

Water-Insoluble Polymers Containing Amine, Sulfonic Acid, and Carboxylic Acid Groups: Synthesis, Characterization, and Metal-Ion-Retention Properties

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ABSTRACT: Crosslinked poly(acryloylmorpholine) and its copolymers poly(acryloyl morpholine-co-acrylic acid) and poly(acryloylmorpholine-co-2-acrylamide-2-methyl-1-propane sulfonic acid) were synthesized by radical polymerization. The resins were completely insoluble in water and were characterized with Fourier transform infrared spectroscopy and thermal analysis. The metal ions Ag(I), Cu(II), Cd(II), Hg(II), Zn(II), Pb(II), Al(III), and Cr(III) were investigated under competitive and noncompetitive conditions

by a batch equilibrium procedure. The resin-metal-ion equilibrium was achieved before 5 min. The recovery of the resin was investigated at 20°C with different concentrations of HNO₃ and HClO₄. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 3266–3274, 2006

Key Words: radical copolymerization; resins; metal-polymer complexes

INTRODUCTION

The development of high-performance adsorbents for removing heavy metal ions from wastewater is considered a research priority in environmental science.^{1–20}

The metal complexation behavior of polymer-supported ligands is critical to their use as analytical reagents and catalysts and in applications related to pollution control. Chelating resins and water-soluble chelating polymers have been used for the selective removal and recovery of heavy-metal ions from drinking and industrial water.

The selective complexation of a targeted metal ion by a given ligand is an important objective for many applications, including catalytic, chromatographic, and metal-ion-recovery processes. The ion-exchange reaction is an extremely versatile reaction and one that is well suited to the complexation of cations and anions through electrostatic binding. As an effective settlement, chelating resins are used for enriching and separating some metal ions from aqueous solutions. They are very useful because they have higher selectivity and larger adsorbing capacities than other adsorbents (e.g., activated carbons and metal oxides), and they are also easy to elute and regenerate.

The desirable properties of chelating exchangers are fourfold:²¹ (1) high capacity for the metal(s) of interest, (2) high selectivity, (3) fast kinetics and rapid equi-

libration with metal-containing solutions, and (4) high mechanical strength and toughness of the exchanger particles.

Metal ions are present in water as hydrated ions or as complex species associated with various anions. In the electroplating industry, chelating agents in wastewater, frequently coexisting with metal ions, exhibit little or no tendency to be transferred to a chelating polymer (ion-exchange resins).²²

This article reports the metal-ion-retention properties of the resin poly(acryloylmorpholine) [P(AMo)] and its copolymers poly(acryloyl morpholine-co-acrylic acid) [P(AMo-co-AA)] and poly(acryloylmorpholine-co-2-acrylamide-2-methyl-1-propane sulfonic acid) [P(AMo-co-APSA)] with the batch equilibrium procedure. The metal ions have been selected according to their environmental impact.

EXPERIMENTAL

Reagents

Acryloylmorpholine (AMo; Aldrich, Milwaukee, WI), acrylic acid (AA; Merck, Stuttgart, Germany), and divinylbenzene (DVB; Merck) were purified by distillation. All other reagents were used without further purification.

Synthesis of the resins

Crosslinked P(AMo)

AMo (10 mL, 0.079 mol), 0.5 mL (0.00318 mol) of DVB, and 0.0665 g (0.000395 mol) of 2,2'-azoisobutyronitrile

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TABLE I
FTIR Characteristic Absorption Bands (cm⁻¹) of the Resins

Resin	Absorption bands (cm ⁻¹)				
P(AMo)	C=O 1637	C—N 1362	C—O 1233	O—CH ₂ 2857	—
P(AMo-co-AA)	C=O 1730	C=O 1629	O—CH ₂ 2862	C—N 1362	C—O 1258
P(AMo-co-APSA)	C=O 1641	N—H 3443	S—O 1226	O—CH ₂ 2869	=C—H 3085

(AIBN) dissolved in 10 mL of dry toluene were added to a polymerization flask. The polymerization reaction was kept under N₂ at 70°C for 8 h. Subsequently, methanol was added. The resin was filtered, washed with abundant water, and dried at 40°C. The yield was 98.0%. The resin was screened, and a particle size of 250–500 μm was used in further runs.

