Polymer Bulletin 57, 445–456 (2006)
DOI 10.1007/s00289-006-0583-6

Polymer Bulletin

The competitive heavy metal removal by hydroxyethyl cellulose-g-poly(acrylic acid) copolymer and its sodium salt: The effect of copper content on the adsorption capacity

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Received: 15 December 2005 / Revised version: 23 March 2006 / Accepted: 27 April 2006

Abstract

Crosslinked hydroxyethyl cellulose-g-poly(acrylic acid) (HEC-g-pAA) graft copolymer was prepared by grafting of acrylic acid (AA) onto hydroxyethyl cellulose (HEC) using $[Ce(NH_4)_2(NO_3)_6]/HNO_3$ initiator system in the presence of poly(ethyleneglycol diacrylate) (PEGDA) crosslinking agent in 1:1 (v/v) mixture of methanol and water at 30°C. Carboxyl content of copolymer was determined by neutralization of –COOH groups with NaOH solution and sodium salt of copolymer (HEC-g-pAANa) was swelled in distilled water in order to determine the equilibrium swelling value of copolymer. Both dry HEC-g-pAA and swollen HEC-g-pAANa copolymers were used in the heavy metal ion removal from three different aqueous ion solutions as follows: a binary ion solution with equal molar contents of $Pb^{2+}$and Cd^{2+}, a triple ion solution with equal molar contents of Pb^{2+}, Cu^{2+} and Cd^{2+}, and a triple ion solution with twice Cu^{2+} molar contents of Pb^{2+} and Cd^{2+}. Higher removal values on swollen HEC-g-pAANa were observed in comparison to those on dry polymer. The presence of Cu^{2+} decreased the adsorption values for Pb^{2+} and Cd^{2+} ions on both types of HEC copolymer. However, with further increase in Cu^{2+} content both dry and swollen copolymers became apparently selective to Cu^{2+} removal and Cu^{2+} removal values exceeded the sum of adsorption values for Pb^{2+} and Cd^{2+}. Maximum metal ion removal capacities were 1.79 and 0.85 mmol $Me^{2+}/g_{polymer}$ on swollen HEC-g-pAANa and dry HEC-g-pAA, respectively.

Introduction

Removal of heavy metal ions such as Pb^{2+}, Cu^{2+}, Cd^{2+} both from wastewater and natural waters has gained importance to solve and minimize the industrial and ecological waste problems. In the removal of heavy metal ions from aqueous solutions, semi-natural polymers such as cellulose and starch graft copolymers and synthetic polymers containing functional groups of carboxylic, sulfonic, amide, amine and iminoacetate have been used [1-7]. The use of cellulose based ion-exchanger polymers in the removal of heavy metal ions from aqueous solutions is the most effective and economic method among the adsorption, extraction, sedimentation, and ion exchange methods.

