ELSEVIER

Polymer 44 (2003) 1785–1793

polymer

www.elsevier.com/locate/polymer

Modified polyacrylamide hydrogels and their application in removal of heavy metal ions

Hasine Kaşgöz*, Saadet Özgümüş, Murat Orbay

Department of Chemical Engineering, Faculty of Engineering, Istanbul University, Avcılar Campus, 34320 Istanbul, Turkey

Received 2 October 2002; received in revised form 3 January 2003; accepted 15 January 2003

Abstract

Modified crosslinked polyacrylamides having different functional groups were prepared by Mannich reaction using different amine compounds such as ethylenediamine (EDA), diethylenetriamine (DETA) and triethylenetetramine (TETA) and sulfomethylation reaction. Products were characterized by determination of their basic group content (BGC), hydroxymethyl group content (HMG), equilibrium degree of swelling (EDS) and FT-IR spectra. For Mannich reactions, BGC and EDS changed with amount of employed amine compounds, reaction time and temperature. Sulfomethylation reactions gave products with high BGC and very high EDS. FT-IR spectroscopic analysis confirmed that a parallel hydrolysis reaction occurred along with the expected modification reactions. The products were used for removal of Cu(II), Cd(II) and Pb(II) ion under competitive and non-competitive conditions at different pH. The metal ion removal capacities changed depending their BGC and EDS. While the Mannich products were selective towards Cu(II) ion, the sulfomethylation products were highly selective to Pb(II) ions. The polymers were used several times by regeneration without loss of adsorption capacity and changing of selectivity properties.

Keywords: Modified polyacrylamide hydrogel; Heavy metal ion removal; Competitive adsorption

1. Introduction

Modified polymers can be obtained by copolymerization of monomers with different functional groups or by post-modification of polymerised products. The second option is generally preferred to prepare materials which are difficult to obtain by direct polymerisation of the corresponding monomers. An example is polyacrylamide with amide groups which are stable in the intermediate (or neutral) pH range that can be converted to $-COOH$ groups by hydrolysis, to $-OH$ containing groups by the reacting with formaldehyde, to $-NH_2$ groups by the Hofmann reaction and to $-SO_3$ containing groups by the sulfomethylation reaction [1–3].

Crosslinked hydrophilic polymers capable of imbibing large volumes of water have found widespread applications in bioengineering, biomedicine, food industry and water purification and separation processes [4]. Modified polyacrylamide hydrogels find various commercial applications such as recovery of secondary oil, stabilization of mineral sedimentation, purification of wastewater and metal extraction [5,6]. In recent years, it was determined that crosslinked polymeric materials having functional groups such as carboxylic acid, amine, hydroxyl and sulfonic acid groups could be used as complexing agents for the removal of metal ions from aqueous solutions. Main advantages of such materials are easy loading and, in most cases, stripping of cations with simple chemicals, reusability and the possibility of semi-continuous operation. Ionic polyacrylamide gels have been used for this purpose [4].

In previous works, modified polyacrylamides have been obtained from linear polyacrylamides by various modification reactions such as Mannich [7], Hofmann [8,9] or by copolymerization of different functional monomers, such as dimethylaminoethyl methacrylate, 2-acrylamidopropane sulfonic acid, 3-acrylamido-3-methylbutanoic acid [10–12]. In this work, Mannich reaction was carried out on crosslinked polyacrylamide using ethylenediamine (EDA), diethylenetriamine (DETA) and triethylenetetramine (TETA) and sulfomethylation reaction was carried out on crosslinked polyacrylamide to obtain ion selective hydrogels having different functional groups, for the first

---

* Corresponding author. Tel.: +90-212-591-24-80; fax: +90-212-591-19-97.

E-mail address: hasineka@istanbul.edu.tr (H. Kaşgöz).

0032-3861/03/$ - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
doi:10.1016/S0032-3861(03)00033-8

time. These modified crosslinked polymers were characterized and used as chelating agents for removal of Cu (II), Cd(II) and Pb(II) ion in competitive and non-competitive conditions, again for the first time.

2. Experimental

2.1. Materials and instruments

Acrylamide (AAm) and *N*,*N*′-methylenebisacrylamide (NMBA) were Merck 'for synthesis'. All of the other reagents used were 'extra pure' chemicals. Bidistilled and distilled water was used for polymerization and for modification reactions, respectively.

The FT-IR spectra were obtained by Perkin–Elmer, Spectrum GX model instrument with ATR technique. The Cu (II), Cd(II) and Pb(II) ions determinations were carried out by atomic absorption spectrometry using Varian Spectro AA 220-FS atomic absorption spectrometer.

2.2. Preparation of crosslinked polyacrylamides and modified products

A crosslinked polyacrylamide (CPAAm1) was prepared by free radical polymerisation of acrylamide (AAm) (50 g) and *N*,*N*′-methylenebisacrylamide (NMBA) (0.5 g) in bidistilled water, using $K_2S_2O_8$ (0.15 g) and $KHSO_3$ (0.15 g) initiator couple at 50 °C, as described previously [13]. The polymerisation was also repeated in methanol–water mixture of 1:1 (v:v), to prepare a crosslinked polyacrylamide having higher EDS (CPAAm2), where the nominal crosslinking degree is 0.46% mole. $K_2S_2O_8$ and $KHSO_3$ were used as initiator couple. The reactions were carried out in a 1 l, five necked glass reaction vessel equipped with a mechanical stirrer, reflux condenser, thermometer and N_2 gas inlet. Dissolved oxygen was removed by bubbling purified nitrogen gas for 30 min through water or methanol–water mixture at ambient temperature. Then AAm (50 g) and NMBA (0.5 g) were added to the reactor. The reaction mixture was heated to 50 °C and $K_2S_2O_8$ (0.15 g) and $KHSO_3$ (0.15 g) were added, then the reaction was continued at this temperature for 5 min. The gel obtained was disintegrated in a blender, washed with water and methanol, filtered and dried under vacuum and at 30 °C to constant weight to give a white fine powder. The extent of reaction was followed by the amount of free monomer residue [14].

