Crosslinked poly(hydroxybutyl acrylate-*co*-acrylamide) based hydrogels: synthesis, characterization, and performance evaluation in heavy metal removal

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Abstract: By radical polymerization, two series of superabsorbent hydrogels of hydroxybutyl acrylate and acrylamide copolymers, poly(HBA-*co*-AAm), were obtained. In the first series, the ratio of hydroxybutyl acrylate to acrylamide was optimized with a constant amount of methylene bisacrylamide (MBA) as a cross-linking agent. In the second series, the amount of MBA was changed at a fixed monomer ratio. The structure of the copolymers was confirmed by the FTIR method. Swelling parameters and mechanical properties were tested. Hydrogels with a high Young's modulus and a high degree of swelling were selected for the study of adsorption properties towards Co^{2+}, Ni^{2+} and Cd^{2+} ions. The influence of basic factors such as adsorbent dose, exposure time and pH on adsorption efficiency was also investigated. The ability to adsorb heavy metal ions changed as follows: $Co^{2+} > Ni^{2+} > Cd^{2+}$.

Keywords: super absorbent polymers, hydroxybutyl acrylate, acrylamide, adsorption properties, heavy metal ions removal.

Hydrożele na bazie usieciowanego poli(akrylanu hydroksybutylo-*co*--akrylamidu): synteza, charakterystyka i ocena zdolności do usuwania metali ciężkich

Streszczenie: Metodą polimeryzacji rodnikowej otrzymano dwie serie superchłonnych hydrożeli kopolimerów akrylanu hydroksybutylu i akryloamidu, poli(HBA-*co*-AAm), otrzymano. W pierwszej serii optymalizowano stosunek akrylanu hydroksybutylu do akryloamidu przy stałej ilości metylenobisakryloamidu (MBA) jako czynnika sieciującego. W drugiej serii przy ustalonym stosunku monomerów zmieniano ilość MBA. Strukturę kopolimerów potwierdzono metodą FTIR. Zbadano parametry pęcznienia oraz właściwości mechaniczne. Do badań właściwości adsorpcyjnych w stosunku do jonów Co^{2+}, Ni^{2+} i Cd^{2+} wytypowano hydrożele o wysokim module Younga i wysokim stopniu pęcznienia. Zbadano również wpływ podstawowych czynników, takich jak dawka adsorbentu, czas ekspozycji i pH na efektywność adsorpcji. Zdolność do adsorpcji jonów metali ciężkich zmieniała się następująco: $Co^{2+} > Ni^{2+} > Cd^{2+}$.

Słowa kluczowe: polimery superchłonne, akrylan hydroksybutylu, akryloamid, właściwości adsorpcyjne, usuwanie jonów metali ciężkich.

In the last two decades, the interest in synthesis of smart hydrogels has expanded because of their unique properties such as high swelling in water and elasticity [1–3]. The swelling response to changes in temperature, pH and ionic strength is another important property of these materials [4, 5]. Crosslinked hydrogels prepared from different hydrophilic monomers have been widely utilized in different fields, including contact lenses, drug delivery, diagnostics, pharmaceutical, wound dressing, gene delivery, agriculture, thermo sensitive materials, and food industry [6-9]. Among them, hydrogels prepared from acrylamide derivatives have been used in various fields such as linear polymers, tissue engineering, film making, smart polymers, heavy metal removal, and dye removal [10–15].