Khalil and Abdel-Halim [2] used alkali-treated poly(methyl acrylate)-starch graft copolymer in the removal of heavy metal ions and determined that metal ion removal capacity of polymer for different metal ions follow the order of $Hg^{2+}>Cu^{2+}>Zn^{2+}>Pb^{2+}$. Rivas and Castro [3] determined that the sulfonic and carboxylic acid groups play different role in the removal of heavy metal ions from aqueous solutions by crosslinked resins containing amino-carboxylic acid and amino-sulfonic acid groups in the side chain. They also observed that the sulfonic acid groups could interact electrostatically with the ions but the carboxylate groups could interact through a complexation. Rivas and Castro [3] concluded that both mechanisms should occur at different magnitudes depending on the pH and at low pH, the contribution of the electrostatic effect is stronger than that at higher pH where the complex formation should be more important. Navarro et al [4,8] used the modified cellulose poly(C-GMAPEI) for the adsorption of Cu^{2+}, Co^{2+} and Zn^{2+} ions, which is obtained by grafting of glycidyl methacrylate (GMA) onto cellulose, followed by the reaction with polyethylene imine (PEI) to introduce nitrogeneous ligands. They determined that Cu^{2+} retention of polymer enhanced with the increase in Cl^- anion concentration in the solution. Zhou et al. [9] used biodegradable cellulose/chitin beads in the competitive removal of Pb^{2+}, Cu^{2+}, Cd^{2+} ions, which is prepared by coagulation a blend of cellulose and chitin in 6 wt % NaOH/5wt % thiourea aqueous solution with 5% H_2SO_4 as coagulant. Their results revealed that the Cu^{2+} ion that has the smaller ion radius (0.072 nm) than those of Cd^{2+} (0.097 nm) and Pb^{2+} (0.120 nm) were more rapidly adsorbed on the sorbents than Pb^{2+} and Cd^{2+}. However, the adsorption capacities of these metals were in the order of $Pb^{2+}>Cu^{2+}>Cd^{2+}$ in a solution with low ion concentration. They have also found that when Cu^{2+} ion concentration exceeded a critical amount, the selectivity to Pb^{2+} ion has disappeared and higher adsorption value for Cu^{2+} than sum of those for Pb^{2+} and Cd^{2+} was observed. Khalil and Farag [10] determined that Cu^{2+} and Cd^{2+} removal efficiencies by poly(acrylamide)-starch graft copolymer was not affected from the initial concentrations of these ions, but the increase in initial concentration of Pb^{2+} ion in the solution improved the adsorption of Pb^{2+}. Beker et al. [11] obtained a semi-ester with an ion removal capacity of 2.57 meq/g resin for Fe^{3+}, Co^{2+}, Cu^{2+} and Zn^{2+}. Fantinel et al. [12] investigated the complexation mechanism (uni-dentate or bi-dentate complex, bridge formation) of Ca^{2+} ion with sodium salts of poly(acrylic acid) with different molecular weights by FTIR method and found that the molecular weight of polymer affects the Ca^{2+} binding mechanism and in the case of higher molecular weight poly(acrylic acid), Ca^{2+} binding to the polymer are stronger in comparison to that for the lower molecular weight fraction of the same polymer. In our previous works [13,14], we studied the effects of the form of cellulose-poly(acrylic acid) (cell-g-pAA) graft copolymer on the metal ion removal efficiency in the competitive and non-competitive removal of Pb^{2+}, Cu^{2+} ve Cd^{2+} ions. In these works, two different types of cellulose-g-pAA were employed. The first copolymer was dry and in the powder form and, containing –COOH groups introduced by grafting of acrylic acid (AA) onto cellulose. The second cellulose sample was in the swollen form and containing –COONa groups obtained by the neutralization of –COOH groups in side chains of cell-g-pAA with NaOH solution and following swelling in distilled water at room temperature. In our previous work [13], we found out that in the removal of Pb^{2+}, Cu^{2+}, and Cd^{2+} ions from aqueous solution containing each ion in equal molar amounts, dry cellulose-g-pAA was selective to Pb^{2+} ion and the removal order for this dry copolymer was $Pb^{2+} > Cu^{2+} > Cd^{2+}$. However, in case of removal of the same ions by swollen cell-g-pAANa copolymer, the adsorption values of Pb^{2+} and Cu^{2+} ions on swollen copolymer were nearly the same. Metal ion removal capacities of dry and swollen cellulose copolymers were found to be 1.06 and 1.34 mmol/$g_{polymer}$, respectively. In the non-competitive removal of these ions by swollen cell-g-pAANa, approximately the equal amounts of removal values for each ion were obtained. In the non-competitive adsorption of the ions on crosslinked dry HEC-g-pAA [14], removal values for each ion decreased with the increase in ionic radius and the removal values were determined to be Cu^{2+} (0.78 mmol/g) > Cd^{2+} (0.62 mmol/g) > Pb^{2+} (0.35 mmol/g).

It is known that initial metal ion concentration plays an important role on the metal ion retention values of polymers. Zhou et al [9] reported that the increase in Cu^{2+} content of the solution up to a critical value led to 3.5-4 fold decreases in Cd^{2+} and Pb^{2+} retentions. In this study, hydroxyethyl cellulose (HEC) was chosen as a cellulose derivative and acrylic acid was grafted onto HEC in the presence of poly(ethyleneglycol diacrylate) crosslinking agent at 30°C in aqueous solution.

The aim of the present work was to investigate the influence of absence and content of Cu^{2+} on the metal ion removal by HEC-g-pAA from a solution containing equal molar amounts of Pb^{2+} and Cd^{2+} ions. To improve both retention and retention rates of copolymers, namely to avoid diffusion limitation of metal ions to dry HEC-g-pAA, it was neutralized with NaOH solution, and then swelled in water at room temperature. Afterwards, swollen HEC-g-pAANa obtained by this procedure was employed in the competitive metal ion removal. To clarify the influence of Cu^{2+} content on the removal capacities of both dry and swollen HEC copolymer, their adsorption values for each ion from the solutions with different Cu^{2+} contents and containing no Cu^{2+} ion were compared.