The Mannich reaction was carried out in reaction system mentioned above by using CPAAm1 and CPAAm2 and different amine compounds. CPAAm1 was swollen in distilled water at ambient temperature for 1.5 h. Then pH was adjusted to 7.0 by addition of dilute HCl and the hydroxymethylation reaction was carried out at 25 °C for 3 h after the addition of HCHO (36.6% (w/w) aqueous solution) to provide a molar ratio of AAm to HCHO 1:0.8. Later the calculated amount of EDA (38.4% aqueous solution) was added to the reactor to provide $r = 1{:}3.2$ and 1:12 ($r =$ the molar ratio of AAm converted into the crosslinked polymer to amine compound). The amination reactions were carried out 50 and 90 °C for 3 and 9 h. The reactions were also repeated with DETA and TETA ($r = 1{:}12$) at 90 °C for 9 h. CPAAm2 was aminomethylated only with EDA ($r = 1{:}12$), at 90 °C for 9 h. For the purification, the gels were disintegrated and suspended in a blender with methanol, filtered and washed with distilled water, until the filtrate was free from amine, as determined by color reaction with ninhydrine [15]. Then, they were washed with methanol and dried under vacuum and at 30 °C, to constant weight to give white fine powders.

The sulfomethylation reactions were carried out in the reaction system used for Mannich reactions. Hydroxymethylation reaction was carried out with HCHO (molar ratio of AAm/HCHO was 1:0.8) at pH = 7.0 followed by the sulfonation reaction with Na_2SO_3 (molar ratio of AAm/Na_2SO_3 was 1:0.8). CPAAm2 was swollen in distilled water at ambient temperature with stirring for 1.5 h and HCHO (36.6% aqueous solution) was added to reaction mixture at pH = 7.0. The reaction mixture was heated to 90 °C and the reaction was continued for either 3 or 9 h. For the purification, the gels were disintegrated and suspended in a blender with a methanol, filtered and washed with distilled water to remove sodium sulfite residue. Then they were washed with methanol, dried under vacuum and at 30 °C to constant weight to give white fine powders.

2.3. Properties of modified crosslinked polyacrylamides

For determination of basic group content. The basic group content (BGC) of modified polymers obtained with EDA and DETA were expressed as amine value (AV). The polymers (50 mg) were swollen in distilled water (25 ml, neutralized against methyl orange indicator) and titrated with HCl (0.1N). The results are given as mmol/g dry polymer. The following procedure [16] was used to determine the amount of total basic group in the sulfomethylated products ($-SO_3Na + -NH_2$ groups) and aminomethylated polymers prepared by using TETA.

The polymers (50 mg) were equilibrated with HCl (20 ml, 0.1N) by stirring for 24 h in a sealed flask, followed by filtration and washing the residue with distilled water to remove unreacted HCl and titration of filtrate with NaOH (0.1N) in the presence of phenolphthalein indicator.

For determination of hydroxymethyl group content. The polymers (50 mg) were kept in NaOH (10 ml, 2N) for 48 h. Then, the pH was adjusted to 4.0 in the presence of bromophenol blue indicator and hydroxylamine hydrochloride (10 ml, 10% aqueous solution) was added and after 5 min the mixture was titrated with KOH (N/3) [17,18]. The results are given as HMG%.

For determination of equilibrium degree of swelling. The polymers were swollen in distilled water for 4 days and the degree of swelling was determined gravimetrically. The amount of water adsorbed under equilibrium conditions is given as the equilibrium degree of swelling (EDS%).

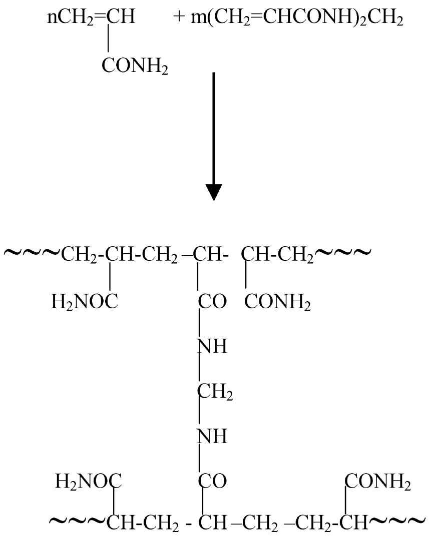
For determination of metal ion removal capacities. The polymers (50 mg) were added to copper (II) sulfate solution (0.01574 mol/l, 25 ml), which had pH of 5.5. The amount of residual metal ion in the solution was determined up to 1 h contact by atomic absorption spectrometry. The capacity results are given as mmol/g dry polymer. Cu(II) ion removal capacity of two polymers (M8 and S2) were also determined by addition of the polymers to Cu(II) solutions, after the pH was brought to 3.0 or 4.5, by dilute HNO_3 addition.

Cu(II), Cd(II) and Pb(II) ion removal capacities of some polymers (M8, M9, M10 and S2) were determined in non-competitive conditions at pH 4.5. Furthermore, the metal ion selectivity properties of these polymers were also determined in solutions containing Cu(II), Cd(II) and Pb(II) ions together at pH = 4.5 and 3.0. The concentration each metal ion was 0.01574 mol/l.

