Removal of anionic phenol red from water solution in the batch system by using N,N-dimethylacrylamide and 3-acrlylamidopropil-trimethyl ammonium chloride-based polymeric hydrogels

Tuba Erşen Dudu

Department of Chemical Engineering, Faculty of Engineering, Van Yuzuncu Yıl University, Van, 65080, Turkey,
tuba_ersen@hotmail.com, ORCID: 0000-0001-5564-2834

A B S T R A C T

p(DMAAm-co-APTMACl)-based hydrogels were synthesized with different molar ratios by the redox polymerization technique using N,N-Dimethylacrylamide (DMAAm) and 3-acrlylamidopropil-trimethyl ammonium chloride (APTMACl) monomers and a crosslinker. In this study, the aim was to improve the swelling properties and dye sorption of the prepared hydrogels. The equilibrium swelling values of hydrogels were determined by the gravimetric method in deionized water and different pH values, and their structural characterizations were examined with Fourier transform infrared spectroscopy (FT-IR) and thermal gravimetric analysis (TGA) techniques. Sorption efficiencies and sorption capacities of the synthesized hydrogels were determined using aqueous solutions containing phenol red dye at 25 °C. In sorption studies, the effects of different concentrations (5-50 ppm) and different pH values (2-12) on sorption were examined. When the swelling analysis in deionized water was examined, there was a significant increase in the equilibrium swelling value of p(DMAAm-co-APTMACl)-based hydrogel as the mole ratio of APTMACl increased. In addition, the increase in the molar ratio of APTMACl was found to increase the phenol red dye sorption capacity and removal percentage. It was observed that p(DMAAm-co-APTMACl) (2:8) hydrogel had maximum sorption capacity in the range of 5-50 ppm and reached 122.2 mg/g. Experimental data showed that the synthesized p (DMAAm-co-APTMACl)-based hydrogels were effective in removing dye from wastewater and could obtain increased dyestuff removal by synthesis with different molar ratios.

A R T I C L E   I N F O

1. Introduction

Today, the increase in industrialization brings some environmental problems. Especially pollution in water has reached threatening dimensions for humans. Dyestuffs usually have synthetic origin and complex aromatic structures. They have a stable structure since they contain more than one double bond and different functional groups. This causes dyestuffs not to easily biodegrade in nature [1-3]. Approximately 700,000 tons/year of dyestuff and pigment are stated to be produced worldwide and some of these are discharged into the environment [4, 5]. This pollutant, which is discharged into the environment and water sources, disrupts the esthetic appearance of the receiving environments, reduces light transmittance and solubility of gases, affects the photosynthetic activity of the water ecosystem and has toxic effects on living organisms [6, 7]. For this reason, it is important to treat wastewater containing dyes before it is released into the environment to minimize the negative effects on the health of humans and living organisms [6].

Different methods such as coagulation-flocculation, oxidation, ozonation, membrane separation, reverse osmosis and adsorption/absorption are used to remove these dyes from wastewater [7-11]. Among these methods, adsorption/absorption comes to the forefront due to high dye removal potential [12, 13]. Especially in recent years, interest in the use of hydrogels as adsorbents/absorbents in the treatment of wastewaters with dyestuffs has increased [14]. Hydrogels are three-dimensional polymeric network structured materials that do not dissolve in water but can swell to an equilibrium volume in aqueous environments and maintain their existing shape [15, 16]. Adsorption/absorption in hydrogels generally results from the presence of ionizable functional groups of monomers forming the hydrogel. Studies about the use of hydrogels containing various types of

functional groups as sorbents in the adsorption/absorption process have gained momentum in recent years [17].

The present study was carried out in three steps. First, p(DMAAm-co-APTMACl)-based hydrogels were synthesized with different molar ratios (as 8:2, 6:4, 4:6, 1:1, 2:8) by the redox polymerization technique. The equilibrium swelling capacities of the hydrogels synthesized in the first stage were examined in pure water and at different pH values, and their structural characterizations were completed with FT-IR and TGA devices. In the last stage of the study, the sorption efficiency of p(DMAAm-co-APTMACl)-based hydrogels for phenol red dye was investigated.