Experimental

Materials

Acrylic acid (AA) (Merck, Schuchardt-Germany) monomer was distilled under vacuum and stored at -8°C until it was used. Hydroxyethyl cellulose (HEC) (145 mPa.s, 1% in H_2O, 20°C) was obtained from Fluka (Buchs-Switzerland). Distilled water was employed in polymerization reactions. Ceric ammonium nitrate hexa hydrate and nitric acid (65% solution), hydroquinone, copper acetate, and lead acetate were obtained from Merck (Darmstadt-Germany), and AnalaR cadmium acetate was purchased from Hopkin and Williams (Chadwell Heath, Essex-England). Polyethyleneglycol (400) diacrylate (PEGDA) was of Sartomer product (Paris-France). Nitrogen gas was purified by passing it through a freshly prepared alkaline pyrogallol solution.

Preparation of HEC-g-pAA polymer

Crosslinked water insoluble HEC-g-pAA copolymer was prepared by using $[Ce(NH_4)_2(NO_3)_6]/HNO_3$ initiator system and polyethyleneglycol diacrylate crosslinker at 30°C in 60 min. Eight grams of HEC was dispersed in 640 mL of $2.5x10^{-3}$ M nitric acid solution in mixture of methanol-water (v/v, 1/1) in a glass reactor. In order to remove the dissolved oxygen, nitrogen was purged for 30 minutes under constant stirring rate (400 rpm). Acrylic acid (40 mL) and PEGDA (1.53 g) were added into the reaction mixture. After the desired reaction time had elapsed, the reaction was stopped by hydroquinone addition, and the product probably containing crosslinked homopolymer pAA beside the HEC-g-pAA was filtered, washed several times with water, and dried under vacuum at 40°C.

Carboxyl content determination

Carboxyl content of HEC-g pAA was determined by neutralization of carboxyl groups in side chains of polymer with 0.1 M NaOH solution. The neutralization reaction is given below:

$$\text{HEC ----}CH_2\text{-}\underset{\displaystyle COOH}{\underset{|}{C}}H_2 + NaOH \longrightarrow \text{HEC ----}CH_2\text{-}\underset{\displaystyle COONa}{\underset{|}{C}}H_2 + H_2O$$

The polymer in a 0.1 M NaBr solution was titrated with a solution of 0.1 M NaOH in the presence of phenolphtalein indicator. The carboxyl content of polymer was calculated using the equation given below:

$$G_v=MxFxS/G_g \tag{1}$$

where G_g is the weight of polymer (g), G_v is carboxyl content of polymer in $mmol/g_{polymer}$, M is molarity of NaOH titration solution (mol/L), S is the volume of NaOH titration solution (mL), and F is the factor of NaOH titration solution. F was determined by the standardization of 0.1 M sodium hydroxide solution in with potassium hydrogen phthalate using phenolphthalein as indicator. Required amount of dried potassium hydrogen phthalate dissolved in 25 mL distilled water and titrated with NaOH solution to the end point of phenolphthalein. Factor of standart NaOH solution was calculated by the following equation.

$$\text{Factor} = \frac{\text{Grams of potassium hydrogen phthalate}}{\text{mL of NaOH x 0.204228 x 0.1}} \tag{2}$$

Determination of equilibrium swelling value of HEC-g-pAA

Neutralized, -COONa form of polymer obtained by the neutralization of –COOH groups on side chains of HEC-g-pAA with NaOH was subjected to swelling in distilled water at room temperature until swelling equilibrium was attained. Equilibrium swelling value (Q in gH_2O/g_{pol}) of polymer was calculated as follows:

$$Q = \frac{\text{Weight of swollen polymer (g) - Weight of dry polymer (g)}}{\text{Weight of dry polymer (g)}} \tag{3}$$

Removal of metal ions

Competitive heavy metal removal from the aqueous solutions with different metal ion compositions was performed by two types of HEC-g-pAA copolymer. The first copolymer was dry and containing carboxyl groups. The second copolymer was neutralized by alkali and then swollen in water. Three different metal ion solutions with different compositions were used in the competitive removal experiments. The concentrations of each ion in the solutions are shown in Table 1.