3. Results and discussion

3.1. Preparation of crosslinked polyacrylamides

The crosslinked polyacrylamide (CPAAm1) which had a significantly high EDS, in comparison with similar polymers [16,19], was prepared by using a low amount of NMBA with polymerisation of the monomers in water, as reported previously [13] (Scheme 1). The crosslinked polyacrylamide (CPAAm2) with an even higher EDS was prepared by solution polymerisation in water–methanol mixture. It is known that, if gel formation takes place in the presence of a good/poor solvent mixture (e.g. water–methanol for polyacrylamide), a phase separation or desolvation of polymer chains can occur. This causes an irreversible process of chain clustering, leading to the formation of a network of a polymer chain aggregates with a permanent macroporous structure [20,21]. Thus, while CPAAm1, which was prepared in water, had an EDS of 3280%, the CPAAm2 prepared in methanol–water mixture had an EDS of 5740% due to higher macroporosity. While CPAAm1 was obtained with a yield of 91.3%, the yield of CPAAm2, as expected, was only 71.7% [22].



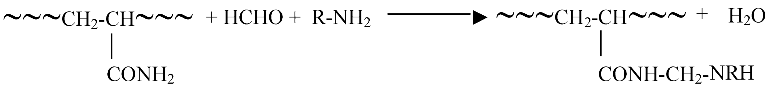
Scheme 1. Preparation of crosslinked polyacrylamide.

3.2. Mannich reaction

The aminomethylated polyacrylamides with secondary and tertiary amino groups can be obtained by Mannich reaction (Scheme 2) and they can be converted to their cationic derivatives by quaternization. The Mannich reaction can be carried out either by initial preparation of Mannich base from formaldehyde and amine followed by reaction with polyacrylamide, or amination of modified polyacrylamide with amine compound after its hydroxymethylation with formaldehyde [3]. When the two-step reaction is carried out, poly(*N*-hydroxymethylacrylamide) is obtained in hydroxymethylation reaction. In the amination reaction, some steric hindrances can be observed, due to the structure of amine used. The reactivities of larger amine molecules were found to be lower than smaller ones [1]. In addition, the use of larger amine molecules increased the crosslink density of the polymers [23].

The conditions of Mannich reactions of crosslinked polyacrylamides and the properties of modified polymers are given in Table 1. The M1–M9 products were obtained by hydroxymethylation with HCHO and followed by amination with different mol ratios of EDA, reaction time and temperature. The AV of these polymers varied between 0.87 and 2.78 mmol/g and increased with the increase of amine content, and also with temperature and reaction time. For example, with increase in reaction time from 3 to 9 h (M1,M2) at 50 °C, the AV increased from 0.87 to 1.34 mmol/g. But increase in the reaction temperature was more effective where AV increased from 0.87 to 1.88 for 3 h (M1–M3) and from 1.34 to 2.52 for 9 h (M2–M4). In addition, when the AAm/amine molar ratio (r) was increased from 3.2 to 12, the AV of the polymers increased. Thus, reactions carried out at higher temperatures, with longer times and employment of larger amount of amine gave the products with the highest AV. In case of the reaction carried out with CPAAm2 and EDA under these conditions (M9), similar properties as with CPAAM1 (M8) were obtained. When the DETA or TETA was used instead of EDA (M10,M11) at 90 °C for 9 h with $r = 12$ the products had similar AV. The amine values of polymers are smaller than the theoretical values, it is probable that steric effects, the slow diffusion rates of high amine molecules into polymer matrix and additional crosslinking of diamines decreased the amine values of polymers.

The EDS, in general, increased with the AV of the polymer. But especially at the higher reaction temperature of 90 °C, increasing the reaction time decreased EDS



$$\sim\sim\sim CH_2\text{-}\underset{\overset{|}{CONH_2}}{CH}\sim\sim\sim + HCHO + R\text{-}NH_2 \longrightarrow \sim\sim\sim CH_2\text{-}\underset{\overset{|}{CONH\text{-}CH_2\text{-}NRH}}{CH}\sim\sim\sim + H_2O$$

Scheme 2. Preparation of Mannich type products.

slightly due to crosslinking reactions (M3,M4 and M7,M8). It is also known that larger amine molecules increase the crosslink density of the polymers [23], and decrease EDS. This is clearly confirmed when TETA was used instead of EDA. This crosslinking reaction was also confirmed by the Mannich reaction, which gave the non-soluble polymers, of linear polyacrylamide. Although the polymers M8 and M11 had similar AV (2.59 and 2.67 mmol/g) EDS was low for the latter (17,300 and 5200%, respectively). The EDA aminomethylated products had approximately 6 times higher EDS than that of the unmodified CPAAm1.

The HMG content of the products (M1–M11) varied between 1.4–6.9. In general, HMG content decreased with the increase of AV. Lower HMG content values were obtained with DETA or TETA than EDA (M8, M10 and M11). This is probably due to the fact that the crosslinking reaction increases in case of larger amine molecules. For the reactions carried out at 90 °C for 3 and 9 h (M3,M4 and M7,M8), the AV of the polymers increased but their HMG contents did not change. This indicates that at this temperature, a parallel transamidation reaction also occurred during the Mannich reaction.

3.3. Sulfomethylation reaction

The anionic derivatives of polyacrylamides can be obtained by sulfomethylation with formaldehyde and sodium bisulfite (or sodium sulfite) [3] (Scheme 3). The sulfomethylation reaction is quite sensitive to pH of the medium. At low pH values, the reaction is almost negligible, but at pH 10 to 12 the reaction is very rapid. So, the reaction is carried out approximately at pH = 12 either by NaOH and sodium bisulfite or with sodium sulfite only, which requires no addition of NaOH due to hydrolysis of sulfite ions to bisulfite and hydroxyl ions. In previous works [1,3], it was mentioned that the reaction is very rapid at high temperatures but the conversion was only 50% due to steric hindrance of bulky sulfomethyl groups [3]. In addition, we have determined that parallel hydrolysis reaction also occurred during the sulfomethylation reaction and carboxylate groups were also present on the polymer chain.

