Synthesis of Water-Insoluble Functional Copolymers Containing Amide, Amine, and Carboxylic Acid Groups and Their Metal-Ion-Uptake Properties

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ABSTRACT: The crosslinked poly[*N*-(3-dimethylamino)-propylmethacrylamide] [P(NDAPA)] and poly[*N*-(3-dimethylamino)propylmethacrylamide-*co*-acrylic acid] [P(NDAPA-*co*-AA)] were synthesized by radical polymerization. The resins were completely insoluble in water. The metal-ion-uptake properties were studied by a batch equilibrium procedure for the following metal ions: silver(I), copper(II), cadmium(II), zinc(II), lead(II), mercury(II), chromium(III), and aluminum(III). The P(NDAPA-*co*-AA) resin showed a lower metal-ion affinity than P(NDAPA), except for Hg(II), which was retained at 71% at pH 2. At pH 5, the resin showed a higher affinity for Pb(II) (80%) and Cu(II) (60%), but its affinity was very low for Zn(II) and Cr(III). The polymer ligand–metal-ion equilibrium was achieved during the first 20 min. By changing the pH, we found it possible to remove between 60 and 70% of Cd(II) and Zn(II) ions with (1*M*, 4*M*) HClO$_4$ and (1*M*, 4*M*) HNO$_3$. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 5232–5239, 2006

Key words: metal-polymer complexes; radical polymerization; resins

INTRODUCTION

Apart from the formation of well-defined complexes, the interactions of polymers with metal ions are a subject of interest because of their potential analytical and technological applications in fields such as environmental science, wastewater treatment, and the metallurgy industry and because of their implications in biological systems. The main uses and applications for an insoluble polymeric matrix are related to metal recovery from dilute solutions.[1–25] Reactive polymeric materials for wastewater treatment and metal recovery have received much attention because metal ions are naturally nonbiodegradable and their intake at a certain level is toxic.[26] Therefore, attempts have been made to incorporate a vast number of chelating groups into polymer networks.

There are different natural and synthetic products that present ion-exchange properties. The organic resins are by far the most important ion exchangers. The main advantages include a high chemical and mechanical stability and a high ion-exchange capacity, and ion-exchange rate. Another advantage is the possibility of the selection of the fixed ligand groups and the degree of crosslinking. However, due to the wide range of materials and synthesis methods, it is not surprising that the chelating exchanger's physical form may vary from a rock-hard material to a soft gel.

The selective separation of metals from different fluids and from contaminated areas presents an interesting, challenging task. The materials used to perform this task should be highly selective, nonhydrophobic, and easy to regenerate. The hard and soft acid base concept[27] and metal complex stability are valuable guidelines for active site selection. The anchoring of the active site to a solid support in a polymer matrix provides an immobilized active surface capable of selective and quantitative separation of the cations from an aqueous solution.

The aim of this study was to examine the ability of two resins containing amide, amine, and carboxylic acid groups to recover metal ions with environmental impact with the batch equilibrium procedure.

EXPERIMENTAL

Reagents

N-(3-dimethylamino)propylmethacrylamide (NDAPA; Aldrich) and acrylic acid (AA; Merck, Aldrich, Milwaukee, WI) were purified by distillation. Ammonium persulfate (Fluka, Germany) and *N,N′*-methylene bisacrylamide (MBA; Aldrich) were used without further purification and were used as the initiator and crosslinking reagent, respectively.

Resin synthesis

Poly[*N*-(3-dimethylamino)propylmethacrylamide] [P(NDAPA)]

NDAPA (10 mL, 0.0552 mol), MBA (0.3552 g, 0.00228 mol), and ammonium persulfate (0.0684 g, 0.000299 mol) dissolved in 10 mL of water were added to a polymerization flask under a nitrogen atmosphere. The polymerization reaction mixture was maintained at 70°C for 8 h. Subsequently, methanol (10 mL) was added. The resin was filtered, washed, and dried until a constant weight was reached (yield = 91%). The resin was screened, and a resin particle size of 250–500 µm was used for the uptake metal-ion studies.

Poly[*N*-(3-dimethylamino)propylmethacrylamide-*co*-acrylic acid] [P(NDAPA-*co*-AA)]

NDAPA (5 mL, 0.0276 mol), AA (2 mL, 0.029 mol), MBA (0.3461 g, 0.0021 mol), and ammonium persulfate (0.0605 g, 0.00027 mol) in 7 mL of water were added to a polymerization flask and kept at 70°C for 8 h under nitrogen. Then, methanol was added. The resin was filtered, washed with abundant distilled water, and dried until a constant weight was reached (yield = 97%). The resin was screened, and a resin particle size of 250–500 µm was used for the metal-ion binding studies.