1. Materials and Methods

1.1. Materials and hydrogel synthesis

In this study, N, N-Dimethylacrylamide (DMAAm, 100%, Sigma Aldrich) and 3-acrlylamidopropil-trimethyl ammonium chloride (APTMACl, 75%, Sigma) as monomers, N, N'-methylene bis acrylamide (MBA, 99%, Merck) as crosslinker, ammonium persulfate (APS, 98%, Merck) as initiator and tetramethylethylenediamine (TEMED, 99%, Merck) as accelerator were used in the preparation of p(DMAAm-co-APTMACl) hydrogel. All chemicals used in the experiments were of analytical purity. Deionized water was obtained from 18.2 MΩ.cm (Millipore Direct-Q3 UV) and used in solution preparation, swelling and sorption experiments. Thermo Scientific pH meter (USA) and ultra-violet spectroscopy (UV-Vis, Thermo Scientific GENESYS 10S, USA) devices were used to measure pH and to quantify amount of phenol red throughout sorption, respectively.

DMAAm and APTMACl-based hydrogels were synthesized at different mole ratios in solution medium according to the redox polymerization technique at 25 °C. MBA was used as crosslinker in the preparation of hydrogels. Typical p(DMAAm-co-APTMACl) (1:1) synthesis was as follows: 3 mg of MBA was dissolved in 1 mL (0.0097 mol) DMAAm monomer, 1.5 mL of distilled water was added to the DMAAm/MBA mixture and mixed well at 2500 rpm. Then this mixture had 2.41 mL (0.0097 mol) APTMACl monomer added and was mixed again. Finally, 5 µL TEMED was used as accelerator and 100 µL ($1.94.10^{-4}$ mol) APS solution was added as initiator. Once the reaction mixture was homogeneously mixed, it was transferred to 6 mm plastic pipettes. The polymerization reaction was allowed to proceed for 4 hours at room temperature (25 °C). These preparation steps are schematically given in Figure 1. After this time period, p(DMAAm-co-APTMACl)-based hydrogels were cut into cylinders and the cylindrical hydrogel pieces were washed by being left in DI water for three days. After the cleaning procedure, hydrogels were dried in an oven at 40 °C to a constant weight and stored for later use [18, 19].

1.2. Characterization

The synthesized hydrogels were ground and powdered and then dried in an oven at 40 °C. The structure of the dried hydrogels and bonding achieved was confirmed using a Thermo Nicolet iS10 FT-IR Spectrometer (USA) in 4000–600 1/cm range.

Thermal gravimetric analyses were conducted with Setaram Labsys Evo Gravimetric Analyzer (TGA/DSC 1600 model, France) in 50-1000 °C range, with 10 °C/min heating rate in an argon atmosphere (flow rate was kept at 100 mL/min).

1.3. Swelling behavior

Swelling characterization of synthesized polymeric hydrogels was carried out by applying dynamic swelling tests at 25 °C in deionized water to cross-linked polymeric samples. Hydrogels based on p(DMAAm-co-APTMACl) in dry form were weighed with a sensitivity of 0.0001 g and placed in a beaker containing distilled water and left to swell. The time when the polymeric hydrogels were immersed in water was taken as t = 0, and the polymeric hydrogels, which were removed from the water at certain intervals, were weighed with the same sensitivity after drying the excess water on the outer surface. Weighing continued regularly until mass values which did not change over time were obtained. With the help of data obtained at the end of dynamic swelling tests, S% - t graphics were drawn and swelling isotherms were created. Equilibrium percentage swelling value was calculated according to the following equation [20-23];

$$S\% = \left(\frac{(M_t - M_0)}{M_0} \right) . 100 \qquad (1)$$

where M_0 is the initial mass (g) of the hydrogel and M_t is the mass of hydrogel at the end of time t. The swelling tests for hydrogels were performed in three replicates and their mean values were used in conjunction with standard deviation values. In order to monitor the change in equilibrium swelling value of p(DMAAm-co-APTMACl)-based hydrogels depending on pH, hydrogels with known dry weights were put in buffer solutions prepared at different pHs (with HCl (0.1 M) and NaOH (0.1 M)) and equilibrium swelling values were calculated according to Equation 1 after 24 hours [22, 23].