The conditions of sulfomethylation reactions and the properties of the polymers are given in Table 2. Both of the products (S1,S2) had the highest BGC and EDS obtained in this work. S1 has the BGC of 3.56 mmol/g and EDS of 196,800%, and the increase in the reaction time increased the BGC and EDS slightly to respectively, 4.08 mmol/g and 203,400%. These values are very high in comparison with the similar polymers used for complexation of metal ions [16,19]. It is interesting that the sulfomethylation reaction products had approximately 35 times higher EDS than the unmodified crosslinked polyacrylamide (CPAAm2). This great increase of EDS is due to ionic repulsion of sulfonate and carboxylate groups.

3.4. FT-IR spectra of polymers

The FT-IR spectra of crosslinked polyacrylamide and two of modified polymers (M8 and S2) are shown in Fig. 1. Crosslinked polyacrylamide exhibits the characteristic absorption peaks of polyacrylamide [24,25]. In the spectrum, absorption peaks at 1650–1660 (C=O group of amide

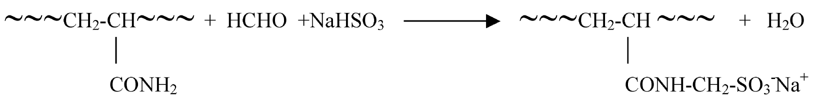
Table 1
The conditions of Mannich reactions of CPAAm1 and the properties of modified polymers

Polymers[a]	Amine	Molar ratio (AAm/HCHO/amine)	Amination[b]		AV (mmol/g)	HMG (%)	EDS[c] (%)	Cu(II) ion removal capacity (mmol/g)
			Temperature (°C)	Time (h)				
M1	EDA	1/0.8/3.2	50	3	0.87	6.9	15,500	0.86
M2	EDA	1/0.8/3.2	50	9	1.34	6.8	16,400	1.19
M3	EDA	1/0.8/3.2	90	3	1.88	5.3	19,400	1.86
M4	EDA	1/0.8/3.2	90	9	2.52	5.3	17,300	2.32
M5	EDA	1/0.8/12	50	3	1.22	5.6	17,500	1.14
M6	EDA	1/0.8/12	50	9	1.48	5.5	17,700	1.36
M7	EDA	1/0.8/12	90	3	2.07	5.1	19,600	1.98
M8	EDA	1/0.8/12	90	9	2.59	5.1	17,300	2.35
M9	EDA	1/0.8/12	90	9	2.78	5	17,400	2.37
M10	DETA	1/0.8/12	90	9	2.77	1.4	16,000	2.76
M11	TETA	1/0.8/12	90	9	2.67	3.8	5200	2.06

[a] M9 was prepared from CPAAm2.

[b] The amination reactions were carried out after hydroxymethylation with formaldehyde at 25 °C for 3 h.

[c] EDS of CPAAm1 and CPAAm2 were 3280 and 5740%, respectively.



$$\sim\sim\sim CH_2\text{-}\underset{\substack{|\\ CONH_2}}{CH}\sim\sim\sim + HCHO + NaHSO_3 \longrightarrow \sim\sim\sim CH_2\text{-}\underset{\substack{|\\ CONH\text{-}CH_2\text{-}SO_3^-Na^+}}{CH}\sim\sim\sim + H_2O$$

Scheme 3. Preparation of sulfomethylation products.

(amide I), 1615 (deformation vibration of $-NH_2$ groups (amide II)), 1450 ($-CH_2$), 1400–1420 and 1170–1190 (deformation vibration of $-NH$ groups), 1315–1320 (stretching vibration of $-NH$ groups) and 1120 cm^{-1} (C–N and N–H bonds (amide III)) are present. In the spectra of M8, in addition to similar absorption peaks, a new absorption peak partially due to C–N bond of hydroxymethylation of primary amide groups [26] and also partially due to carboxylate groups appeared at 1540 cm^{-1}. This peak and the other new peak observed at 1395 cm^{-1} (due to carboxylate groups) [26] show that a parallel hydrolysis reaction occurred during the modification reactions. In addition, compared to crosslinked polyacrylamide, the intensity of the peaks at ~1650 cm^{-1} (C=O groups of amide) decreased and those of at 1315 cm^{-1} (NH groups of amide) increased, due to the effect of amine groups bonded to the polymer chain. Additionally, absorption peaks at 994 and 948 cm^{-1} due to primary amine groups exist. In the spectrum of S2, the new absorption peaks around 1040–1060 and at 680 cm^{-1} are due to sulfonate groups [26]. Furthermore, the presence of peaks at 1551 and 1399 cm^{-1} again confirm the parallel hydrolysis reaction.

3.5. Metal ion removal capacities of modified polymers

3.5.1. Non-competitive conditions

The complexion of heavy metal ions by a chelating ligand is strongly dependent on the pH of the medium [27]. This effect can be observed especially the formation of the coordination bond between nitrogen and metal atoms. M8 and S2 were added to Cu(II) solutions of pH = 3.0, 4.5 and 5.5 to investigate the effect of pH (Fig. 2). As expected, the Cu(II) ion removal capacity increased with increase in pH, especially in case of S2. High adsorption at higher pH values shows that copper ions interact with unprotonated amine groups by chelating [28]. In addition, at low pH, the carboxylic groups are mostly present in non-ionized form and no interaction can occur between the carboxylic groups and the metal ions. On increasing the pH, the carboxylic groups are ionized and spaced along the polymeric chains which increase the probability of interaction between the carboxylic groups and metal ions in the solution. Thus the Cu(II) ion removal capacities of the products were determined by batch equilibrium technique at moderate pH of 5.5. This was considered to be optimal, since copper precipitates as cupric hydroxide at pH >6, at ambient temperature.