Metal-ion uptake

Aqueous solutions containing metal ions were prepared from nitrate metal salts (Merck) of silver(I), copper(II), cadmium(II), zinc(II), lead(II), mercury(II), chromium(III), and aluminum(III) (Merck). This solution (5 mL) was added to 0.05 g of dry resin. The resin ligand–metal-ion ratio was 20 : 1.0 mol/mol. The flask was closed and kept at 20°C with constant stirring for 1 h. Then, it was filtered and washed with abundant distilled water. The filtered volume was collected in a 100-mL container. The metal-ion retention was determined by atomic absorption spectrometry (AAS).

To study the time effect on metal-ion retention, 5 mL of an aqueous solution with 50 mg of resin (with a resin/metal-ion ratio of 20 : 1 mol/mol maintained) were placed in a flask at 20°C for 5, 15, 30, and 120 min. Subsequently, the mixture was filtered, and the resin was washed with abundant twice-distilled water. The metal ions were analyzed in the filtrate by AAS.

Measurements

A Julabo air-batch shaker was used to shake the solution at a desired temperature. The pH was measured with a digital H. Jürgens & Co. pH meter. A Unicam Solaar 5M series atomic absorption spectrometer (UK) was used to determine the presence of single and mixed metal ions. The Fourier transform infrared (FTIR) spectra of the sample were recorded with a Magna Nicolet 550 spectrophotometer (UK). The thermograms of the loaded and unloaded resins were recorded on a STA-625 thermoanalyzer (Polymer Laboratories). Approximately 5 mg of the dry sample was heated at 10°C/min heating rate under a dynamic nitrogen atmosphere.

Similarly, the temperature effect on the metal-ion-uptake behavior was studied at 20, 25, 30, and 40°C.

To determine the maximum retention capacity (MRC), aqueous solutions were prepared from nitrate salts of Ag(I), Cu(II), Cd(II), Zn(II), Pb(II), Hg(II), Cr(III), and Al(III) (Merck) at optimum pH. A 1 g/L aqueous solution (25 mL) with 0.5 g of dry resin was placed in the flask at 20°C for 1 h. The solution was filtered and transferred to a 100-mL flask. The resin was washed with twice-distilled water. The process was repeated twice, and the metal-ion retention was determined by AAS.

To study resin recovery, 0.1 g of metal-ion-loaded resin was placed in contact with 10 mL of eluent at 20°C. The solution was filtered, and the metal-ion retention was determined as indicated previously.

To carry out the charge–discharge cycles, 10 mL of a metal-ion solution with 0.1 g of dry resin are stirred for 1 h at 20°C and was then filtered and transferred to a 100-mL flask; we completed the volume with water at the same pH. Then, the resin was placed in 10 mL of eluent for 1 h at 20°C. It was filtered and completed to 100 mL. This procedure was repeated three times. The metal-ion retention was determined as indicated previously.

RESULTS AND DISCUSSION

Two water-insoluble resins containing different ligand groups were synthesized by radical polymerization. P(NDAPA) and P(NDAPA-*co*-AA) were obtained with yields higher than 90%. The structures are shown next:
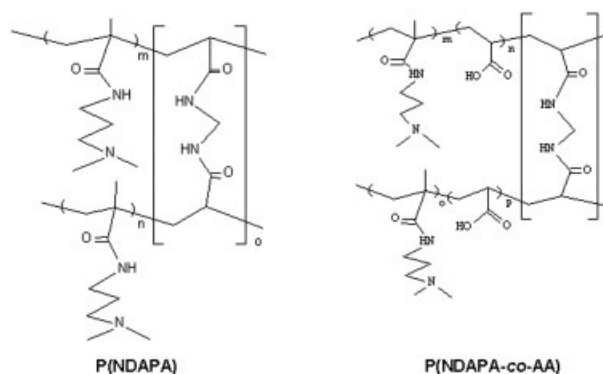

P(NDAPA)   P(NDAPA-co-AA)

TABLE I
FTIR Characteristic Absorption Bands for the Resins P(NDAPA)
and P(NDAPA-*co*-AA)

Resin	Absorption bands (cm^{-1})				
P(NDAPA)	C=O	C—H	N—H	CH_3—N	—
	1642	2943	3436	2864	
P(NDAPA-*co*-AA)	C=O	CH_3—N	C—N	C—O	N—H
	1634	2949	1382	1282	3442

These resins were synthesized with a constant amount of crosslinking reagent. However, it is well known that these polymer–metal-ion reactions are diffusion-controlled; therefore, as the crosslinking degree increases, usually the water adsorption and the available ligand sites at the surface decrease, which results in lower metal-ion retention.[8] This effect should be not very important when the metal ions are retained by a mechanism other than coordination.

The most characteristic FTIR absorption bands are summarized in Table I and are shown in Figure 1. The copolymer composition for the resin P(NDAPA-*co*-AA) was determined by elemental analysis according to nitrogen content. The value obtained, 1 : 0.98 (NDAPA/AA), was very close to the monomer ratio in the feed and agreed with the copolymerization yield of 97%. The copolymer's weight loss was higher than that of P(NDAPA) due to the incorporation of the carboxylic acid moiety at the copolymer and probable CO_2 evolution (see Table II).