Swelling kinetics curves drawn as a result of dynamic swelling tests were generally assumed to be second-order and were calculated with the following equation [24].

$$\frac{dS}{dt} = k_s . (S_{mak} - S)^2 \qquad (2)$$

where dS/dt is the swelling rate of hydrogels; S_{max} is the swelling value of hydrogel at equilibrium ($g_{water}/g_{hydrogel}$); S is the swelling value at time t ($g_{water}/g_{hydrogel}$); k_s represents

swelling rate constant ($g_{hydrogel}/(g_{water}.min)$); and r_0 is the initial swelling rate ($g_{water}/(g_{hydrogel}.min)$).

As a result of the mathematical arrangement of the equation at the boundary conditions S=0 for t=0 and S=S_{max} for t= t_{eq};

$$\frac{t}{S} = A + B.t \tag{3}$$

In this equation, A ($=1/(S_{max}^2.k_s)$) is the opposite of the initial swelling rate ($1/r_0$) and B ($=1/S_{max}$) is the opposite of the largest swelling value [24].

The basic laws used in explaining swelling kinetics and diffusion type of polymeric structures are Fick's laws. Swelling kinetics of hydrogels with swelling properties were examined with the help of the equation below [25].

$$F = \left(\frac{M_t}{M_e}\right) = k.t^n \tag{4}$$

where M_e represents the mass of hydrogels that have reached equilibrium (g); k is a specific rate constant; n is a constant which shows the diffusion exponent; and t is time (min). In order to determine the diffusion type, the parameter n must be known. The diffusion exponent n can be found from the slope of the line on the lnF-lnt graph when swelling has not yet reached equilibrium and in the time it takes for 60% of the solvent mass to enter the gel [25].

1.4. Sorption studies

Pollutants from industries such as textile, printing, plastic, food, paper, pharmaceutical, cosmetic and leather tanning are rich in dyes. Dyes are non-biodegradable, complex organic molecules and even carcinogenic. Therefore, the discharge of these pollutants into water sources, especially, causes environmental pollution of water and soil [26, 27]. In order to explain the phenol red dye sorption quantitatively, the effects of different initial concentrations (ppm) and pH values on sorption were examined. In all sorption studies, the sorption temperature, sorption time and mixing rate were kept constant at 25 °C, 24 hours and 150 rpm, respectively. After the interaction of 50 mg dry hydrogels with 50 mL solutions containing 5-50 ppm phenol red dye concentrations, the dye concentrations in the equilibrium solution were measured. In experiments, the sorption pH was chosen as the pH of phenol red. Moreover, dry hydrogels (50 mg) interacted with 50 mL of 50 ppm phenol red solutions with pH adjusted between 2-12 using HCl and NaOH, and the amounts of phenol red in equilibrium solutions were determined. In all sorption studies, the batch technique was used, and dye sorption capacities of hydrogels were determined at 428 nm wavenumber by UV-VIS measurements. The amounts of absorbed phenol red per unit mass of the hydrogels, qe (mg/g), were calculated by the following equation [28];

$$q_e = \frac{(C_o - C_e).V}{M} \tag{5}$$

Where C_o represents the initial concentration of phenol red (ppm); C_e is the equilibrium concentration of phenol red (ppm); V represents the solution volume (L); and M is the hydrogel mass (g).

1.4.1. Sorption isotherms

The adsorption isotherm is generally the name given to the relationship between the amount of substance sorbed by the unit mass of the sorbent at constant temperature and the concentration of the solution at equilibrium. Therefore, sorption isotherms are used to create equilibrium isotherm models and to design sorption systems [29]. In this study, experimental isotherms showing the change in sorption with concentration were created and related parameters were derived by making use of their compatibility with Langmuir (Eq. (6)) [30] and Freundlich (Eq. (7)) [31] sorption models (see Table 1 for equations).