CPAAm1 and CPAAm2 were not effective in removal of Cu(II) ions since amide groups alone cannot form complexes with copper ions [29]. The Cu(II) ion removal capacities of CPAAm1 and CPAAm2 were 2.7×10^{-2} and 2.4×10^{-2} mmol/g, respectively.

As seen from Table 1, products of Mannich reaction obtained from EDA (M1–M9) show quite a linear relationship of increase in ion removal capacity with increase in AV, reaching a maximum of 2.37 mmol/g Cu(II) ion removal capacity for the 2.78 mmol/g AV (Fig. 3, Table 1). In general, a molar ratio of approximately 1:1 of Cu(II) ion to amine group in a chelating agent was observed as mentioned in a previous article [19], although Cu(II) ions could have been partially chelated with the carboxylate groups as well as the amine groups [30]. The EDS of products also effects their Cu (II) ion removal capacities. For instance, the product obtained with TETA (M-11) has lower Cu(II)ion removal capacity than EDA (M8) due to its lower EDS, although it has higher AV.

Among the sulfomethylation reaction products, S1 had a quite high Cu(II) ion removal capacity (3.56 mmol/g) due to its high basic group content (sulfonate and carboxylate groups) and high EDS (Table 2). The Cu(II) ion removal capacity was found to be even higher (4.07 mmol/g) for S2 due to further increase of the same properties, making it the most efficient sample among these modified polyacrylamides.

There was no previous work in literature on such aminomethylated and sulfomethylated polyacrylamide hydrogels and their application in metal ion removal. On the other hand, in some works [16,19], aminofunctionalized polyacrylamides prepared by transamidation reaction and these polymers had maximal Cu(II) ion removal capacities

Table 2
The conditions of sulfomethylation reaction of CPAAm2 and the properties of modified polymers

Polymers	Sulfonation[a]		BGC (mmol/g)	HMG (%)	EDS[b] (%)	Cu(II) ion removal capacity (mmol/g)
	Temperature (°C)	Time (h)				
S1	90	3	3.56	3.05	196,800	3.56
S2	90	9	4.08	2.92	203,400	4.07

[a] Sulfonation reaction was carried out after hydroxymethylation with formaldehyde at 25 °C for 3 h.

[b] The EDS of CPAAm2 was 5740%.

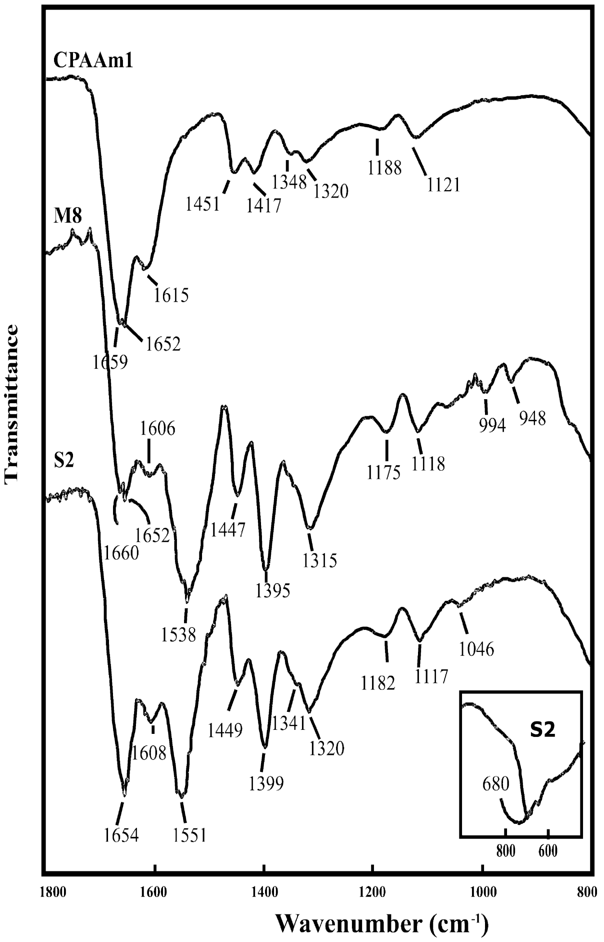


Fig. 1. The FT-IR spectra of CPAAm1 and modified polymers M8 and S2.

of 1.67–2.41 mmol/g. The aminomethylated and sulfomethylated polyacrylamides prepared in this work had maximal ion removal capacities of 2.78 and 4.07 mmol/g, respectively. It is interesting that, Cu(II) ion removal capacities of these polymers are considerably higher than the other products mentioned above.

Cu(II), Cd(II) and Pb(II) ion removal capacities of some polymers (M8, M10, M11 and S2) from the single metal aqueous solutions was also investigated with batch equilibrium technique under similar conditions at pH = 4.5. Although the capacities of chelating agents increase with increasing pH [16,31], since lead hydroxide precipitated above pH = 4.5, at this relatively high concentration, experiments were carried out at this pH. As seen from Table 3, the removal capacities of polymers were lower than expected from their amine values (basic group content for S2). This must be due to the lower pH since the Cu(II) ion removal capacities of all polymers were lower than those at pH = 5.5. The polymers' Cu(II) ion removal capacity was higher than those of the other ions. M10 and M11 polymers had the highest Cu(II) and Pb(II) removal capacities, respectively. The Cd(II) ion removal capacities of all polymers were low in all cases.