Metal-ion-uptake properties

The batch equilibrium procedure was used to study the metal-ion retention properties for both resins.

The polymer P(NDAPA) contained amine and amide groups, whereas P(NDAPA-*co*-AA) contained amine, amide, and carboxylic acid groups. The effect of pH on metal-ion retention for both resins is shown in Figures 2 and 3. Hg(I) was the only cation studied at pH 2. In general, the retention increased as pH increased. This result could be explained by metal-ion competition with protons at low pH; when the pH increased, the electron pair of the nitrogen amine–ligand group from P(NDAPA) was more available to interact with metal ions. Similarly; at higher pH, the carboxylate groups from P(NDAPA-*co*-AA) presented a higher metal-ion affinity to form polymer–metal complexes.

These results suggest that the ligand interaction should have been stronger with the carboxylate and amine groups than with the amide group.

Depending on the pH value, ionized carboxylic acid may form complexes with D_{2h} or D_{4h} (dimmer) symmetry.[28,29] At high pH values, the polymer chain has a drawn shape because of the electrostatic repulsion of charged carboxylate groups, where metal ions are then binding with either one or two neighboring groups. At a pH close to 4.5, the macromolecular coil contracts and the metal ions are able to coordinate two to four carboxylic groups [see Scheme 1(a)].

Amino groups form stable complexes through the free electron pair of the nitrogen atom. Consequently, complex stability depends strongly on the
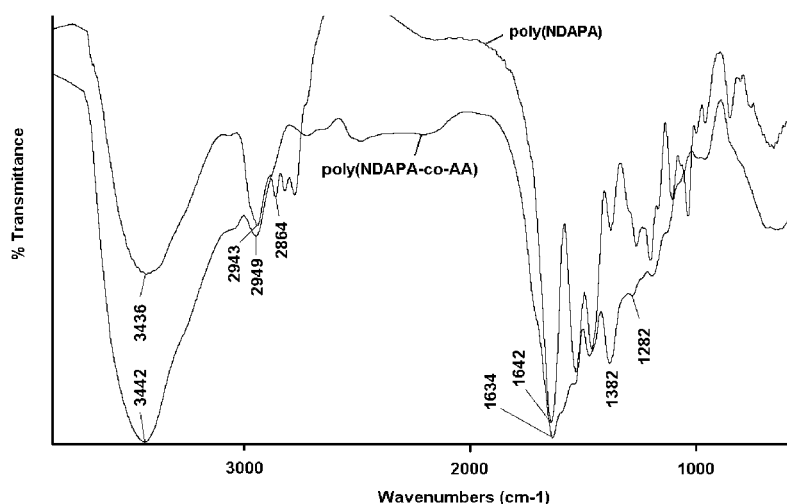

Figure 1 FTIR spectra of P(NDAPA) and [P(NDAPA-*co*-AA).

Resin	Weight loss (%) at different temperatures				
	100°C	200°C	300°C	400°C	500°C
P(NDAPA)	0.0	2.47	14.63	44.46	82.05
P(NDAPA-*co*-AA)	0.0	14.49	25.25	54.31	95.53

pH. At low pH, where the majority of the amino groups are protonated, the metal-ion affinity is poor, and the complex stability is low. As the pH increases, the affinity and stability of the polymer–metal complexes increases[8] [see Scheme 1(b)].

The participation of both amine and carboxylate groups is also possible in the interaction, especially at higher pH values [see Scheme 1(c)].

At pH 1, the P(NDAPA) resin presented a poor affinity (< 35%) for all metal ions, which meant that the amine groups needed the free electron pair to form complexes with the metal ions. Consequently, complexes were only formed at higher pH. Hg(II) was studied only up to pH 2 to avoid precipitation, and at this pH, the retention was only close to 45%. The highest retention (near 100%) was observed for Zn(II), Cu(II), and Pb(II) at pH 5. These results were in agreement with the results obtained for amine-group-containing polymers, such as crosslinked polyethylenimine.[8]

P(NDAPA-*co*-AA) contained three potential ligand groups (amine, amide, and carboxylic acid groups) and presented a lower metal-ion affinity than P(NDAPA), except for Hg(II), which was retained in 71% at pH 2. These results indicate that carboxylate groups should be better ligands than amine groups for Hg(II) ions. At pH 5, the resin showed the highest

affinity for Pb(II) (80%) and Cu(II) (60%), although the affinity was very low for Cr(III) and for Zn(II). The higher affinity for Pb(II) and Cu(II) should have been due to the action of amine and carboxylate groups. Because of the easily polarized nature of their d-electron shells due to orbital valences, first-row transition-metal ions such as Cu(II) and Pb(II) function as borderline acids according to the Lewis acid–Lewis base concepts of Pearson;[27] they, thus, exhibit a preference for nonbonding pair electrons from nitrogen atoms in aliphatic amino-containing ligands.