Table 1. Composition of the solutions (mmol/L) used in the metal removal.

Solution	Ion Concentration (mmol/L)		
	Pb^{2+}	Cd^{2+}	Cu^{2+}
I	4.72	4.72	-
II	4.72	4.72	4.72
III	4.72	4.72	9.44

Each solution was prepared by dissolving the metal acetate salt in distilled water. A weighed amount of dry or water-swollen polymer was added in a given amount of metal ion solution and the mixture was stirred by a magnetic stirrer during the adsorption experiments. The total metal ion amount contacted with HEC-g-pAA or its Na salt was kept constant at 28.32 mmol by varying the volume of each solution. The concentration of residual metal ions in the aliquots of withdrawn from the solution was determined by an atomic absorption spectrophotometer (Varian Spectro AA 220-FS). The amount of metal ion adsorbed per gram of polymer was determined by the difference between initial and final concentrations of ion in the solution. Metal ion removal capacities of the polymers were calculated according to equation given below:

$$\text{Removal Capacity } (\text{mmol/g}_{\text{polymer}}) = \Sigma\,(C_i - C_f)\,/\,m_{\text{polymer}} \qquad (4)$$

where C_i :initial concentration of each metal ion in the solution (mmol metal ion/L), C_f: the concentration of each metal ion in the solution after adsorption (mmol metal ion/L), m_{polymer} : weight of polymer.

In order to investigate the variation in the pH of metal ion solution with time during the removal of metal ions, the solution pH was measured by a pH-meter (Orion 720A+, Thermo Electron Corporation, USA) in the predetermined time intervals.

Results and discussion

Carboxyl content and equilibrium swelling value of crosslinked HEC-g-pAA were found to be 7.4 mmol –COOH/g_{polymer} and 13.0 g H_2O/g_{polymer} , respectively. Metal ion removal capacities by both dry (HEC-g-pAA)and swollen (HEC-g-pAANa) copolymers after 10 hours are shown in Table 2.

A comparison of removal capacity of dry HEC-g-pAA with those of swollen HEC-g-pAANa from solution I is given in Figure 1-2. The equilibrium state occur after 10 hour for both dry and swollen copolymer. The equilibrium ion removal capacity of swollen HEC-g-pAANa is higher than that of dry HEC-g-pAA and approximately more than double that of the latter.

Table 2. The Ion removal capacities of HEC-g-pAA and HEC-g-pAANa copolymers.

Solution	Ion Removal Capacity (mmol $Me^{2+}/g_{polymer}$)						Total Removal Capacity (mmol $Me^{2+}/g_{polymer}$)	
	Pb^{2+}		Cu^{2+}		Cd^{2+}			
	Dry	Swollen	Dry	Swollen	Dry	Swollen	Dry	Swollen
I	0.37	0.85	-	-	0.18	0.43	0.55	1.28
II	0.31	0.60	0.33	0.78	0.13	0.33	0.77	1.70
III	0.26	0.43	0.49	1.10	0.10	0.26	0.85	1.79

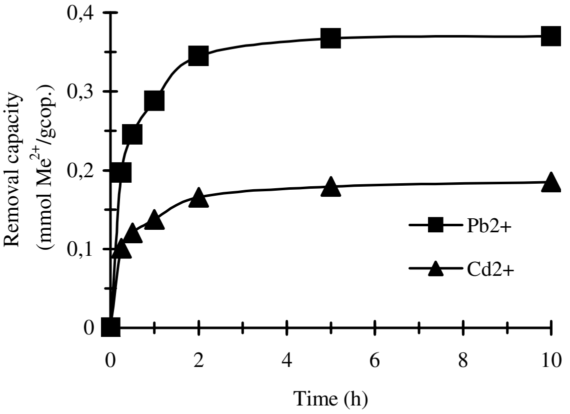

Figure 1. Removal of metal ions from solution I by dry HEC-g-pAA.