2. Results and discussion

2.1. Characterization

FT-IR spectra of p(DMAAm-co-APTMACl)-based hydrogels synthesized with different molar ratios are given in Figure 2. As seen in Figure 2, as the mole ratio of DMAAm monomer decreased and the mole ratio of APTMACl monomer increased, the intensity of some peaks changed and some peaks shifted. The characteristic peaks observed at 3391 1/cm, 2932 1/cm, 1617 1/cm and 1255 1/cm for all spectra were related to N–H stretching, C–H stretching, C=O and C–N stretching, respectively. In a study by Ersen Dudu et al. (2019), it was shown that p (DMAAm) hydrogel has characteristic N–H stretching, C–H stretching and C=O stretching peaks at 3467 1/cm, 2927 1/cm and 1616 1/cm, respectively [19]. In a study by Ersen Dudu et al. (2015), it was shown that p (APTMACl) hydrogel has characteristic N-H stretching, C-H stretching, C=O stretching and C-N stretching peaks at 3276 1/cm, 2926 1/cm, 1643 1/cm and 1480 1/cm, respectively [23]. It was determined that the obtained spectra were in agreement with the literature.

Investigation of the thermal behavior of polymeric samples is important for polymers to be selected for their intended use and location. The results of the thermo-gravimetric analysis for the characterization and thermal stability of the network structure are shown in Figure 3. Hydrogels based on p(DMAAm) and p(APTMACl) were shown to undergo thermal degradation in one step up to 500 °C and in three steps up to 700°C, respectively [19, 23]. The results obtained in this study were compatible with the literature [19, 21, 32]. p(DMAAm-co-APTMACl) (8:2) was stable until 229 °C; however, above 229 °C there was a substantial loss in copolymer weight. p(DMAAm-co-APTMACl) (6:4),

p(DMAAm-co-APTMACl) (4:6), p(DMAAm-co-APTMACl) (1:1) and p(DMAAm-co-APTMACl) (2:8) hydrogels, on the other hand, did not show stable behavior against temperature increase and the first degradation occurred at 50 °C. p(DMAAm-co-APTMACl) (8:2) and p(DMAAm-co-APTMACl) (4:6) hydrogels had a total of three decay steps and a total mass loss of 53.5% occurred up to 663 °C and 100% up to 484 °C, respectively. p(DMAAm-co-APTMACl) (6:4), p(DMAAm-co-APTMACl) (1:1) and p(DMAAm-co-APTMACl) (2:8) hydrogels had a total of four decay steps and a total mass loss of 100% up to 606 °C, 95.6% up to 832 °C and 92.1% up to 731 °C, respectively. In addition, the structural resistance of the copolymers decreased with the increase in temperature as the APTMACl mole ratio increased.

2.2. Swelling behavior

In the characterization of network structured polymers with swelling behavior, it is important to examine the swelling kinetics and to clarify the diffusion type and mechanism. The swelling values and equilibrium swelling data in deionized water of the hydrogels synthesized with different molar ratios are given in Figure 4a. As seen in Figure 4a, as the APTMACl ratio in the copolymer hydrogel increased, the equilibrium swelling values of the hydrogels increased. The main reason for this is that more hydrophilic groups are present in the APTMACl monomer than the DMAAm monomer [19, 21, 33]. As a result of the calculations made using Equation 1, the highest swelling value was obtained for p(DMAAm-co-APTMACl) hydrogel prepared at a ratio of 2:8 moles and this value were found to be 10601% after 540 minutes. According to Figure 4a, the hydrogel with the lowest equilibrium swelling value was p(DMAAm-co-APTMACl) (8:2) which reached 5383% after 480 minutes.