According to the low solubility properties of mercury species at pH values higher then 2, this metal ion was not investigated at higher pH values, whereas all the other metal ions were investigated at pH 1, 3, and 5, according to the solubility properties of their species.

Figures 4 and 5 present the uptake behavior of both resins at pH 2 under competitive conditions. This pH was selected because it allowed us to study the possibility of the separation of Hg(II) from the other ions. The retention behavior was determined with regard to the initial amount of each metal ion and the total initial amount of both metal ions. In the last case, the total amount of metal ions (moles) was considered. The Hg(II) ion retention decreased with respect to the value measured under noncompetitive conditions and for both resins. Neither resin presented selectivity for Hg(II) because the reten-
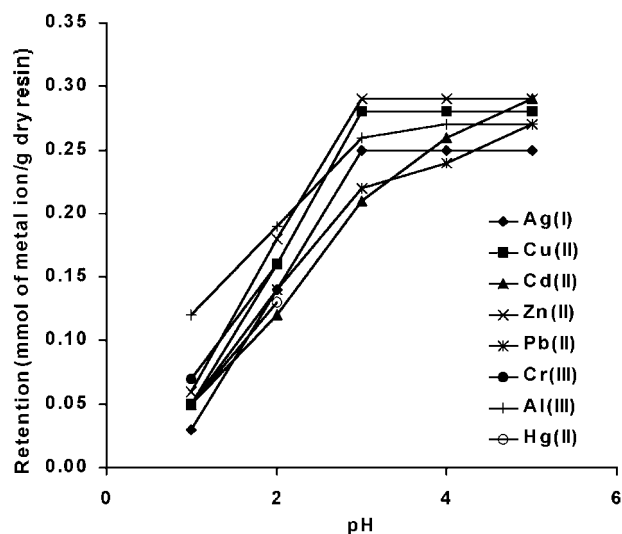

Figure 2 Effect of pH on the metal-ion retention properties for the resin P(NDAPA) (initial amount of metal ion = 0.29 mmol/g of dry resin).
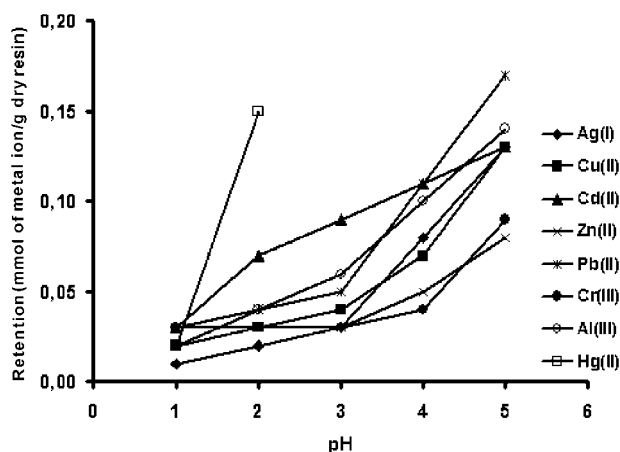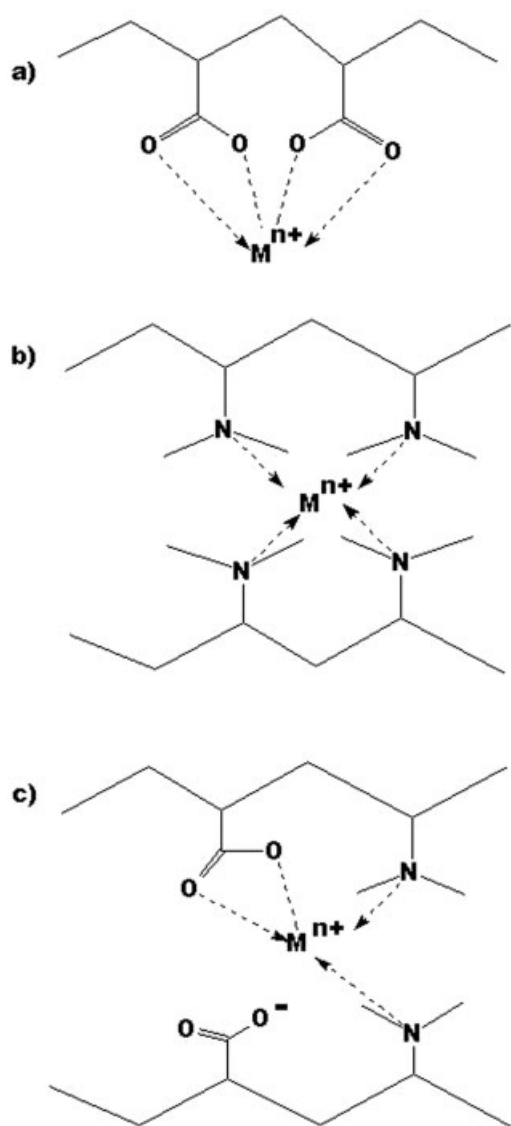

Figure 3 Effect of pH on the metal-ion retention properties for the resin P(NDAPA-*co*-AA) (initial amount of metal ion = 0.21 mmol/g of dry resin).