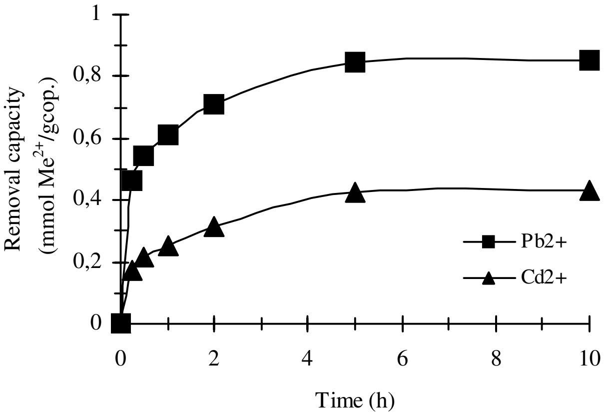

Figure 2. Removal of metal ions from solution I by swollen HEC-g-pAANa.

The temporal variations of the ion removal capacity from solution II for dry and swollen HEC copolymers are shown in Figures 3-4. Figure 3 shows that the competitive removal capacities of dry polymer for Pb^{2+} and Cu^{2+} ions are the same and they are apparently higher than Cd^{2+} retention. While Cd^{2+} adsorption remained almost constant after 1-hour treatment of dry polymer with solution II, Pb^{2+} and Cu^{2+}

adsorptions progressed further with the increase in treatment time. However, the same behavior was not observed for swollen copolymer, and thus the removal values for each ion increased even in a low amount with the treatment duration.

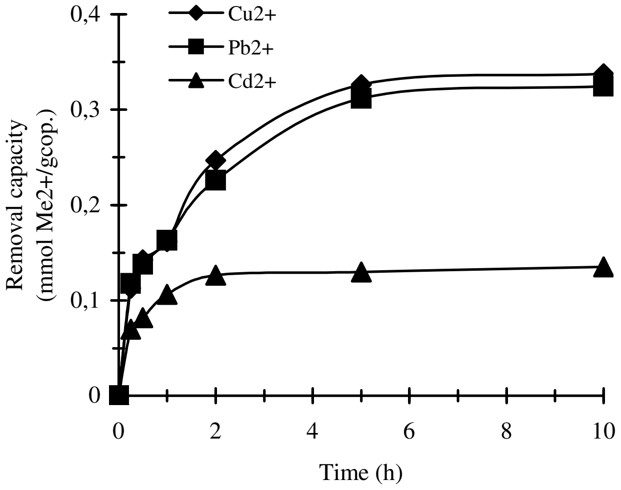

Figure 3. Removal of metal ions from solution II by dry HEC-g-pAA.

Data from Figure 4 show that the case of competitive removal by sodium salt of crosslinked HEC-g-pAA swollen in water, removal values of polymer for each ion are higher than those of dry copolymer as can be expected. Adsorption values of swollen polymer for Pb^{2+}, Cu^{2+}, and Cd^{2+} ions are 1.9, 2.4, and 2.5 times higher than those of dry polymer, respectively. While the removal order for dry copolymer is $Pb^{2+} \sim Cu^{2+} > Cd^{2+}$, in case of swollen polymer it follows $Pb^{2+} > Cu^{2+} > Cd^{2+}$ order. Since swollen copolymer has very weak diffusion limitation for metal ions, COO^-Na^+ groups of copolymer are more accessible by metal ions in comparison to –COOH groups in un-neutralized and dry polymer due to ionization of former groups.

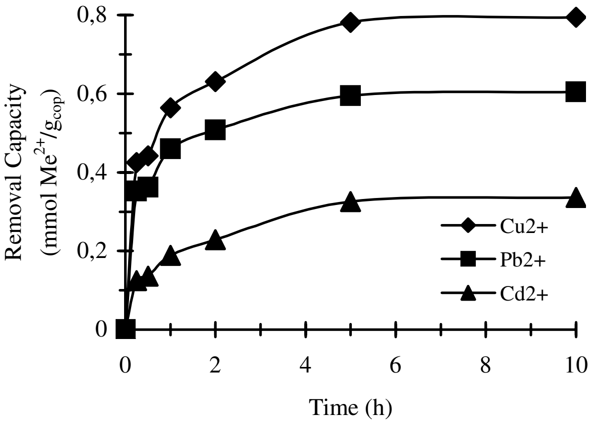

Figure 4. Removal of metal ions from solution II by swollen HEC-g-pAANa.

In the competitive removal of metal ions by dry and water swollen crosslinked HEC-g-pAA polymer from solution III containing excess Cu^{2+}, the variations of removal values with time are seen in Figures 5- 6.