Presence of heavy metal ions in water caused by industrial and agricultural processes, even at low concentrations, leads to many environmental and biological problems [16]. Extraction and separation of these ions from wastewater with polymeric materials is one of the most popular methods used in this field [17]. Homopolymer or copolymer hydrogels containing electron donating atoms like oxygen, sulfur and nitrogen can bind heavy metal ions such as Co^{2+}, Ni^{2+}, Cd^{2+}, Mn^{2+} and Cu^{2+} by forming coordinate bonds with

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them; thus, they are widely applied in purification of wastewater [18, 19]. Many studies have reported on synthesis of hydrogels based on acrylamide and acrylate derivatives, which can be used for this purpose. Ayatzhan *et al*. prepared hydrogel composed of poly(N,N-dimethylacrylamide) homopolymer, the prepared hydrogel showed good performance in removing Pb^{2+} from aqueous solution [20]. Essawy and Ibrahim observed that poly(vinylpyrrolidone-*co*-methylacrylate) hydrogel extracted Cu^{2+} more than Cd^{2+} from synthetic wastewater [21]. Hydrogels based on natural polymers such as sodium alginate, diethylaminoethyl dextran, chitosan and starch have also been used as effective materials for removing some heavy metal ions from their solutions [22–24], the amount of extracted heavy metal ions by using diethylaminoethyl dextran ordered as $Zn^{2+} > Mn^{2+} > Pb^{2+} > Cd^{2+}$.

In the present work, we report the synthesis and characterization of crosslinked hydroxybutyl acrylate/acrylamide copolymer with different compositions. The properties of prepared hydrogels were also studied. The capacity of prepared hydrogels to remove heavy metal ions from wastewater was investigated under different conditions.

EXPERIMENTAL PART

Materials

The monomers: hydroxybutyl acrylate and acrylamide were supplied by Aldrich-OMA Chemical Co. Hydroxybutyl acrylate was shaken 2–3 times with 10% NaOH to eliminate hydroquinone inhibitor, and then dried over anhydrous $CaCl_2$ for 10 h. Methylene bisacrylamide as crosslinker was purchased from Merck Chemical Co. The initiator potassium persulphate was provided by Aldrich-OMA Chemical Co., it was recrystallized twice from methanol prior to use. Hydrochloric acid, sodium hydroxide, Nickel chloride hexahydrate, cadmium chloride hexahydrate, and cobalt chloride hexahydrate were purchased from Merck Chemical Co. All solvents were provided by Aldrich-OMA Chemical Co. and used as received.

Methods

Perkin Elmer-1650 spectrophotometer complete with data processing facilities was used to determine the functional groups in the copolymers using a KBr disk method at wavenumber range of 400 to 4000 cm^{-1}. The concentration of heavy metal ions after adsorbing by hydrogels was estimated by using Shimadzu-3600 UV according to the standard procedure. Tensile test of prepared hydrogels was achieved by using Instron 3366 machine analyzer with 3 mm/min as crosshead speed. After plotting strain ($\lambda - 1$) versus stress (τ), the following relation was employed to obtain Young's modulus (E) [25].

$$\tau = E\,(\lambda - 1) \tag{1}$$

where λ – deformed length/undeformed length and τ – applied force.

The equilibrium water content (*EWC*) of a hydrogel was calculated using the weight of fully hydrated samples (W_S) and the weight of the same discs after drying (W_d) in an oven at 50°C for 48 h:

$$EWC\,\% = \frac{W_S - W_d}{W_S} \cdot 100 \tag{2}$$

The following relation was used to calculate the weight reduction of the xerogels:

$$\text{Weight loss during swelling} = \frac{W_0 - W_d}{W_0} \cdot 100 \tag{3}$$

where: W_0 and W_d are the weights of the sample before and after drying, respectively.

Preparation of hydrogels

Two series of hydrogels were prepared, corresponding to the monomers, imitator, and crosslinking agent concentrations. Monomers mixture was made up gravimetrically and dissolved in water/ethanol (80/20) mixture, according to the desired composition (Table 1) in a small stopper flask. The mixture was stirred magnetically for 15 minutes before being moved to glass ampoules. Prior to the reaction, all oxygen was removed from the tubes by purging them with nitrogen for 15 minutes. To ensure complete conversion of the monomers to polymer forms, normally free radical initiated reactions were preferred at conventional temperatures, which ranged from about room temperature to about 100°C. To minimize formation of bubbles in the polymers, polymerization was usually started at a temperature of 70–80°C. The glass ampoules were closed firmly, placed in a 70°C water bath and allowed to polymerize for two days. After that, the temperature was increased, and the tubes were put in