In addition to swelling values of p(DMAAm-co-APTMACl)-based hydrogels in deionized water, which were investigated for use as dye sorption material, the swelling behaviors in different pH media were examined and the results are given in Figure 4b. According to the results, the swelling properties of the synthesized hydrogels varied depending on the pH and the swelling capacities of the hydrogels were observed to increase as the amount of APTMACl monomer, which is known to be pH-sensitive, increased. According to the experimental results, it was established that the highest swelling value was reached by p(DMAAm-co-APTMACl) (2:8) and p(DMAAm-co-APTMACl) (4:6) hydrogels. As seen in Figure 4b, maximum swelling capacities of p(DMAAm-co-APTMACl) (2:8) and p(DMAAm-co-APTMACl) (4:6) hydrogels reached 11091% and 10870% at pH 6, respectively.

The swelling rate constant (k_s), the initial swelling rate (r_0) and the theoretical equilibrium swelling value (S_{max}), which determines the swelling rate of the crosslinked hydrogels, were calculated with the help of Equation 3 and presented in Table 2. To calculate these values, the slopes and intersections of the lines obtained by drawing t/S - t graphs were used. When Table 2 is examined, the initial swelling rate for p(DMAAm-co-APTMACl) (8:2) hydrogel was smaller compared to p(DMAAm-co-APTMACl) (2:8) and p(DMAAm-co-APTMACl) (4:6) hydrogels; however, this value increased with increasing functional monomer ratio in the copolymer structure. On the other hand, another intersection is the compatibility between the theoretical S_{max} values calculated from the second-order kinetic equation and the experimental S_{max} values. This also showed the suitability of the kinetic model applied to experimental data.

Examination of the diffusion mechanism of water and determination of the relevant parameters are important in many areas where hydrogels are used. Water diffusion in hydrogels in this study was examined using Fick's Law (Equation 4). The diffusion exponential n and diffusion constant k were found by calculating the slopes and intersections of the line obtained from the $\ln(M_t/M_e)$-lnt graphs, respectively (Table 3). Depending on the value of the diffusion exponent, the diffusion mechanism can be explained. If n <0.5, Fick-type diffusion mechanism is valid and if this value is between 0.5 and 1.0, non-Fick-type diffusion is valid [30]. When Table 3 is analyzed, n values vary between 0.52 and 0.67. In this case, swelling processes for all copolymer hydrogels could be explained by non-Fick type diffusion. In non-Fickian diffusion, diffusion rate and rinse rate are approximately the same, and swelling is controlled by both diffusion and relaxation [34, 35].

2.3. Effect of concentration and pH on sorption

It is known that hydrogels, which are crosslinked polymeric systems, are very good water holders, as well as being used as absorbents in some applications. The sorption of phenol red dye from aqueous solutions was investigated using p(DMAAm-co-APTMACl)-based hydrogels and positive results were obtained. The graph showing the percent removal of phenol red from the synthesized polymeric hydrogels is given in Figure 5a and the isotherm analyses of absorbent are summarized in Table 4. In Figure 5a, the phenol red sorption capacity of hydrogels increased, but this increase decreased after a certain concentration. In addition, p(DMAAm-co-APTMACl) (2:8) hydrogel was found to have higher phenol red sorption capacity and removal percentage than other copolymeric hydrogels. In light of the data obtained, as the amount of APTMACl monomer increased, the number of functional groups increased and as a result, the sorption capacity of the hydrogel increased. The maximum sorption capacities of p(DMAAm-co-APTMACl) (2:8), p(DMAAm-co-APTMACl) (4:6), p(DMAAm-co-APTMACl) (6:4), p(DMAAm-co-APTMACl) (1:1) and p(DMAAm-co-APTMACl) (8:2) for removal of phenol red were 122.2 mg/g, 109.7 mg/g, 95.5 mg/g, 90.7 mg/g and 68.7 mg/g, respectively.