Scheme 1 Possible ligand–metal-ion interactions: (a) carboxylate, (b) amine, and (c) amine and carboxylate groups.

tions for Cd(II), Zn(II), and Pb(II) were very similar and were only slightly higher for Hg(II). Therefore, under these experimental conditions, it should be not possible to selectively retain Hg(II) from a mixture of these metal ions.

Figures 6 and 7 demonstrate that the polymer ligand–metal-ion equilibrium was achieved during the first 20 min. This was a fast reaction if one considers that it occurred in a heterogeneous phase and, basically, with those ligand sites located at the resin's surface. This behavior demonstrates that the ligand groups had a high affinity for the metal ions.

For the copolymer P(NDAPA-*co*-AA), the two divalent cations Pb(II) and Hg(II) were selected as models to study the temperature effect on the retention at pH values of 5 and 2, respectively. These cations were selected because there was no significant difference with the retention behavior of the other
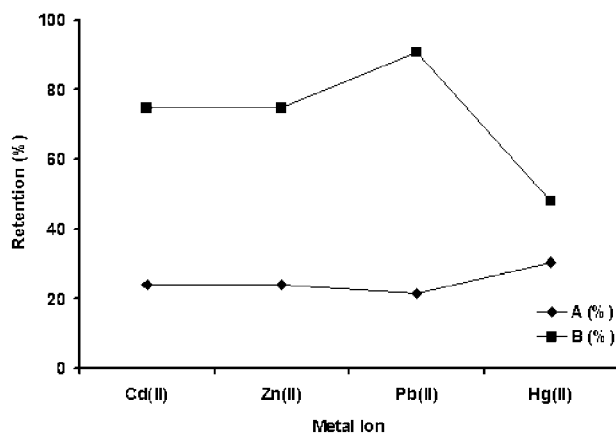

Figure 4 Metal-ion retention behavior from a mixture of the resin P(NDAPA) (conditions: 0.0179 mmol of each metal ion and 0.00715 mmol with respect to the total, pH = 2) with regard to (A) the total amount in the mixture and (B) the amount of each metal ion.

metal ions and both were also very important environmental pollutants. The temperature effect on the metal-ion uptake is shown in Figures 8 and 9. No important effect was produced in the temperature range (20–40°C) for all of the metal ions, and this result was probably due to the polymer–ligand interaction that occurred primarily through a chemical process.

On the basis of these results, the MRC was determined at pH 5 for all of the metal ions, except for Hg(II), which was determined at pH 2. It was determined after three contacts and with a fresh aqueous solution each time. The highest MRC values for the resin P(NDAPA) corresponded to Al(III), Cu(II), and Zn(II) (see Fig. 10). MRC values for the resin P(NDAPA-*co*-AA) were lower than those corresponding to P(NDAPA). For the resin P(NDAPA-*co*-AA),
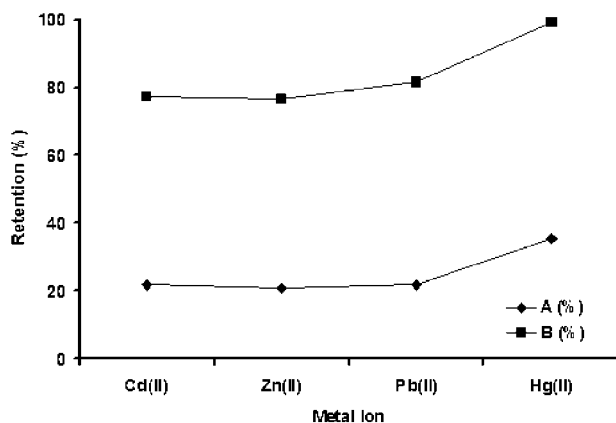

Figure 5 Metal-ion retention behavior from a mixture of the resin P(NDAPA-*co*-AA) (conditions: 0.00154 mmol of each metal ion and 0.00619 mmol respect to the total, pH = 2) with regard to (A) the total amount in the mixture and (B) the amount of each metal ion.
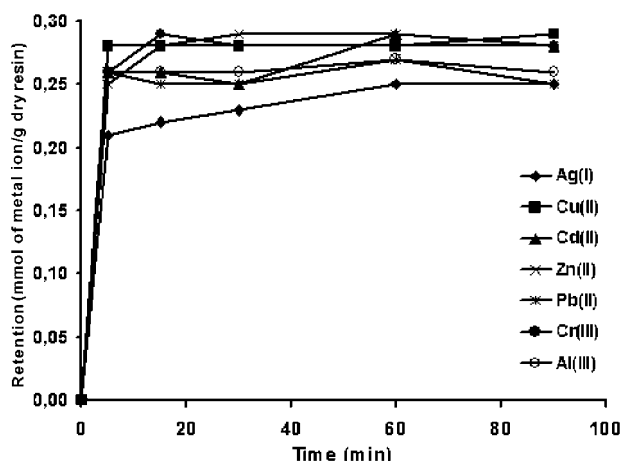
Figure 6 Effect of time on the metal-ion retention of P(NDAPA) [metal ions: Ag(I), Cu(II), Cd(II), Zn(II), Pb(II), Cr(III), and Al(III); pH 5].