Crosslinked P(AMo-co-AA)

AMo (5 mL, 0.04 mol), 3 mL (0.04 mol) of AA, 0.5 mL (0.0035 mol) of DVB, and 0.0651 g (0.00039 mol) of AIBN dissolved in 8 mL of dry toluene were added to a polymerization flask. The polymerization mixture was kept under N₂ at 70°C for 8 h. Then, methanol was added, and the resin was filtered, washed, and dried at 40°C until a constant weight. The yield was 95%. The resin was screened, and a particle size of 250–500 μm was employed for the following runs.

Crosslinked P(AMo-co-APSA)

AMo (5 mL, 0.04 mol), 8.1900 g (0.03951 mol) of 2-acrylamide-2-methyl-1-propane sulfonic acid (APSA), 0.5 mL (0.0035 mol) of DVB, and 0.0648 g (0.00039 mol) of AIBN dissolved in 5 mL of dried toluene were added to a polymerization flask. The flask was kept under N₂ (g) at 70°C for 8 h. The resin was filtered, washed with abundant water, and dried until a constant weight. The yield was 99.0%. The resin was screened, and a particle size of 250–500 μm was employed for the following runs.

Resin/metal-ion uptake

The batch metal uptake experiments were performed with standard metal salts AgNO₃, Cu(NO₃)₂, CdCl₂, HgCl₂, Zn(NO₃)₂, Pb(NO₃)₂, Al(NO₃)₃, and Cr(NO₃)₃ at pH 1–5 (the value depended on the metal ion). All experiments were performed in flasks mounted on a shaker at 25°C. The resin ligand/metal-ion ratio (mol) was 20 : 1. The retention ability for Ag(I), Cu(II), Cd(II), Zn(II), Hg(II), Pb(II), Al(III), and Cr(III), under noncompetitive and competitive conditions, was determined as a function of the pH. Batches of 0.05 g of the resin were used, together with a mixture of 5 mL of the metal-ion solution. After a shaking time of 1 h, the samples were filtered, washed with abundant water, and dried in vacuo at 40°C. The mixture in the

flask was filtered and washed with water, and the solution was transferred into calibrated 100-mL flasks. The metal ion was determined by atomic absorption spectrometry (AAS).

In the regeneration experiments, 1, 2, and 4M HNO₃ and 1, 2, and 4M HClO₄ were tested for their stripping potential. It was studied by the batch method. Batches of 0.05 g of the resin were loaded with mercury ions with a metal-ion solution at pH 2 under stirring for a period of 1 h. The loaded resin was washed with water, and the filtrates were collected.

To study the metal-ion-retention properties under competitive conditions, 5 mL of a mixture of metal ions (from nitrate salts) at the desired pH was brought into contact with 0.05 g of the dried resin at 20°C for 1 h. After a shaking time of 1 h, the samples were further handled as described for the noncompetitive experiments.

The necessary time to achieve the equilibrium was investigated by 5 mL of a metal-ion solution being brought into contact with 0.05 g of the resin at 20°C for 5, 15, 30, and 120 min at the corresponding pH.

To study the effect of the temperature on the metal-ion-retention properties, 5 mL of a metal-ion solution (from nitrate salts) at the desired pH was brought into contact with 0.05 g of the dried resin for 1 h at 20, 25, 30, 35, and 40°C.

To determine the maximum load capacity, solutions of Ag(I), Cu(II), Cd(II), Zn(II), Pb(II), Hg(II), Cr(III), and Al(III) (nitrate salt) at the optimum pH were prepared. The metal-ion solutions (25 mL, 1 g/L) were brought into contact with 0.5 g of the resin for 1 h at 20°C. They were filtered in 100-mL flasks. The process was repeated twice.