In experiments about determining the appropriate pH value to remove anionic dyes from aqueous solutions, the equilibrium dye-holding capacities for phenol red were determined by studying in different pH media. The results are presented in Figure 5b. As can be seen from Figure 5b, the highest phenol red dye holding capacity values were obtained for all hydrogels at pH 10. In addition, it was determined that the equilibrium dye sorption capacity increased with the addition of APTMACl. Among the copolymeric hydrogels, p(DMAAm-co-APTMACl) (2:8) hydrogel had the highest phenol red sorption capacity and this value was 40.9 mg/g at pH 10. These differences observed in the sorption capacities and rates of hydrogels as the amount of APTMACl increased were due to the increase in crosslink points within the copolymer hydrogel structure and the interaction of the dye molecules and hydrophilic groups of the hydrogel.

2.3.1. Sorption Isotherm

In order to determine the sorption behavior of p(DMAAm-co-APTMACl)-based hydrogels, hydrogels of certain weights were exposed to phenol red solutions with different concentrations. With the help of the experimental data obtained, the suitability of hydrogel sorption behaviors was examined using Langmuir and Freundlich isotherms. Data for Langmuir and Freundlich isotherms are shown in Table 4. As can be seen from Table 4, all of the R^2 values calculated for the Freundlich isotherm were between 0.9683 and 0.9902 and higher than the calculated R^2 values for the Langmuir isotherm. When these results are evaluated, the sorption of phenol red dye from aqueous solutions fitted the Freundlich isotherm when p(DMAAm-co-APTMACl)-based hydrogels were used. 1/n is a heterogeneity parameter and is commonly applied to correlate sorption data. The smaller the value of 1/n, the greater the expected heterogeneity [36].

3.   Conclusion

In order to investigate the effect of monomer ratio on swelling and dye removal efficacy, p(DMAAm-co-APTMACl)-based hydrogels were synthesized with different molar ratios by the redox polymerization technique using DMAAm and APTMACl monomers. The presence of functional groups in the copolymer structures and their temperature sensitivity were demonstrated qualitatively and/or quantitatively by FTIR and TGA analyses. The presence of APTMACl monomer containing functional groups with hydrophilic character increased the rate of equilibrium swelling in copolymeric hydrogels and the experimental Smax value of p(DMAAm-co-APTMACl) (2:8) hydrogel was observed to reach 10601%. Evaluations to determine the diffusion mechanism revealed that both diffusion and relaxation control (non-Fick type) was valid for all copolymer hydrogels. In order to investigate the sorption properties of cationic hydrogels, phenol red, which has anionic property, was chosen as a model dye. The sorption properties of hydrogels

were investigated in terms of the effect of phenol red concentration, pH value and mole ratios of monomers. In the sorption experiments, the maximum sorption capacity was reached with p(DMAAm-co-APTMACl) (2:8) hydrogel and this value was 122.2 mg/g. The APTMACl monomer, which showed more hydrophilic properties in light of the obtained data, was found to increase the equilibrium sorption values of the copolymer hydrogels. As a result of evaluating the equilibrium data, it was determined that the phenol red removal process fitted the Freundlich isotherm. As a result, these copolymeric hydrogel structures have the potential to be used in various separation and purification processes, especially in environmental applications.

References

[1]. Gong R.M., Li M., Yang C., Sun Y.Z., Chen J., "Removal of cationic dyes from aqueous solution by adsorption on peanut hull", Journal of Hazard Mater, 121, (2005), 247-250.

[2]. Sudipta C., Dae S.L., Min W.L., Seung H.W., "Congo red adsorption from aqueous solutions by using chitosan hydrogel beads impregnated with nonionic or anionic surfactant", Bioresource Technology, 100, (2009), 3862-3868.

[3]. Wen-Tien T., Kuo-Jong H., Hsin-Chieh H., "Adsorption of organic compounds from aqueous solution onto the synthesized zeolite", Journal of Hazardous Materials, 166, (2009), 635-641.

[4]. Aksakal O., Ucun H., "Equilibrium, kinetic and thermodynamic studies of the biosorption of textile dye (Reactive Red 195) onto Pinus sylvestris L", Journal of Hazardous Materials, 181, (2010), 666-672.