Removal values for dry HEC-g-pAA polymer is in the order of 0.49 mmol $Cu^{2+}/g_{polymer} > 0.26$ mmol $Pb^{2+}/g_{polymer} > 0.10$ mmol $Cd^{2+}/g_{polymer}$ (Figure 5). The same order for swollen HEC-g-pAANa was obtained as 1.10 mmol $Cu^{2+}/g_{polymer} > 0.43$ mmol $Pb^{2+}/g_{polymer} > 0.26$ mmol $Cd^{2+}/g_{polymer}$ and the removal capacities for each ion (Figure 6) are twice those of dry copolymer. The low removal capacity of dry polymer in comparison to swollen copolymer results from the difficulty to form complex or bridge of ions with COOH groups.

Table 2 shows that the percentage of equilibrium sorption of Pb^{2+} and Cd^{2+} on both dry and on swollen copolymer decrease with increasing Cu^{2+} content in the solutions. The adsorption values of swollen HEC-g-pAANa for each ion are approximately twice of dry HEC-g-pAA. In case of solution I, the sorption values of dry HEC-g-pAA

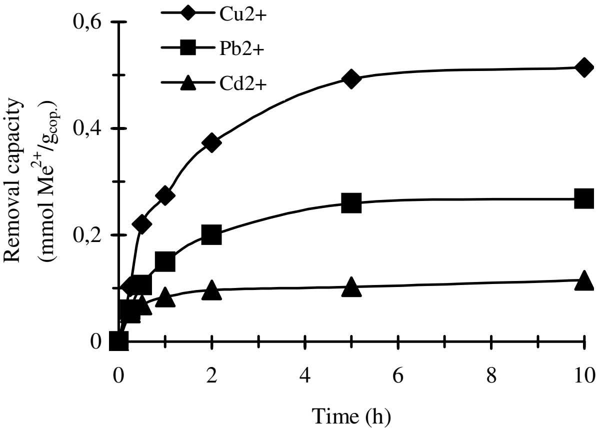

Figure 5. Removal of metal ions from solution III by dry HEC-g-pAA.

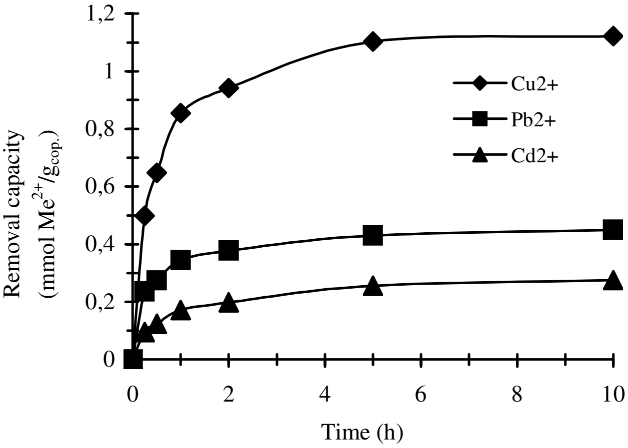

Figure 6. Removal of metal ions from solution III by water swollen HEC-g-pAANa.

polymer for Pb^{2+} and Cd^{2+} ions were 0.37 and 0.18 mmol/g, respectively and total metal ion adsorption capacity of dry polymer is 0.55 mmol/g polymer.

However, when equal molar amount of Cu^{2+} with Pb^{2+} and Cd^{2+} ions was present in the solution, 16 % and 30% decrease in Pb^{2+} adsorption on dry HEC-g-pAA and swollen HEC-g-pAANa polymers were observed , respectively. Further increase in Cu^{2+} content up to twice of Pb^{2+} and Cd^{2+} molar amounts led to 30 and 50 % decrease in Pb^{2+} adsorption on the same polymers, respectively. Doubling the amount of Cu^{2+} ion worsened Cd^{2+} retention capacity of dry and swollen copolymers at the same extent . Cd^{2+} adsorption values on dry HEC-g-pAA from solution II and III decreased 28 and 45 %, respectively. The decreases in Cd^{2+} adsorption values of dry HEC-g-pAA were due to the presence of equal molar amount of Cu^{2+} in solution II and excess Cu^{2+} in solution III, and they are higher than those for Pb^{2+} ion. In other words, the presence of Cu^{2+} affects Cd^{2+} removal more than that of Pb^{2+} in case of dry polymer. On the contrary, Cd^{2+} removal by swollen HEC-g-pAANa was affected less by the presence of Cu^{2+} in comparison to that for Pb^{2+} by the same polymer. Cd^{2+} adsorption by swollen HEC-g-pAANa decreased 23 and 40% due to presence and increase in Cu^{2+} content in the solution, respectively, in comparison to that from binary metal ion solution.