T a b l e 1. Compositions of the synthesized copolymeric hydrogels

Sample	HBA wt%	AAm wt%	MBA wt%	PPS wt%	Water/Ethanol 80/20 ml
Copolymer 1	70	30	1	0.01	10
Copolymer 2	50	50	1	0.01	10
Copolymer 3	30	70	1	0.01	10
Copolymer 4	70	30	1.5	0.01	10
Copolymer 5	70	30	2	0.01	10

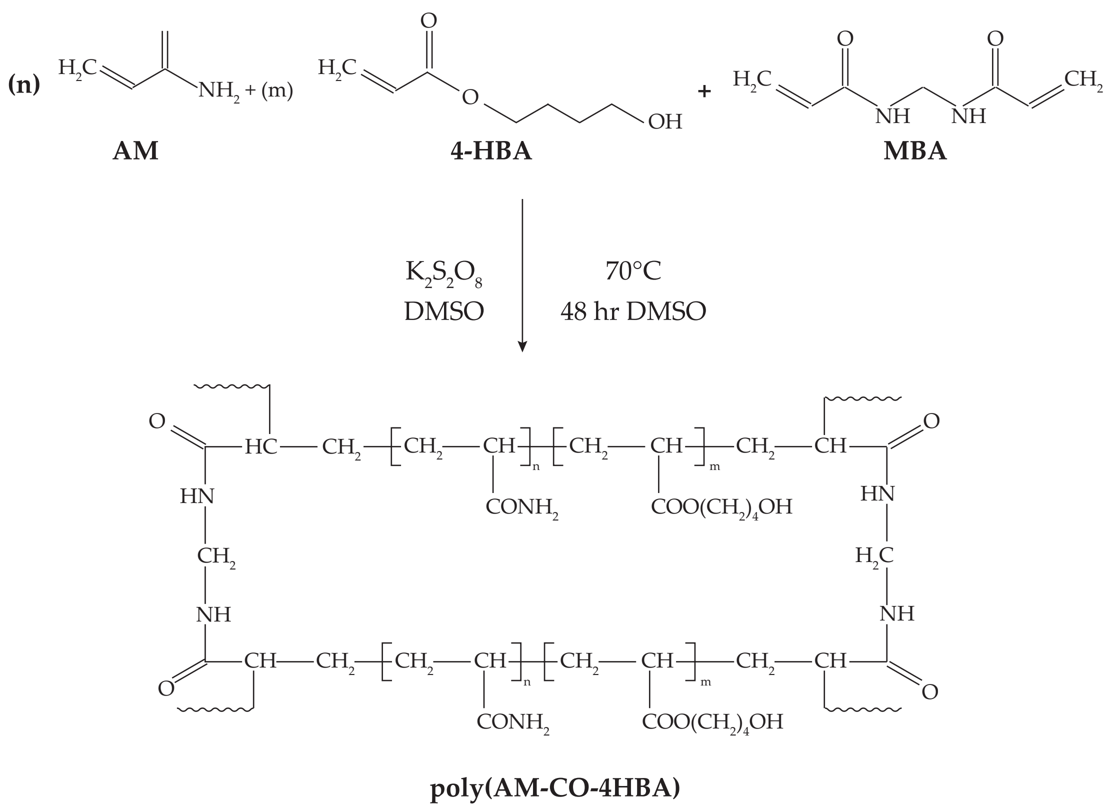

Fig. 1. Reaction scheme of poly(AM-co-4HBA) crosslinking

an oven at 90°C for one more day. Polymerization was usually completed by the end of this time. The reaction scheme is shown in Fig. 1.