[5]. Deveci T., Unyayar A., Mazmanci M.A., "Production of Remazol Brilliant Blue R decolourising oxygenase from the culture filtrate of Funalia trogii ATCC 200800", Journal of Molecular Catalysis B: Enzymatic, 30, (2004), 25-32.

[6]. Badu M., Boateng I.W., Boadi N.O., "Evaluation of adsorption of textile dyes by wood sawdust", Research Journal of Physical and Applied Sciences, 3(1) (2014), 6-14.

[7]. Dulman V., Cucu-Man S.M., "Sorption of some textile dyes by beech wood sawdust", Journal of Hazardous Materials, 162, (2009), 1457-1464.

[8]. Yang Y., Wyatt D.T., Bahorshky M., "Decolorization of dyes using UV/H2O2 photochemical oxidation", Textile Chemist and Colorist, 30, (1998), 27-35.

[9]. Konsowa A.H., "Decolorization of wastewater containing direct dye by ozonation in a batch bubble column reactor", Desalination, 158, (2003), 233-240.

[10]. Ong S.A, Toorisaka E., Hirata M., Hano T., "Treatment of azo dye orange II in aerobic and anaerobic-SBR systems", Process Biochemistry, 40, (2005), 2097-2914.

[11]. Kim T.H., Park C., Kim S., "Water recycling from desalination and purification process of reactive dye manufacturing industry by combined membrane filtration", Journal of Cleaner Production, 13, (2005), 779-786.

[12]. Shirsath D.S., Shrivastava V.S., "Removal of hazardous dye Ponceau-S by using chitin: An organic bioadsorbent", African Journal of Environmental Science and Technology, 6(2), (2012), 115-124.

[13]. Mohsen M., Maziad N.A., Gomaa E., Hassan Aly E., Mohammed R., "Characterization of some hydrogels used in water purification: correlation of swelling and free-volume properties", Open Journal of Organic Polymer Materials, 5, (2015), 79-88.

[14]. Kavaklı P.A., Yılmaz Z., Şen M., "Investigation of heavy metal ion adsorption characteristics of poly(N,N Dimethylamino Ethylmethacrylate) hydrogels", Separation Science and Technology, 42, (2007), 1245-1254.

[15]. Al-qudah Y.H.F., Mahmoud G.A., Abdel Khalek M.A., "Radiation crosslinked poly (vinyl alcohol)/acrylic acid copolymer for removal of heavy metal ions from aqueous solutions", Journal of Radiation Research and Applied Sciences, 7, (2014), 135-145.

[16]. Wang W.B., Huang D.J., Kang Y.R., Wang A.Q., "One-step in situ fabrication of a granular semi-IPN hydrogel based on chitosan and gelatin for fast and efficient adsorption of Cu2+ ion", Colloids and Surfaces B: Biointerfaces, 106, (2013), 51-59.

[17]. Demirbilek C., Özdemir Dinc C., "Synthesis of diethylaminoethyl dextran hydrogel and its heavy metal ion adsorption characteristics", Carbohydrate Polymers, 90, (2012), 1159-1167.

[18]. Ersen Dudu T., Alpaslan D., Uzun Y., Aktas N., "Utilization of hydrogel-fungus composites as absorbents for removal of textile dyes from aqueous media", International Journal of Environmental Research, 11, (2017), 557-568.

[19]. Ersen Dudu T., Alpaslan D., Aktas N., "Urea uptake and release by novel macrogels from dimethylacrylamide", Communications in Soil Science and Plant Analysis, 50, (2019), 2278-2293.

[20]. Chang C., Duan B., Cai J., Zhang L., "Superabsorbent hydrogels based on cellulose for smart swelling and controllable delivery", European Polymer Journal, 46, (2010), 92-100.