Figure 8 Effect of temperature on the metal-ion retention of P(NDAPA) [metal ions: Ag(II), Cu(II), Cd(II), Zn(II), Pb(II), and Al(III) were studied at pH 5, and Hg(II) was studied at pH 2].

the highest MRC value was obtained for Al(III) ions (4.1 mmol/g of dry resin). This resin's MRC value for Hg(II) was higher than the value obtained for P(NDAPA) (see Fig. 11).

For the resin P(NDAPA-co-AA), there were two possible explanations: the ligand sites located at the surfaces were very quickly saturated and it was impossible for it to retain more metal ions, and/or the amine groups had a higher affinity than the carboxylate groups for Cu(II), Zn(II), and Al(III).

The eluents can be base or acid compounds. To remove the metal ions, HNO_3 and $HClO_4$ were used because these produce a change in pH and form a more stable salt with the metal ions. To recover the resin from the loaded metal-ion resins, the resins were eluted in acid media with protonic acid at different concentrations (see Figs. 12 and 13). By changing the pH, we could remove between 60 and 70% of Cd(II) and Zn(II) ions with ($1M$, $4M$) $HClO_4$ and
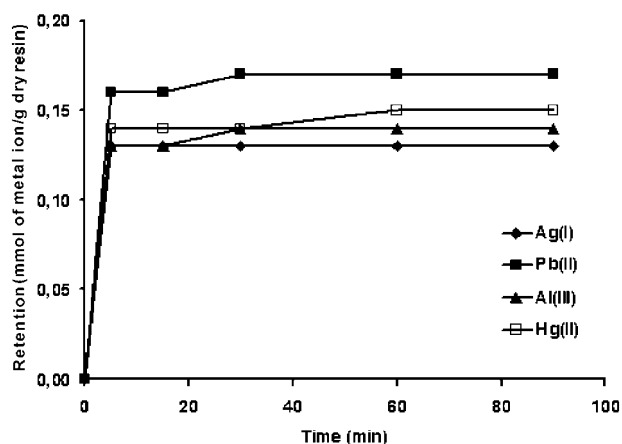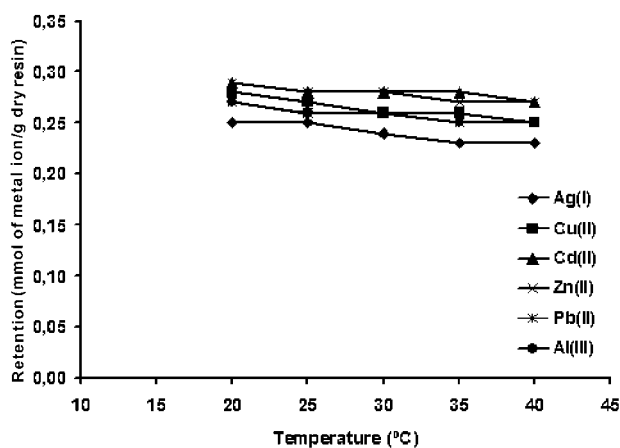
($1M$, $4M$) HNO_3. All of the other metal ions formed more stable complexes because only up to 50% of the metal ions were removed (see Fig. 12).

Figure 13 shows that Pb(II) ion removal was above 80% when we used $4M$ HNO_3 and the resin P(NDAPA).

To quantitatively remove the metal ions, higher concentrations or other eluents would be necessary.

To obtain resin reusability, the sorption–desorption cycle was repeated four times with the same adsorbent. This study was only performed with the resin P(NDAPA) and two metal ions. The aim was to investigate this polymer as a model for this run. In principle, if the study included the other resin, the Pb(II) and Hg(II) cations should have been investigated. The divalent cations Zn(II) and Cd(II) were selected to carry out the charge–discharge cycles on the basis of their retention and elution results. The charge–discharge cycles for the other metal ions

