

**Conclusion**

Poly(DMA-co-AAc) hydrogels were prepared using free radical polymerization in water media. All the hydrogel copolymers are characterized by swelling properties. Highly swelling ratios distinguish the hydrogel copolymers in the crosslinking agent where is the highest content of crosslinking gave the highest swelling ratios. The optimum time for synthesis of hydrogel was studied. Synthesis time (20 minutes) was the optimum time for hydrogel, but 10 minutes gave soft hydrogel and 40 minutes gave rigid hydrogel. The potential capability of hydrogel in the treatment of oil-contaminated water was investigated. Hydrogel gave the highest swelling ratio for solution containing lowest concentration of Cu (II) ion than for solution containing highest concentration of Cu (II) ion. Based on the results of the study, Poly(DMA-co-AAc) hydrogel can be applied to remove oil from oil-contaminated water.

**References**

1 Ashok Kumar, Akshay Srivastava, Igor Yu Galaev, Bo Mattiasson. (2007) Smart polymers: Physical forms and bioengineering applications. Progress in Polymer Science. Vol 32, № 10, PP 1205-1237 https://doi.org/10.1016/j.progpolymsci.2007.05.003

2 Louise Van Gheluwe, Igor Chourpa, Coline Gaigne and Emilie Munnier (2021) Polymer-Based Smart Drug Delivery Systems for Skin Application and Demonstration of Stimuli-Responsiveness. Polymers 13(8), 1285; https://doi.org/10.3390/polym13081285

3 Qu Jin, Zhao Xin, Ma Peter X., Guo Baolin. (2018) Injectable antibacterial conductive hydrogels with dual response to an electric field and pH for localized “smart” drug release. Acta Biomaterialia. Vol.72, PP. 55–69. http://dx.doi.org/10.1016/j.actbio.2018.03.018.

4 Srivastava A, Yadav, T, Sharma, S, Nayak, A, Akanksha Kumari, A. and Mishra, N. (2016) Polymers in Drug Delivery. Journal of Biosciences and Medicines, №4, PP. 69-84. doi: 10.4236/jbm.2016.41009.

5 Brighenti R, Li Y and Vernerey F.J (2020) Smart Polymers for Advanced Applications: A Mechanical Perspective Review. Front. Mater. №7, P.196. doi: 10.3389/fmats.2020.00196

6 Maria V. Martinez, Maria Molina, (2018) Poly(N-isopropylacrylamide) cross-linked gels as intrinsic amphiphilic materials: swelling properties used to build novel interphases. J. Phys. Chem. B vol.122, № 38, P.9038–9048. https://doi.org/10.1021/acs.jpcb.8b07625

7 Nakam, U.; Mun, G.A.; Shaikhudtinov, E.M.; Bieerkehazhi, S.; El-Sayed, (2020) Hydrogels based on N-isopropylacrylamide and 2-hydroxyethyl acrylate: Synthesis, characterization, and investigation of their antibacterial activity. Polym. Int. VI. 69, PP. 1220–1226. https://doi.org/10.1002/pi.6065.

8 Nakam, U.; Mun, G.A. (2021) Thermosensitive N-isopropylacrylamide-co-2-hydroxyethyl acrylate hydrogels interactions with Poly(acrylic acid) and surfactants. Polym. Adv. Technol. Vol. 32, PP.2676–2681. https://doi.org/10.1002/pat.5070.

9 Mao, J.; Yu, Q.J.; Wang, S. (2021) Preparation of multifunctional hydrogels with pore channels using agarose sacrificial templates and its applications. Polym. Adv. Technol. Vol.32, PP. 1752–1762. https://doi.org/10.1002/pat.5211.

10 Nakam U, K Rahmetullaeva, A Mun, M Shaikhudtinov, Zh Yeligbaeva, El-Sayed Moussa. (2016) Linear Copolymer of N-Isopropylacrylamide and 2-Hydroxyethylacrylate: Synthesis, Characterization and Monomer Reactivity Ratios. Oriental Journal of Chemistry. Vol.5, № 32, PP. 2347–2354. http://dx.doi.org/10.13005/ojc/320505

11 Sadia Afroz, Farha Afrose, A. K. M. M. Alam, Ruhul A. Khan & Md. Ashraf AlAMIL. (2019) Synthesis and characterization of polyethylene oxide (PEO)-N,N-dimethylacrylamide (DMA) hydrogel by gamma radiation. Advanced Composites and Hybrid Materials vol. 2, pp.133–141 DOI: 10.1007/s42114-018-0058-x

12 Ullantay Nakam, Balgyn Tolky, Dinara AdikanoBAT, El-Sayed Moussa Negim, (2021) Characterization and swelling properties of copolymer Poly(N, N-dimethyl acrylamide-co-acrylic acid) and homopolymer Poly (acrylic acid) // Egyptian Journal of Chemistry DOI: 10.21608/ ejchem.2021.95005.4465
12 Ayatzhan Akhmetzhan, Nurgeldi Abeu, Sotirios Nik. Longinos. (2021) Synthesis and Heavy Metal Sorption Studies of N,N-Dimethylacrylamide Based Hydrogels Polymers №13, PP 3084. https://doi.org/10.3390/polym13183084

13 Shahid Bashir, Fatin Saiha Omar, Maryam Hina, Arshid Numan, Javed Iqbal, S. Ramesh, K. Ramesh, (2020) Synthesis and characterization of hybrid poly (N,N-dimethylacrylamide) composite hydrogel electrolytes and their performance in supercapacitor. Electrochimica Acta, vol. 332, P. 135438. https://doi.org/10.1016/j.electacta.2019.135438

14 Ulantay Nakan.; Bieerkehazhi, S.; Tolkyn, B.; Mun, G.A.; Assanov, M; Nursultanov, M.E.; (2021) Synthesis, characterization and antibacterial application of copolymers based on N,N-dimethyl acrylamide and acrylic acid. Materials, №14, P.6191. https://doi.org/10.3390/ma14206191

15 A.R. Hernandez-Martínez, J.A. Lujan-Montelongo, C. Silva-Cuevasb, Josué D. Mota-Moralessa (2018) Swelling and methylene blue adsorption of poly(N,N-dimethylacrylamide-co-2-hydroxyethyl methacrylate) hydrogel. Reactive and Functional Polymers Vol. 122, Pages 75-84 https://doi.org/10.1016/j.reactfunctpolym.2017.11.008

16 Fariba Ganji, Samira Vasheghani-Farahani, and Ebrahim Vasheghani-Farahani (2010). Theoretical Description of Hydrogel Swelling: Iranian Polymer Journal vol.5, №19, PP. 375-398

17 Nermin Orakdogen, Talin Boyaci Charge density dependence of elasticity of anionically modified N,N-dimethylacrylamide-based gels with (meth)acrylic acid segments: an insight by quantitative analysis of electrostatic contributions, European Polymer Journal 2017; 94; 484-500 https://doi.org/10.1016/j.eurpolymj.2017.07.032