Heavy metal removal studies

Since xerogel of composition 70HBA/30AAm/1.5MBA (Co4) had the highest swelling degree and Young's modulus values, it was selected to investigate its performance in heavy metal removal. Salts of $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, and $CdCl_2 \cdot H_2O$ were used to prepare different concentrations of the stock solutions of Co^{2+}, Ni^{2+}, Cr^{2+}, and Cd^{2+}, respectively. Heavy metal solutions were adjusted to pH values of 3, 5, 7, and 9 using sodium hydroxide and hydrochloric acid. The effect of pH value of adsorbed solution, contact time of metal ions with adsorbed solution, and metal ions concentration on the adsorption efficiency of hydrogels was conducted at a temperature of 30°C. All parameters are shown in Table 2.

50 mg of prepared xerogel was placed into 50 ml of aqueous solution of Co. $^+$, Ni^{2+}, and Cd^{2+}. UV spectrophotometer was used to determine the residual of heavy metal ions using their standard curves. The following equation was used to calculate the amount of adsorbed Co^{2+}, Ni^{2+}, and Cd^{2+} (mg) per g of hydrogel:

$$\text{Aa (mg/g)} = \frac{V(C_1 - C_2)}{m} \quad (4)$$

where: C_1 and C_2 are concentration of Co^{2+}, Ni^{2+}, and Cd^{2+} in their aqueous solution before and after removal. m is the mass of dry 70 HBA/30 AAm/1.5 MBA xerogel, and V is the volume of aqueous solution containing heavy metal ions.

RESULTS AND DISCUSSION

FTIR spectra of 70HBA/30AAm xerogel before and after adsorption of Co^{2+}, Ni^{2+}, and Cd^{2+} are shown in Figure 2. The structure of HBA/AAm copolymer before adsorption is shown in Figure 2 (spectrum a). The absorption bands which appear in the FTIR spectra of the copolymer belong to the stretching vibration in different functional groups of their corresponding monomers, and as follows: a band at 1712^{-1} corresponding to ester C=O, 3290 cm^{-1} (amide N-H), 2962 cm^{-1} (alkane C-H), 1678 cm^{-1} (amide C=O), and 1145 cm^{-1} (amide C-N), 1022 cm^{-1} (ester C-O-C).

Figures 2b-d show FTIR spectra of 70HBA/30AAm xerogel with adsorbed Co^{2+}, Ni^{2+}, and Cd^{2+}, respectively. The absorption bands of OH and NH_2 were shifted about

T a b l e 2. pH value, contact time, and metal ion concentration of heavy metal ions adsorption

Metal ion	pH value				Contact time, h	Adsorbent dose, ppm			
Co^{2+}	3	5	7	9		30	500	2000	3000
Ni^{2+}	3	5	7	9	1–24	30	500	2000	3000
Cd^{2+}	3	5	7	9		30	500	2000	3000