Figure 7 Effect of time on the metal-ion retention of resin P(NDAPA-co-AA) [metal ions: Ag(I), Pb(II), Hg(II), and Al(III); pH 2].
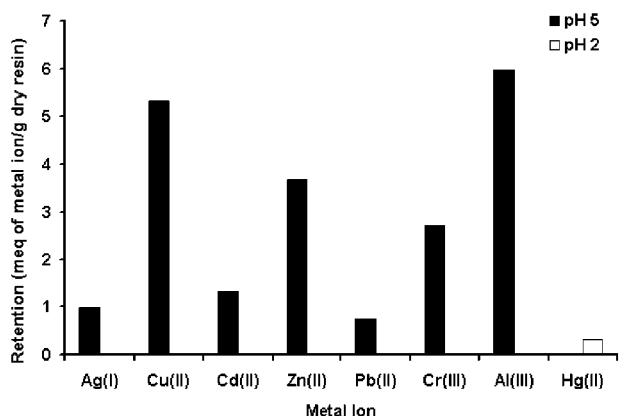

Figure 9 Effect of temperature on the metal-ion retention of P(NDAPA-co-AA). The metal ions Hg(II) and Pb(II) were studied at pH 2 and pH 5, respectively.
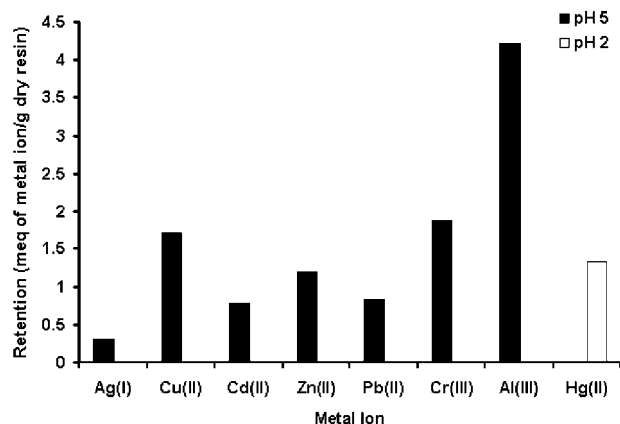
Figure 10 MRC (mequiv of metal ion/g of dry resin) for the resin P(NDAPA) [metal ions: Ag(I), Cu(II), Cd(II), Zn(II), Pb(II), Cr(III), and Al(III) were studied at pH 5, and Hg(II) was studied at pH 2].

Figure 12 Metal-ion recovery from the loaded resin P(NDAPA) by treatment with $HClO_4$ and HNO_3 [metal ions: Ag(II), Cu(II), Cd(II), Zn(II), Pb(II), Cr(III), and Al(III) were studied at pH 5, and Hg(II) was studied at pH 2].

were not performed due to the retention–elution results. Initial amounts of Zn(II) and Cd(II) were used to load the resin. Each cycle was carried out at pH 5 for 1 h. The Zn(II) retention decreased to near 30% with the second cycle, whereas Cd(II) decreased to only about 10%. However, the elution of both metal ions decreased only during the fourth cycle (see Fig. 14). During this process, the ligand sites should have been partially destroyed.

CONCLUSIONS

Water-insoluble resins containing amine, amide, and carboxylic acid groups were synthesized by radical polymerization. The copolymer resin showed a composition 1 : 0.97, which was very close to the comonomer ratio in the feed. The metal-ion retention,
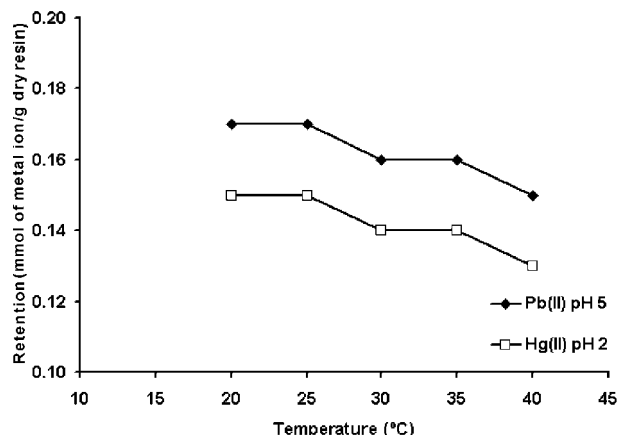
studied by a batch equilibrium procedure, depended on the pH. At higher pH values, the metal-ion uptake increased. The resin ligand–metal ion was achieved during the first 20 min, which was relatively fast when one considers that the ligand–metal-ion interaction occurred in the heterogeneous phase. The P(NDAPA-co-AA) resin presented a lower metal-ion affinity than P(NDAPA), except for Hg(II), which was retained at 71% at pH 2. This result means that carboxylate anions should be better ligands than the amine groups for Hg(II) ions, and it can be attributed to the probable electrostatic interactions among the carboxylic acid with amine groups decreasing the content of ligand sites to bind metal ions.

These results suggest that the most active groups to bind metal ions corresponded to amine and carboxylate groups and that complex formation was favored in both cases.