Doubling the Cu content of solution enhanced the metal removal capacity of both dry HEC-g-pAA and swollen HEC-g-pAANa copolymers almost at the same level, 1.5 and 1.3x, respectively.

Cu^{2+} removal values on both types HEC copolymer exceeded the sum of those for Pb^{2+} and Cd^{2+}. This finding for Cu^{2+} sorption coincides with the finding of Zhou et al [9].

About 1.5 times improvements in total metal ion adsorption capacities of dry and swollen polymers were observed with the increase in metal ion concentration. However, while this improvement was linear for dry polymer, it enhanced for swollen polymer up to the composition of solution II and remained almost constant with further increase in ion concentration from solution II to solution III.

The variation in the solution pH with time during the removal of metal ions by dry HEC-g-pAA and the swollen HEC-g-pAANa was illustrated in Figure 7.

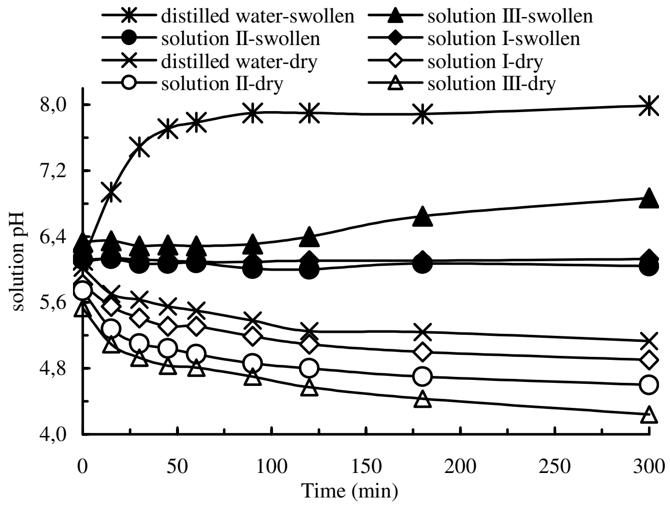

Figure 7. The variation in solution pH with time during the adsorption experiments.

In the case of the removal of metal ions by dry HEC-g-pAA, the reaction equation can be written as follows without taking the complexation mechanism of ions into consideration:

$$2\ –COOH + Cu^{2+} + Pb^{2+} + Cd^{2+} \longrightarrow -(COO^{-})_2(Cu^{2+} + Pb^{2+} + Cd^{2+}) + 2H^{+} \quad (5)$$

As seen from the equation 5 and Figure 7, as a result of complexation or ion exchange between the carboxyl groups and metal ions, the acidity of the solution increases. Therefore, the pH of solution decreases with the increase in contact time of HEC-g-pAA with the metal ion solutions. Although the total metal ion amounts in mmol contacted with polymer was equal to each other in case of each solution, the presence of Cu^{2+} (solution II) and the increase in its concentration (solution III) enhanced the metal ion removal capacity of the polymer. In the case of dry polymer, the decreases in pH for solution I to III as a result of H^{+} release coincide with the increase in the removal capacities of the polymer.

It has been suggested[12] that three types of coordination complexes between the carboxylate groups ($-COO^{-}$) and metal ions occur: unidentate, bidentate, and the bridging complexes. In the unidentate, only one oxygen is bound to the metal ion; in the bidentate both oxygen of the $-COO^{-}$ group are coordinating to the metal in a chelating structure; in the bridging type the two oxygens of the COO^{-} group are coordinated to different ions. In addition, unidentate and pseudobridge complexes are soluble while the bidentate ones precipitates.