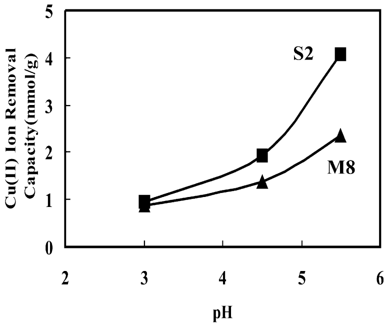


Fig. 2. The effect of pH on the Cu(II) ion removal capacities of M8 and S2.

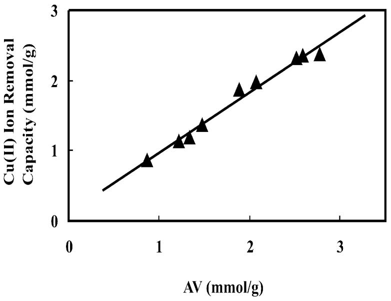


Fig. 3. The effect of amine value (AV) on the Cu(II) ion removal capacity for the Mannich reaction products (M1–M8).

3.5.2. Competitive conditions

It is be hoped that in the presence of different metal ions, one metal ion could be selectively adsorbed by a chelating agent. Adsorption capacity of a polymeric ligand towards the different metal ions, effect of pH of the feed metal solutions, adsorption equilibrium time are important factors over the selectivity properties of ligands in competitive adsorption. To investigate such items, competitive adsorption of Cu(II), Cd(II) and Pb(II) ions by the M8, M10, M11 and S2 polymers from solutions containing them together was carried out. The concentration of each metal ion in the mixture was again 0.01574 mol/l. The pH of this solution was adjusted to either 4.5 or 3.0 by addition of dilute HNO_3. In experiments, a fixed amount of polymer was equilibrated with the mixture of metal ion solutions and the adsorption of each metal ion was followed up to 1 h contact time. The removal capacities of these polymers in ternary mixture of

Table 3
The metal ion removal capacities of modified polyacrylamides in single solutions at pH = 4.5

Polymer	Metal ion removal capacity (mmol/g)			Amine value (mmol/g)
	Cu(II)	Cd(II)	Pb(II)	
M8	1.37	0.53	1.20	2.59
M10	1.99	0.62	0.42	2.77
M11	1.82	0.60	1.53	2.67
S2	1.93	0.42	1.42	4.08[a]

[a] Basic group content.

metal ions at pH = 4.5 are given in Fig. 4. The metal ion removal capacity is expressed as mmol/g and the percentages given on top of the bars are selectivities found from adsorption ratios.

As expected, the total metal ion adsorption capacities of CPAAM1 and CPAAM2 were again practically nil. However, the modified crosslinked polyacrylamides had high metal ion removal capacities and different selectivities as seen from Fig. 4. The M8 polymer which was prepared with EDA had the total metal removal capacity of 2.45 mmol/l and was not significantly selective to any metal ion. The other Mannich product prepared with DETA (M10) possessed higher removal capacity and was distinctly selective towards Cu(II) ions. It is quite probable that this selectivity is due to the secondary amine groups in the polymer. It is interesting that M11 polymer prepared with TETA had the lower selectivity towards Cu(II) ion compared to M10, although TETA has higher amount of secondary amine groups than DETA. This must be the result of lower amine value and decrease in swelling due to crosslinking during the Mannich reaction. S2 polymer, on the other hand, showed a very distinct selectivity towards Pb(II) ions due to the presence of sulfomethylated and carboxylate groups in the polymer.

The Cu(II) ion selectivity of the Mannich products shifts to Pb(II) ions at pH = 3.0 (Fig. 5) since Cu(II) ion cannot form efficient complexes between amine and carboxylate groups at low pH [28,31]. This effect is clearly seen from Fig. 6 where adsorption of ions from ternary mixtures by M8 polymer at pH = 3.0, 4.0 and 4.5 is given. The total metal ion removal capacity of polymer decreased with decreasing pH and selectivity shifted from Cu(II) ion to Pb(II) ion as the pH is lowered.

The sulfomethylation product (S2) at pH = 4.5 had a low metal ion removal capacity despite its high basic group value. It may be suggested that the polymer forms a dense complex on the surface which prevents the diffusion of metal ions into the polymer. But partial precipitation of $Pb(OH)_2$ complexes at this pH might have also contributed to 'shell' formation. This is confirmed by higher ion removal at lower pH of 3. The same must be true for M11 polymer which shows an increase of ~600% higher Pb(II) ion removal at pH = 3.0, contrary to the other Mannich products. Also, ionization at the amine and carboxylate groups at this pH results in increase in swelling which would permit diffusion of more ions into the polymer.

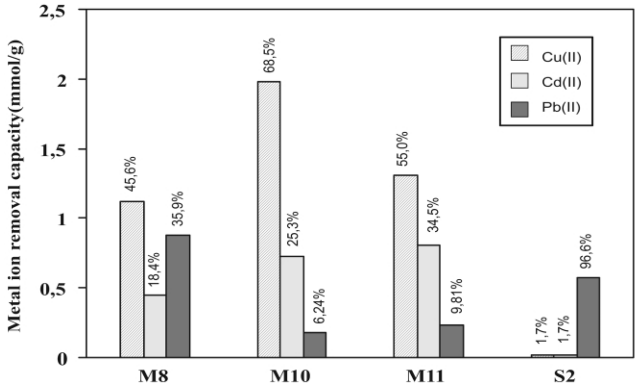


Fig. 4. The metal ion removal capacities and selectivity properties of M8, M10, M11 and S2 polymers in ternary mixtures at pH = 4.5. (Total metal ion rem.cap.(mmol/g): M8 = 2.45, M10 = 2.89, M11 = 2.35, S2 = 0.59 and selectivity (%) = adsorbed metal ion for each metal ion/total adsorbed metal ions).