Figure 11 MRC (mequiv of metal ion/g dry resin) for the resin P(NDAPA-co-AA) [metal ions: Ag(I), Cu(II), Cd(II), Zn(II), Pb(II), Cr(III), and Al(III) were studied at pH 5, and Hg(II) was studied at pH 2].
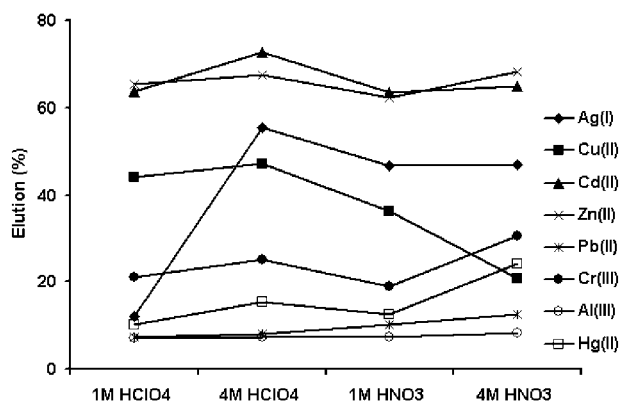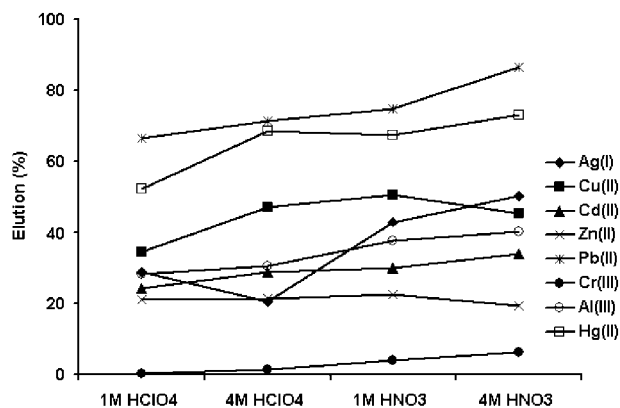

Figure 13 Metal-ion recovery from the loaded resin [P(NDAPA-co-AA) by treatment with $HClO_4$ and HNO_3 [metal ions: Ag(II), Cu(II), Cd(II), Zn(II), Pb(II), Cr(III), and Al(III) were studied at pH 5, and Hg(II) was studied at pH 2].
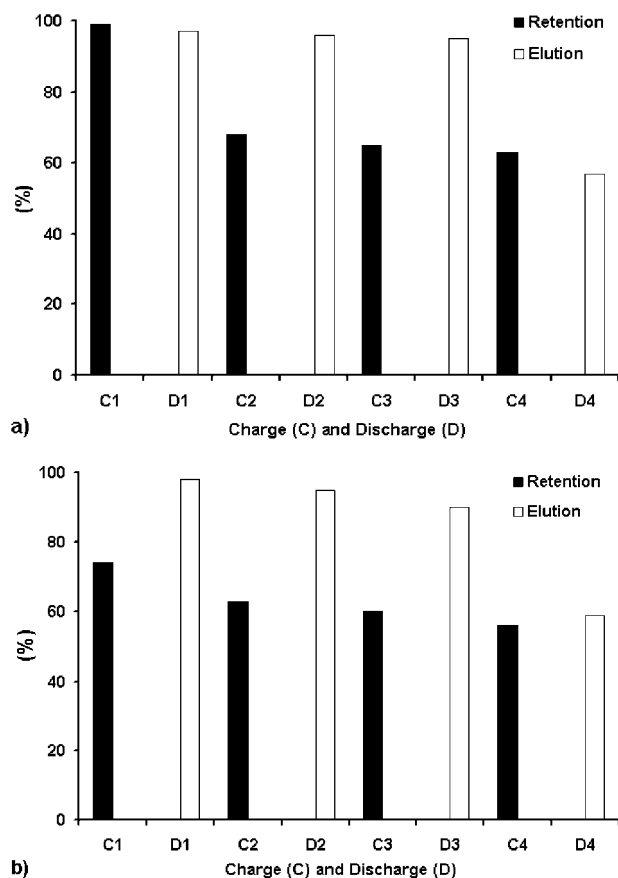
Figure 14 Charge and discharge cycles for (a) Zn(II) and (b) Cd(II) of the resin P(NDAPA) (eluent: $4M$ HNO_3, 0.0299 mmol of Zn(II) and Cd(II), 0.1 g of dry resin, pH 5).

By changing the pH, we could remove between 60 and 70% of Cd(II) and Zn(II) ions with ($1M$, $4M$) $HClO_4$ and ($1M$, $4M$) HNO_3. For the remaining metal ions, more than 80% of Pb(II) ions were removed by treatment with the P(NDAPA-*co*-AA) resin from the resin P(NDAPA). Hg(II) and Zn(II) were eluted between 70 and 80% by treatment with $4M$ HNO_3 from the loaded P(NDAPA-*co*-AA) resin.

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