Gerente et al[15] investigated the removal of Cu^{2+}, Pb^{2+}, and Ni^{2+} ions at pH 4 by carboxylic moieties. They found that the first fixed copper ions favors the fixation of the following ions, and the fixation of Cu^{2+} ions was occurred mainly by ion exchange (95%) and a negligible amount of adsorption, 5%. On the other hand, Pb^{2+} removal took place predominantly by ion exchange (75%), in addition to 25% adsorption mechanism. In case of our work, the decrease in pH of the mixture of distilled water and dry polymer is the least in comparison with those of the mixtures of dry polymer with metal ion solutions due to less ionization as a result of high affinity of carboxyl groups to protons as expected (Figure 7). It is also known[15] that when the pH of solution increases, removal capacities are improved due to the lower competition between the protons and Cu^{2+}.

As expected and seen in Table 2, the removal capacities of swollen HEC-g-pAANa are higher than those of dry HEC-g-pAA due to higher extent in the ionization of carboxylate groups on the former polymer. In case of acrylic polymers, the extent in the ionization of –COOH groups, and the pH of swelling medium determines the water absorption capacity of the polymer. The swelling capacity of pAA is higher at alkaline pHs due to repulsion of negative charged $–COO^{-}$ groups each other. In case of lower pHs, the carboxyl groups of pAA are in protonated form and consequently their swelling and metal removal values are low.

In the removal of metal ions by swollen HEC-g-pAANa, there is no change in pH with time for solution I and II, and a small increase in pH after 2 hours-contact time of polymer with solution III due to Na^{+} release to the solution (equation 6). The pHs of all the solutions are higher than those of the solutions contacted with dry HEC-g-pAA.

$$-COO^{-}Na^{+} + Cu^{2+} + Pb^{2+} + Cd^{2+} \longrightarrow -(COO)_2(Cu^{2+} + Pb^{2+} + Cd^{2+}) + Na^{+} \quad (6)$$

The pH of the mixture of the distilled water and swollen HEC-g-pAANa increases (eq. 7) and attains in equilibrium approximately in one hour which means maximum ionization.

$$\text{-COO}^{-}\text{Na}^{+} + \text{H}_2\text{O} \longrightarrow \text{-COOH} + \text{Na}^{+}\text{OH}^{-} \qquad (7)$$

François et al[16] studied the interactions of PAA with Cu^{2+} ions in aqueous solutions by electron paramagnetic resonance spectroscopy as a function of ionization degree. They found that pAA forms two types of complexes with Cu^{2+} depending on the pH, preponderantly binuclear complexes (copper:carboxylate,2/4) at low pHs, and preponderantly mononuclear complexes (copper:carboxylate, 1/2) at higher ionization at high pHs. They observed also that the fraction of Cu^{2+} complexed with pAA increased with the ionization degree and the fraction of free Cu^{2+} became zero at ionization degree of 0.25. The formation of binuclear complexes is more difficult in comparison with that of mononuclear ones since the former requires more available carboxyl groups and metal ions. In addition, at low pHs the protons competes with metal ions for carboxyl groups. For that reason, the increase in the sorption of Cu^{2+} by swollen polymer may be attributed to the favored complexation of carboxyl groups with Cu^{2+} in comparison to rest of ions.

Conclusion

Swollen HEC-g-pAANa polymer adsorbs more than 2 times metal ions in comparison to dry HEC-g-pAA. Metal ion sorption values on both dry HEC-g-pAA and swollen HEC-g-pAANa polymers enhanced with time even after 1 hour contact time of polymer with metal ion solution except that for Cd^{2+} on dry HEC-g-pAA. The addition of Cu^{2+} in equal molar amounts of Pb^{2+} and Cd^{2+} into their binary solution improved the adsorption values 1.3-1.4x on both HEC copolymers. The increase in Cu content up to twice from solution II to III increased the metal ion sorption capacity on dry polymer, however it remained almost constant for swollen HEC-g-pAANa. Maximum metal ion removal (1.79 and 0.85 $mmol/g_{polymer}$) by both forms of HEC copolymer was performed from solution III with maximum metal ion concentration. In the presence of excess Cu^{2+}, Cu^{2+} adsorption on both dry and swollen HEC copolymer exceeded the sum of those for Pb^{2+} and Cd^{2+} and the polymer became apparently selective to Cu^{2+}. Although the complexation mechanism of Pb^{2+} and Cd^{2+} ions with carboxyl groups are not reported as in for Cu^{2+}, the increase in copper removal may be assigned to the easy complex formation between the copper and carboxyl groups in comparison to that for former ions.

Acknowledgement. This work was supported by the Research Fund of Istanbul University, Project No: UDP-315/25052004.

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