To recover the resin, 0.1 g of the loaded resin at the optimum pH was brought into contact with 10 mL of an eluent for 1 h at 20°C. Then, it was filtered, and the metal ion was analyzed by AAS.

TABLE II
Thermal Stability of the Resins

Resin	Weight loss (%) at different temperatures (°C)				
	100	200	300	400	500
P(AMo)	0.00	1.47	3.62	21.03	82.76
P(AMo-co-AA)	0.88	7.98	34.08	64.46	82.68
P(AMo-co-APSA)	0.00	2.35	8.83	37.15	86.62

Heating rate = 10°C/min.

To carry out charge–discharge cycles, 0.1 g of the dried resin with 10 mL of a metal-ion solution was stirred at the desired pH at 20°C for 1 h. Then, it was filtered on 100-mL flasks, completing the volume. Then, the loaded resin was brought into contact with 10 mL of the eluent solution at 20°C and filtered on a 100-mL flask. The volume was completed with twice distilled water. The process was repeated three times..

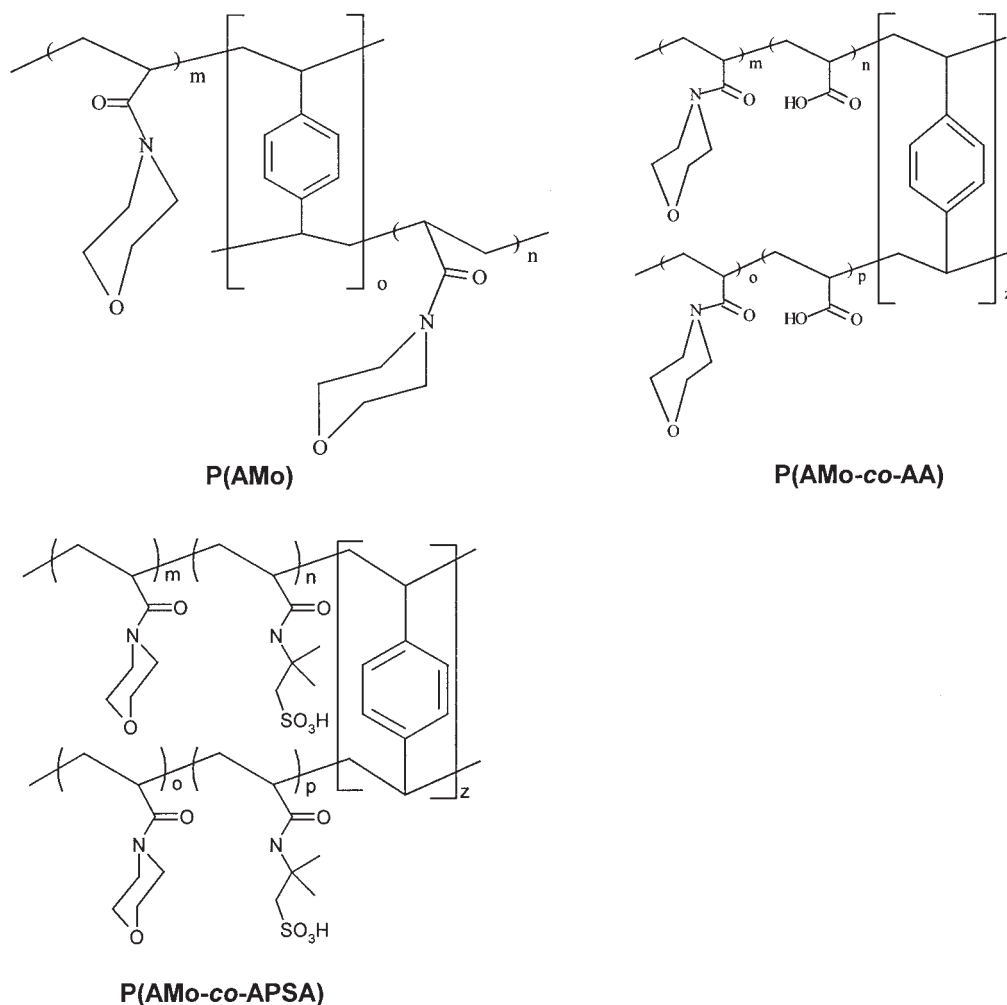
Measurements

A Julabo air-batch shaker (Julabo Labortechnik, GmbH, Germany) was used for shaking the solution at the desired temperature. The pH was measured with a H. Jurgens & Co. digital pH meter. A Unicam (United Kingdom) Solaar 5M series atomic absorption spectrometer