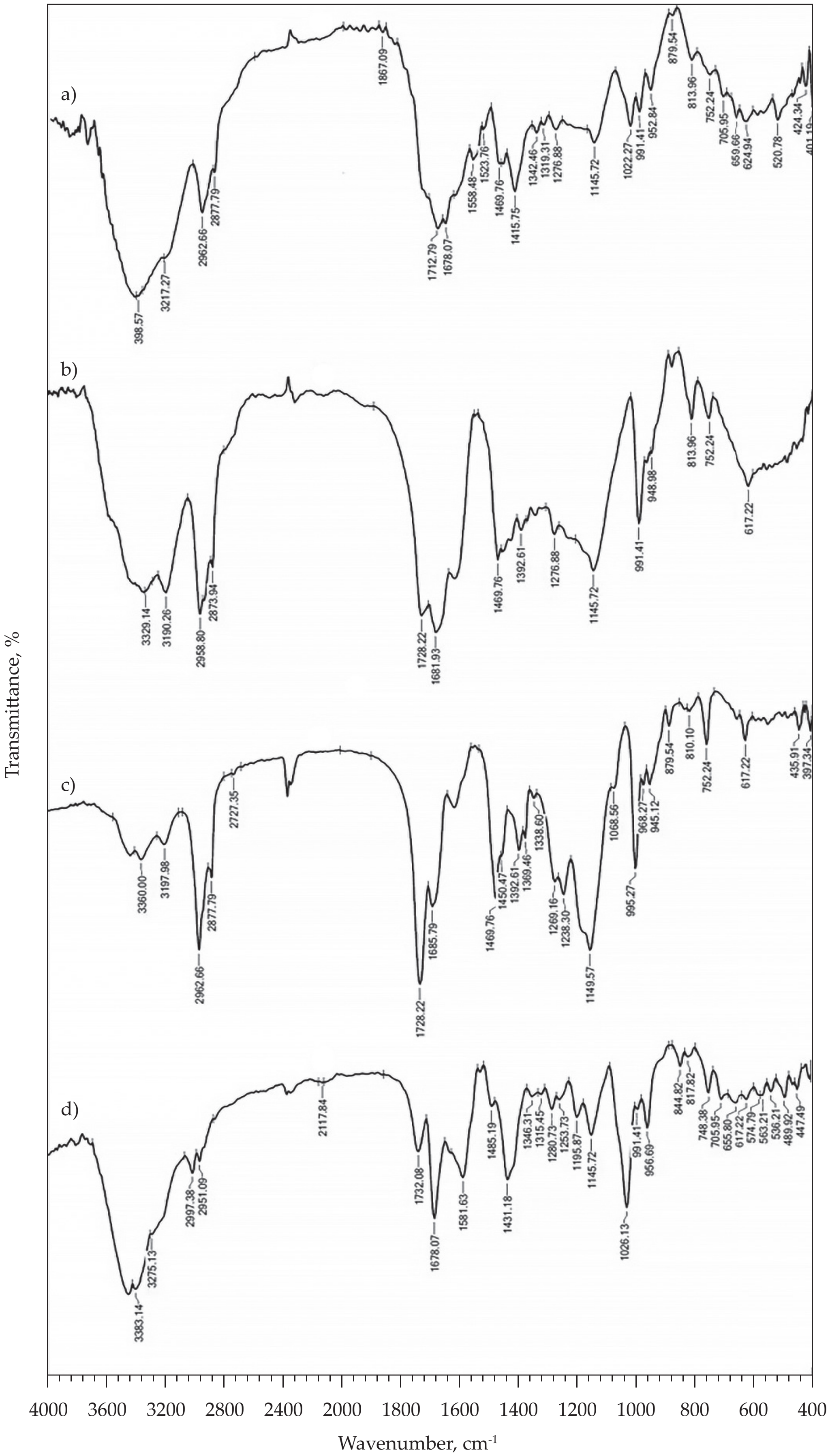

Fig. 2. FTIR spectra of: 70HBA/30AAm hydrogel before (a) and after adsorption of (b) Co^{2+}, (c) Ni^{2+}, and (d) Cd^{2+}

T a b l e 3. Swelling parameters and mechanical properties of prepared hydrogels

Sample code	EWC	Weight loss, %	Young's modulus, kPa
Copolymer 1	96	11	1.23
Copolymer 2	91	9	1.44
Copolymer 3	84	8	1.35
Copolymer 4	93	11	2.06
Copolymer 5	90	10	2.09

15–60 and 10–25 units, respectively, towards lower wave numbers compared with the same bands of original xerogel before heavy metal adsorption.

Swelling parameters

The equilibrium water content (EWC) values of the hydrogels are listed in Table 3, they are in the range of (84–96%). 30HBA/30AAm/1MBA (Copolymer 3) had the lowest swelling capacity, while 70HBA/30AAm/1MBA (Copolymer 1) had the highest EWC. A decrease in the amount of crosslinker MBA allows an easy diffusion of water molecules outside of the gel phase. As expected, the amount of weight loss during swelling in the prepared hydrogels decreases with increasing MBA content. The same behavior was observed when the swelling property of copolymer of N, N-dimethyl acrylamide with acrylic acid (poly(DMA-*co*-AAc) was studied [26].