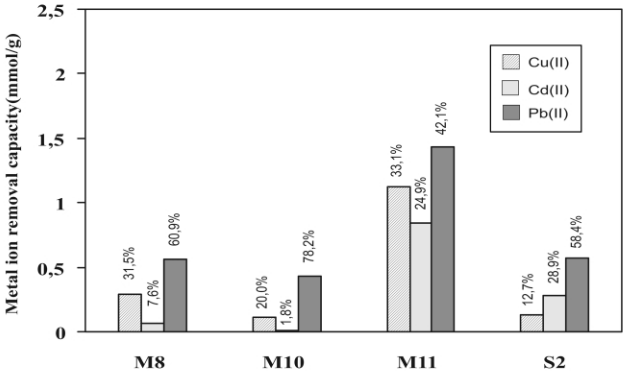


Fig. 5. The metal ion removal capacities and selectivity properties of M8, M10, M11 and S2 polymers in ternary mixtures at pH = 3.0. (Total metal ion rem.cap.(mmol/g): M8 = 0.92, M10 = 0.55, M11 = 3.39, S2 = 0.98 and selectivity (%) = adsorbed metal ion for each metal ion/total adsorbed metal ions).

3.5.3. Adsorption rate

The rapid adsorption of metal ions by the adsorbent is important for practical use, shortening the treatment of wastewater during filtration. The change in amount of adsorbed metal ions with time for of M8 and S2 are shown in Figs. 7 and 8, respectively. It was observed that the adsorption process was very fast and the equilibrium was approached within the first 5 min of the process. After this period, the adsorption rate was very slow and saturation was reached within approximately 20 min for all metal ions. This high initial rate suggests that the adsorption occurs mainly on the polymer surface.

Previously prepared polymeric sorbents have adsorbed different metal ions from solutions in competitive or non-competitive conditions with different adsorption rates changing between 30 min and 24 h [16,19,32]. The

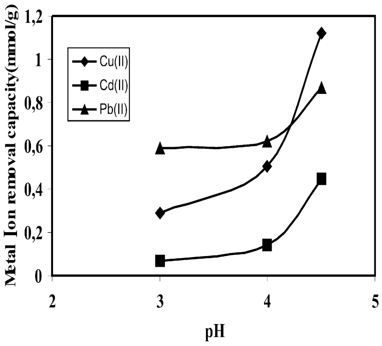


Fig. 6. The effect of pH on the metal ion removal capacities of M8 in competitive conditions.

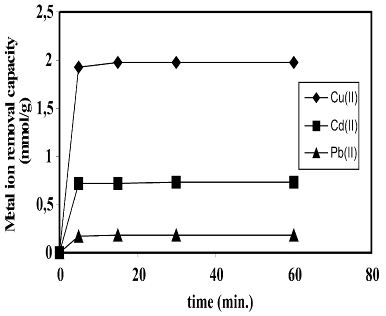


Fig. 7. Adsorption rates of metal ions by M8 polymer.

modified crosslinked polyacrylamides are interesting that the adsorption rates for removal of Cu(II), Cd(II) and Pb(II) ion from solutions are very fast compared with previous works [16,19].

3.5.4. Regeneration studies

To be viable materials for practical use, the modified polyacrylamides must be easily desorbed under suitable conditions and reusable. Desorption of the adsorbed metal ions from polymers was also studied with a batch equilibrium technique. In case of Cu(II) ions polymers were left in contact with 0.1N HCl for about 1 h and then filtered, washed for removal of excess HCl and neutralized with 0.1N NaOH, filtered and washed again for removal of excess NaOH. The regeneration process was repeated for 3 cycles. As seen in Table 4, the polymers showed stable Cu(II) ion removal capacities after repeated regeneration. Regeneration of the M8 polymer was also carried out with ternary mixture of metal ions (Table 5) and it was observed that the polymer selectivity and adsorption capacities did not change with regeneration.

4. Conclusion

The Mannich and sulfomethylation reactions of crosslinked polyacrylamides obtained in water or water–methanol mixtures were investigated under various conditions. In Mannich reactions, the AV of products increased with the amount of amine compound used, reaction temperature and time. The EDS of Mannich products were

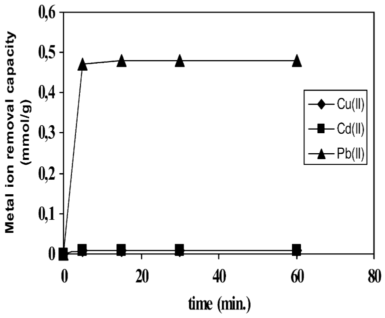


Fig. 8. Adsorption rates of metal ions by S2 polymer.

Table 4
The amounts of Cu(II) ions adsorbed/desorbed by some modified crosslinked polyacrylamides

Cycle[a]	M8		M10		M11		S2	
	Adsorbed Cu(II) ion (mmol/g)	Desorbed Cu(II) ion (mmol/g)	Adsorbed Cu(II) ion (mmol/g)	Desorbed Cu(II) ion (mmol/g)	Adsorbed Cu(II) ion (mmol/g)	Desorbed Cu(II) ion (mmol/g)	Adsorbed Cu(II) ion (mmol/g)	Desorbed Cu(II) ion (mmol/g)
1	2.35	2.31	2.76	2.75	2.06	2.03	4.07	4.03
2	2.38	2.36	2.78	2.74	2.11	2.08	4.09	4.05
3	2.36	2.34	2.78	2.76	2.08	2.04	4.08	4.06

[a] See text for the cycle procedure.