was used for the determination of single and mixed metal ions. The Fourier transform infrared (FTIR) spectra of the sample were recorded with a Magna Nicolet 550 spectrophotometer. The thermograms of the loaded and unloaded resins were recorded on an STA-625 thermoanalyzer (Polymer Laboratories). Approximately 5 mg of the dry sample was heated at a 10°C/min heating rate under a dynamic nitrogen atmosphere.

RESULTS AND DISCUSSION

Water-insoluble functional resins containing tertiary amine, sulfonic acid, and carboxylic acid groups by radical polymerization were synthesized. These resins contained either weak or strong acids coming from AA or APSA moieties, respectively:



The resins were characterized with FTIR spectroscopy and thermal analysis. Table I summarizes the most characteristic absorption bands.

Table II demonstrates that P(AMo) was the most thermally stable resin. It lost only 22% at 400°C. When the AMo moiety was copolymerized with AA and

APSA, the thermal stability decreased, particularly for the resin P(AMo-co-AA), probably because of the evolution of CO₂.

The metal-ion-retention properties were studied by the batch equilibrium procedure. The resin P(AMo) showed a low affinity for the metal ions in the pH

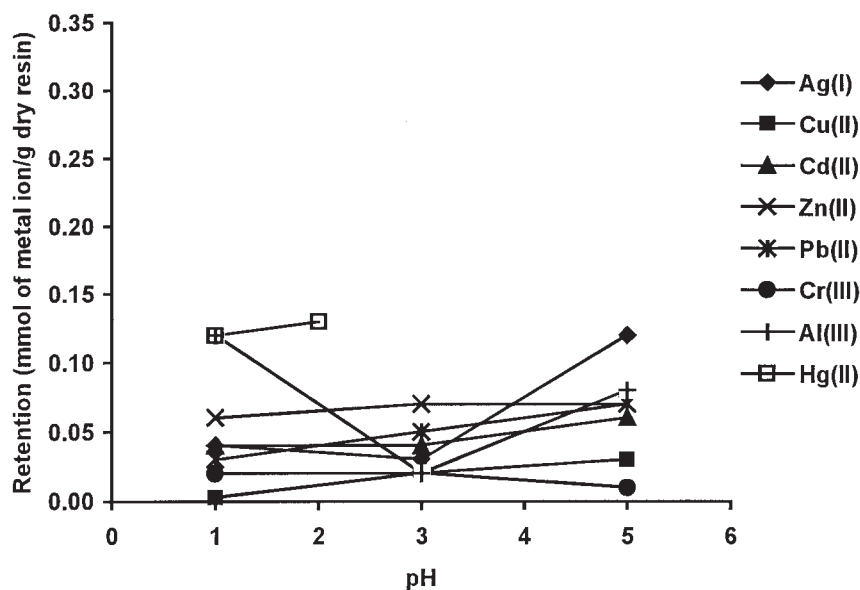


Figure 1 Retention (mol of metal ion/g of dry resin) versus pH for the resin poly(4-acryloylmorpholine). The initial amount of the metal ion was 0.35 mmol/g of dry resin.

range analyzed (see Fig. 1). This could be explained by the steric hindrance by the cycle, which reduced the availability of the tertiary amine groups to bind metal ions. By the incorporation of the moieties containing carboxylic acid (AA) and sulfonic acid (APSA), the metal-ion-retention capability was increased (see Figs. 2 and 3). In general, there was an effect of the pH on the cation retention: as the pH increased, the retention of metal ions increased. The highest retention values

were observed at pH 5, except for Hg(II) at pH 2. The resin P(AMo-co-AA) showed a higher affinity (0.20 mmol/g of dry resin) for Hg(II) ions at pH 2. At this pH, the carboxylic acid groups were not dissociated; therefore, complex formation with carboxylate groups should not have been possible, but the ion-exchange process would have been favored.