Mechanical properties

Mechanical properties are also considered as an important characteristic of crosslinked polymers [27, 28]. Tensile test of the 70HBA/30AAm hydrogels, with different concentration of MBA, was performed and the results are listed in Table 3. The results show that as the crosslinking agent increases, the values of Young's modulus increase. The crosslinker restricts the mobility of polymer chains; thus, stronger polymers are obtained.

Heavy metal removal results

Since sample 70HBA/30AAm/1.5MBA of hydrogel showed high degree of swelling and good mechanical properties, it was selected to study its ability as heavy metal adsorbent.

Effect of pH values

As shown in Figure 3, adsorption of Co^{2+}, Ni^{2+}, and Cd^{2+} by 70HBA/30AAm/1.5MBA hydrogel was studied using different pH values (3, 5, 7, and 9). All measurements were carried out using 2000 ppm of adsorbent dose for 24 h. When the pH of the solution is increased from 3 to 5, a greater rise in the adsorption capacity of hydrogel for Co^{2+}, Ni^{2+} and Cd^{2+} occurs. The amino groups of acrylamide undergo protonation at low pH values, which results in electrostatic repulsion with metal ions and reduce the metal's adsorption ability through the complexation process. At higher pH value (9), all heavy metal ions form insoluble metal hydroxides, $Co(OH)_2$, $Ni(OH)_2$, and $Cd(OH)_2$; thus, the adsorption capacity decreases.

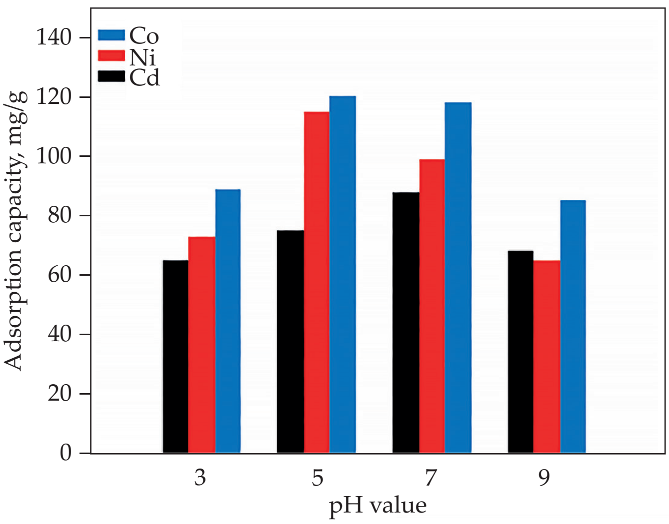

Fig. 3. Effect of pH on removal of Ni^{2+}, Cd^{2+}, and Co^{2+} by 70HBA/30AAm/1.5 MBA hydrogel

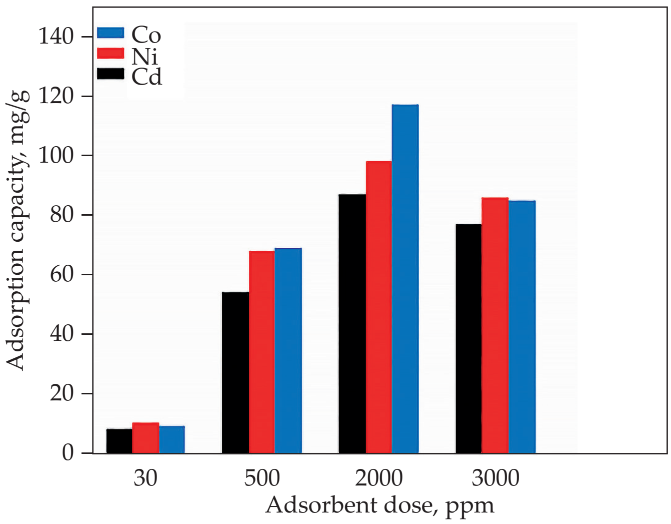

Fig. 4. Effect of adsorbent dose on removal of Ni^{2+}, Cd^{2+}, and Co^{2+} by 70HBA/30AAm/1.5MBA hydrogel