[21]. Olak T., Turan A., Alpaslan D., Ersen Dudu T., Aktas N., "Developing poly(Agar-co-Glycerol-co-Thyme Oil) based Organo-hydrogels for the controlled drug release applications", Journal of Drug Delivery Science and Technology, (2020), https://doi.org/10.1016/j.jddst.2020.102088.

[22]. Alpaslan D., Ersen Dudu T., Aktas N., "Synthesis of smart food packaging from poly(gelatin-co-dimethyl acrylamide)/citric acid-red apple peel extract", Soft Materials, (2020), https://doi.org/10.1080/1539445X.2020.1765802.

[23]. Ersen Dudu T., Sahiner M., Alpaslan D., Demirci S., Aktas N., "Removal of As(V), Cr(III) and Cr(VI) from aqueous environments by poly(acrylonitril-co-acrylamidopropyl-trimethyl ammonium chloride)-based hydrogels", Journal of environmental management, 161, (2015), 243-251.

[24]. Kundakcı S., Öğüt H.G., Üzüm Ö.B., Karadağ E., "Equilibrium swelling characterization and dye uptake studies of acrylamide-co-methylenesuccinic acid hydrogels and semi-IPNs with PEG", Polymer-Plastic Technology and Engineering, 50, (2011), 947-956.

[25]. Yanfeng C., Min Y., "Swelling kinetics and stimuli-responsiveness of poly(DMAEMA) hydrogels prepared by UV-irradiation", Radiation Physics and Chemistry, 61, (2001), 65-68.

[26]. Ji F., Li C., Tang B., Xu J., Lu G., Liu P., "Preparation of cellulose acetate/zeolite composite fiber and its adsorption behavior for heavy metal ions in aqueous solution", Chemical Engineering Journal, 209, (2012), 325-333.

[27]. Kurniawan A., Sisnandy V.O.A., Trilestari K., Sunarso J., Indraswati N., Ismadji S., "Performance of durian shell waste as high capacity biosorbent for Cr(VI) removal from synthetic wastewater", Ecological Engineering, 37, (2011), 940-947.

[28]. Maziad N.A., Mohsen M., Gomaa E., Mohammed R., "Radiation copolymerization of hydrogels based in polyacrylic acid/polyvinyl alcohol applied in water treatment processes", Journal of Materials Science and Engineering A, 5(11-12), (2015), 381-390.

[29]. Kuang Y., Zhang X., Zhou S., "Adsorption of methylene blue in water onto activated carbon by surfactant modification", Water, 12, (2020), 587. doi:10.3390/w12020587.

[30]. Langmuir I., "The adsorption of gases on plane surfaces of glass, mica and platinum", Journal of the American Chemical Society, 40, (1918), 1361.

[31]. Freundlich H.M.F., "Uber die adsorption in losungen", Zeitschrift für Physikalische Chemie, 57, (1906), 385-470.

[32]. Alpaslan D., Ersen Dudu T., Sahiner N., Aktas N., "Synthesis and preparation of responsive poly(Dimethyl acrylamide/gelatin and pomegranat extract) as a novel food packaging material", Materials Science & Engineering C, 108, (2020), 110339.

[33]. Alpaslan D., Ersen Dudu T., Aktas N., "Synthesis, Characterization and Modification of Novel Food Packaging Material from Dimethyl acrylamide/Gelatin and Purple Cabbage Extract", MANAS Journal of Engineering, 6(2), (2018), 110-128.

[34]. Khare A.R., Peppas N.A., "Swelling/deswelling of anionic copolymer gels", Biomaterials, 16(7), (1995), 559-567.

[35]. Aydınoğlu D., "Investigation of pH-dependent swelling behavior and kinetic parameters of novel poly(acrylamide-co-acrylic acid) hydrogels with spirulina", e-Polymers, 15(2), (2015), 81-93.

[36]. Nethaji S., Sivasamy A., Mandal A.B., "Adsorption isotherms, kinetics and mechanism for the adsorption of cationic and anionic dyes onto carbonaceous particles prepared from Juglans regia shell biomass", International Journal of Environmental Science and Technology, 10, (2013), 231-242.