To determine metal-ion retention under competitive conditions, 0.050 g of the resin was brought into con-

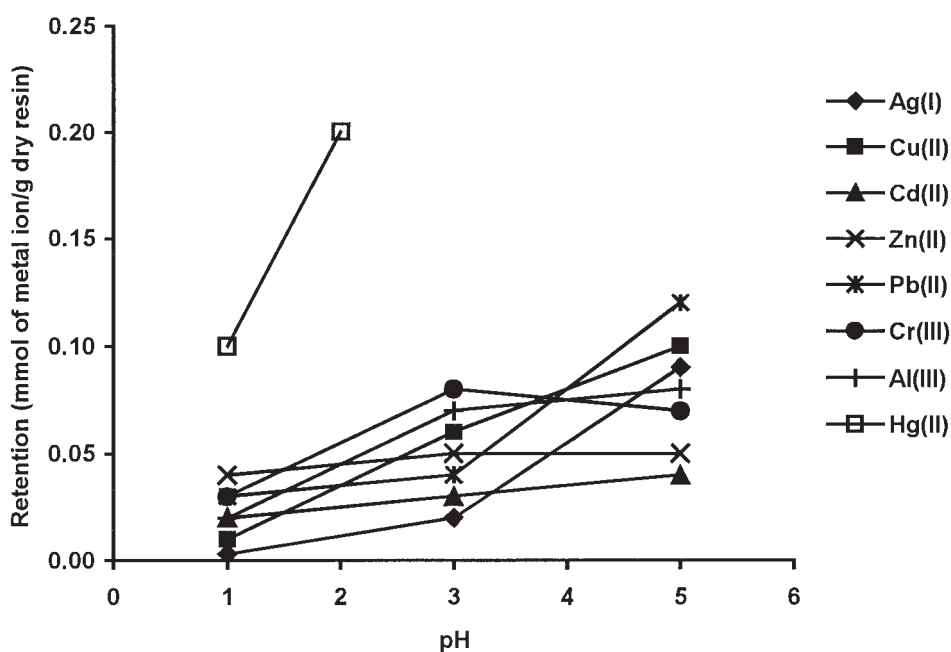


Figure 2 Retention (mmol of metal ion/g of dry resin) versus pH for the resin P(AMo-co-AA). The initial amount of the metal ion was 0.23 mmol/g of dry resin.