Table 5
The amounts of metal ions adsorbed/desorbed by M8 polymer and the selectivity properties after regeneration

Cycle	Adsorbed metal ions (mmol/g)				Desorbed metal ions (mmol/g)			
	Cu(II)	Cd(II)	Pb(II)	Total	Cu(II)	Cd(II)	Pb(II)	Total
1	1.12	0.45	0.88	2.45	1.11	0.43	0.88	2.42
2	1.13	0.44	0.89	2.46	1.12	0.41	0.86	2.39

approximately six times higher than those of the crosslinked polyacrylamides. Employment of larger amine molecules increased crosslinking and decreased the EDS of the polymers. Hydrolysis reaction occurred along with the expected modification reaction and the polymers also had carboxylate groups. The products obtained from CPAAm2 with sulfomethylation reaction had quite high BGC and very high EDS (approximately 35 times higher than CPAAm2).

These modified polyacrylamides were used for removal of Cu(II), Cd(II) and Pb(II) ions under competitive and non-competitive conditions. Their removal capacities changed mainly according to their AV (BGC) and EDS, and as expected increased with increase in pH. The maximum Cu(II) ion removal capacity of 4.07 mmol/g was obtained with sulfomethylation reaction products. While the Mannich products were mainly selective towards Cu(II) ions the sulfomethylation products were distinctly selective towards Pb(II) ions.

Acknowledgements

This work was supported by Research Fund of The University of Istanbul. Project number: Ö-1018/07062001. We also thank Dr İrfan Ünlüsayın from Mustafa Nevzat İlaç San. A.Ş. for help in FT-IR analysis and Dr Kubilay Güçlü from The University of İstanbul, Department Chemistry for AAS analysis.

References

[1] Kawaguchi H, Hoshino H. J Colloid Interface Sci 1984;97(2): 465–75.
[2] Kamel AA, Ma CM, El-Aasser MS, Micale FJ, Vanderhoff JW. J Dispersion Sci Technol 1981;2:315.
[3] Schiller AM, Suen TJ. Ind Engng Chem 1956;48:2132.
[4] Finch CA. Specialty polymers. New York: Wiley; 1982.
[5] Wu XY, Hunkeler D, Haniele AE, Pelton RH, Woods DR. J Appl Polym Sci 1991;42:2081.
[6] Warshawsky A. Polymeric ligands in hydrometallurgy. In: Sherrington DC, Hodge P, editors. Synthesis and separations using functional polymers. Chichester: Wiley; 1988. p. 325.
[7] Pelton RH. J Polym Sci, Polym Chem Ed 1984;22:3955–6.
[8] Tanaka H, Ödberg L. J Polym Sci, Part A: Polym Chem 1989;27: 4329–30.
[9] Tanaka H. J Polym Sci, Polym Chem Ed 1979;17:1239–45.
[10] Dusek K, Janacek J. J Appl Polym Sci 1975;19:3061–75.
[11] Kremer M, Pothmann E, Rössler T, Baker J, Yee A, Blanch H, Prusnitz JM. Macromolecules 1994;27:2965–73.
[12] Yao KJ, Zhou WJ. J Appl Polym Sci 1994;53:1533–8.
[13] Kaşgöz H, Özgümüş S, Orbay M. Polymer 2001;42:7497–502.
[14] Snell FD, Ettre LC, Encyclopedia of industrial chemical analysis, vol. 4. New York: Wiley-Interscience; 1973. p. 160.
[15] Spackman PH, Stein WH, Moore S. Anal Chem 1958;30:1190.
[16] Latha AG, George BK, Kannan KG, Ninnan KN. J Appl Polym Sci 1991;43(6):1159–63.
[17] Urbanski J, Czerwinski W, Janicka K, Majewska F, Zowall H. Amino resins. Handbook of analysis of synthetic polymers and plastics, New York: Wiley; 1977. p. 194–211.
[18] De Jong JI. Rec Trav Chim 1953;72:653–4.
[19] Mathew B, Pillai VNR. Polymer 1993;34(12):2650–8.
[20] Jervis L. Polymers in affinity chromatography. In: Sherrington DC, Hodge P, editors. Synthesis and separations using functional polymers. New York: Wiley; 1988. p. 265–304.
[21] Okay O. Prog Polym Sci 2000;25:711–79.
[22] Jose L, Mathew B, Pillai VNR. Polymer 1993;34(18):3963–5.
[23] Shambhu MB, Theodorakis MC. J Polym Sci, Polym Chem Ed 1977; 15:525–31.
[24] Hummel DO. Atlas Der Kunststoff-Analyse. Munchen: Carl Hanser; 1968.
[25] Hummel DO, Scholl KF. Infrared analysis of polymers, resins and additives on atlas. Munchen: Carl Hanser; 1973.
[26] Bellamy LJ, The infrared spectra of complex molecules, vol. 1. London: Chapman & Hall; 1975.
[27] Denizli A, Tanyolaç D, Salih B, Aydınlar E, Özdural A, Pişkin E. J Membr Sci 1997;1:137.
[28] Denizli A, Özkan G, Arıca MY. J Appl Polym Sci 2000;78:81–9.
[29] Siegel H, Martin RB. Chem Rev 1982;82:385–426.
[30] Kolarz BN, Jezierska J, Bartkowiak D, Gortarcyzk A. React Polym 1994;23:53–61.
[31] George B, Pillai VNR, Mathew B. J Appl Polym Sci 1999;74: 3432–44.
[32] Godjevargova T, Simeonova A, Dimov A. J Appl Polym Sci 2001;79: 283–8.