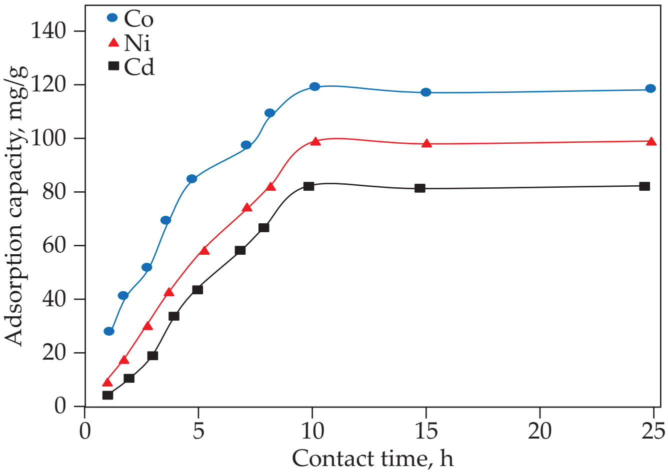

Fig. 5. Effect of contact time on removal of Ni^{2+}, Cd^{2+}, and Co^{2+} by 70HBA/30AAm/1.5 MBA hydrogel

Effect of heavy metal concentration

Figure 4 shows the adsorption capability of the cross-linked copolymer towards Co^{2+}, Ni^{2+}, and Cd^{2+} with various initial adsorbent dose ranging from 30 to 3000 ppm. The experiments were carried out at pH 7 for 24 h. It is clearly observed that, as the initial metal concentration increases, the metal absorption increases rapidly. The absorption then levels off after reaching a maximum at 2000 ppm. The maximum load capacities can be easily determined as 118.6, 99.5 and 88.2 mg/g xerogel for Co^{2+}, Ni^{2+}, and Cd^{2+}, respectively. These findings demonstrated the potential industrial use of HBA/AAm/MBA copolymers for removal of such metals from wastewater.

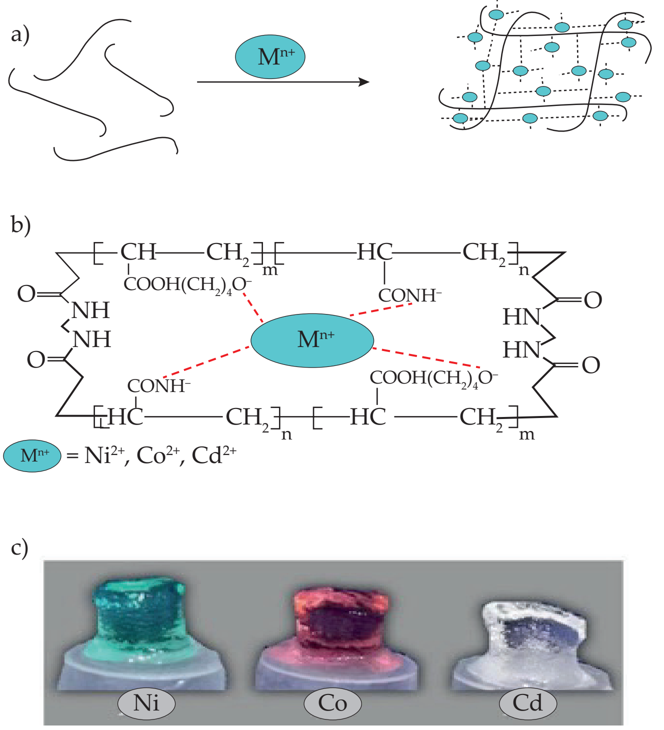

Fig. 6. The interaction between hydrogels and metals: a) and b) the proposed mechanism, c) photographs of hydrogels after heavy metals adsorption

Effect of contact time

The capability of 70HBA/30AAm/1.5MBA hydrogel to remove Co^{2+}, Ni^{2+}, and Cd^{2+} was also studied at different contact times. The pH value and metal ions concentration were kept constant at 7 and 2000 ppm, respectively. The highest binding of all metal ions occurred within the first 10 hours and remained constant for the following 14 hours, as can be seen in Fig. 5.