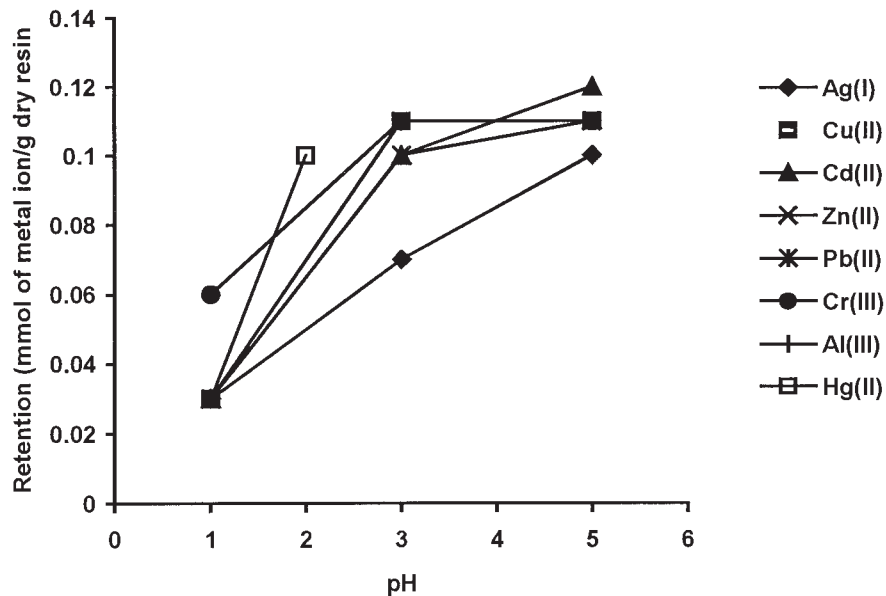


Figure 3 Retention (mmol of metal ion/g of dry resin) versus pH for the resin P(AMo-co-APSA). The initial amount of the metal ion was 0.14 mmol/g of dry resin.

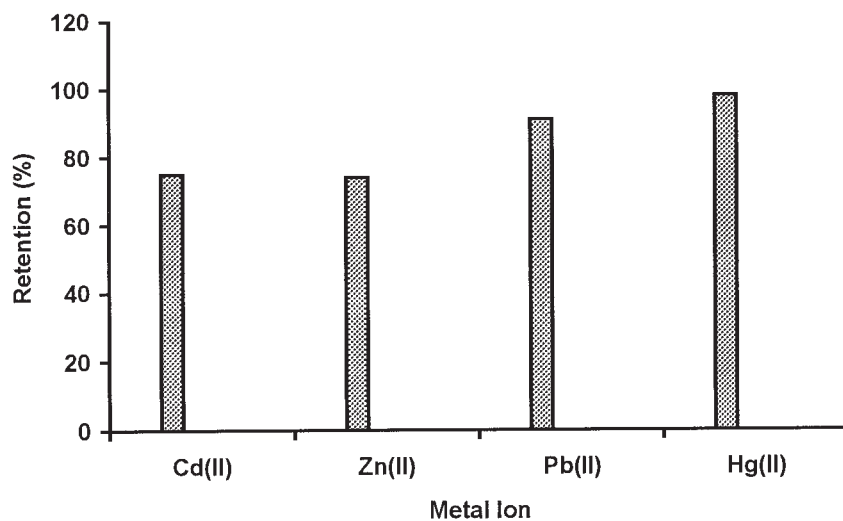


Figure 4 Metal-ion retention (%) from a mixture for the resin P(AMo-co-AA). The initial amount of the metal ion was 0.00219 mmol at pH 2.