In all cases of changing pH, adsorbent dose, and contact time, it was clearly observed that 70HBA/30AAm/1.5MBA hydrogel was more effective in adsorption Co^{2+} and Ni^{2+} than adsorption of Cd^{2+}. This occurs because polymeric hydrogels form complexes more easily with metal ions which have a small radius, such as Co^{2+} and Ni^{2+}. Similar findings have been obtained in Arzo Yakar study when poly(N-methyl methacrylamide) and its copolymer with vinyl sulfonic acid were used in removing Co^{2+} and Ni^{2+}. Fig.6 shows the proposed interaction mechanism between hydrogels and heavy metal ions in addition to photographs of hydrogels after heavy metals adsorption.

Thermal analysis

TGA data for 70HBA/30AAm/1.5MBA before and after forming complexes with heavy metals are shown in Fig. 7. In all cases, the sharp increase in weight loss started at about 350°C. Generally, the xerogel before heavy metals adsorption is less stable than complexes with 60% weight loss of 70HBA/30AAm/1.5MBA at about 446°C, which is lower than 482°C, 550°C, and 555°C of 70HBA/30AAm/1.5MBA-Cd, 70HBA/30AAm/1.5MBA-Ni, and 70HBA/30AAm/1.5MBA-Co, respectively. These results could be explained in terms of Co, Ni, and Cd

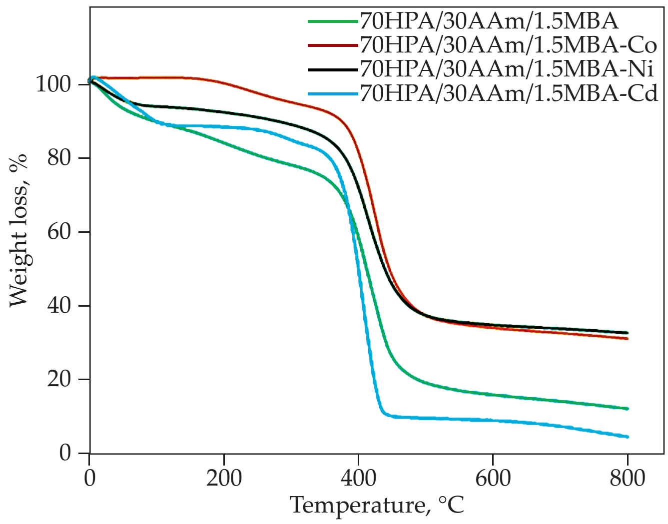

Fig. 7. TGA thermograms of 70HBA/30AAm/1.5MBA, 70HBA/30AAm/1.5MBA-Cd, 70HBA/30AAm/1.5MBA-Ni, and 70HBA/30AAm/1.5MBA-Co

metals remaining undecomposed even at high temperature. In addition, thermal stability of the three complexes indicates that the amount of removed heavy metals ordered as $Co^{2+} > Ni^{2+} > Cd^{2+}$, which is in agreement with the results obtained from experiments.

CONCLUSIONS

Five compositions of poly(hydroxybutyl acrylate-*co*-acrylamide), poly(HBA-*co*-AAm), was successfully synthesized in the presence of different amounts of methylene bisacrylamide as crosslinker. Swelling in water and mechanical properties of the prepared hydrogels were tested to select the most suitable composition, 70HBA/30AAm/1.5MBA, for removal of Co^{2+}, Ni^{2+}, and Cd^{2+} from synthetic wastewater. The effect of using different pH, contact time, and adsorbent dose on the adsorption capacity of the selected xerogel was also studied. Generally, the selected xerogel showed good performance in removing most of heavy metals from synthetic wastewater. Presence of metals in the structure of copolymeric xerogels increased their thermal stability.

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