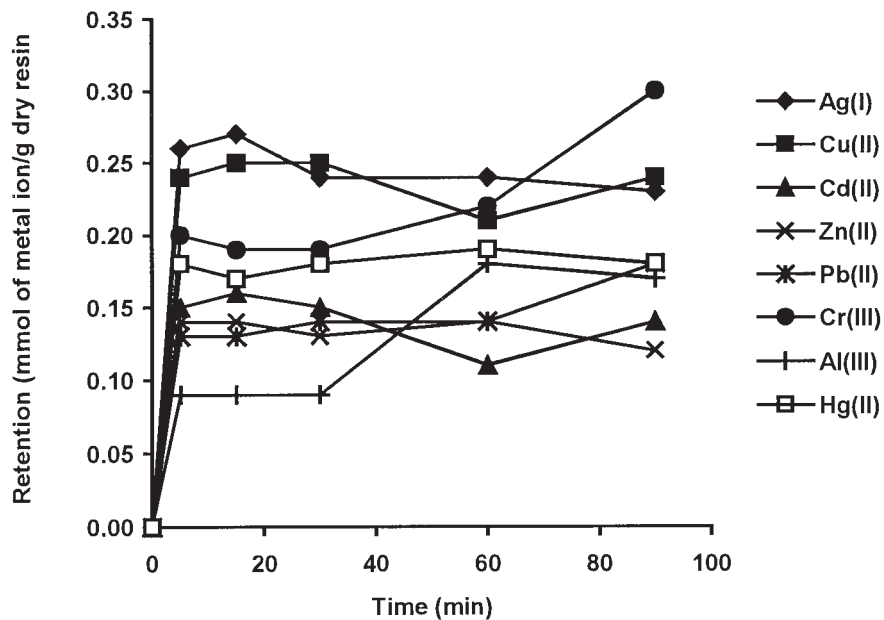


Figure 5 Effect of the time on the retention (mol of metal ion/g of dry resin) for the resin P(AMo-co-APSA). Ag(I), Cu(II), Cd(II), Zn(II), Pb(II), Cr(III), and Al(III) were studied at pH 5, and Hg(II) was studied at pH 2.

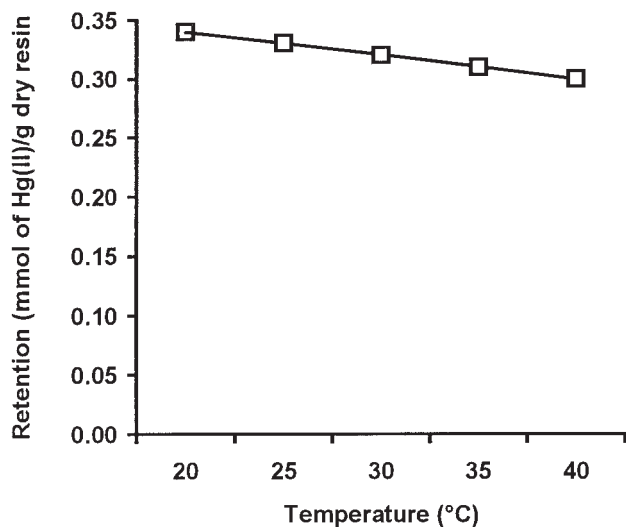


Figure 6 Effect of the temperature on the retention [mmol of Hg(II)/g of dry resin] for the resin P(AMo-co-AA).

tact at pH 2 for 1 h with 5 mL of an aqueous solution containing the same concentration of each metal ion. The resin showed the highest affinity for Hg(II) with respect to the other metal ions, Cd(II), Pb(II), and Zn(II) (see Fig. 4).

Figure 5 shows that the polymer ligand/metal-ion equilibrium was achieved before 5 min; this was very fast, in that the reaction occurred in a heterogeneous medium.

Figure 6 shows that there was not an important effect of the temperature on the mercury-ion retention for P(AMo-co-AA) with the batch equilibrium proce-

dure. There was only a decrease close to 10% as the temperature increased from 20 to 40°C. The resin P(AMo-co-APSA) showed a similar effect for all the metal ions, except for Pb(II), which decreased by almost 30%; this indicated that the ligand/metal-ion interaction occurred at the surface but not only by a chemisorption process (see Fig. 7).

To explore the applications of a resin, it is very important to obtain knowledge about the sorption capacity of the resin toward all metal ions, and according to that, the maximum retention load (MRL) of the resins P(AMo-co-AA) and P(AMo-co-APSA) was determined at pH 5 and at pH 2 for Hg(II) ions (see Figs. 8 and 9). The resin P(AMo-co-AA) showed the highest MRL value for Hg(II) and MRL values close to 1.3 mequiv/g of dry resin for the trivalent cations Al and Cr. The MRL values for the other metal ions were lower than 0.5 mequiv/g of dry resin. On the contrary, the resin P(AMo-co-APSA) showed higher MRL values than P(AMo-co-AA) because of a higher affinity of the sulfonic/sulfonate functional groups through electrostatic interactions with the metal ions.

To be useful in the ion-recycling process, the metal ion adsorbed by the resin should be easily released under appropriate conditions. The batch desorption studies were conducted via the loading of samples of the resin with each metal ion followed by a treatment with an excess of the extracting reagent. Two extractants, HClO₄ and HNO₃, were chosen at two concentrations. The two reagents acted in similar ways.

The effect of the eluent was higher for P(AMo-co-AA) than P(AMo-co-APSA) (see Figs. 10 and 11).

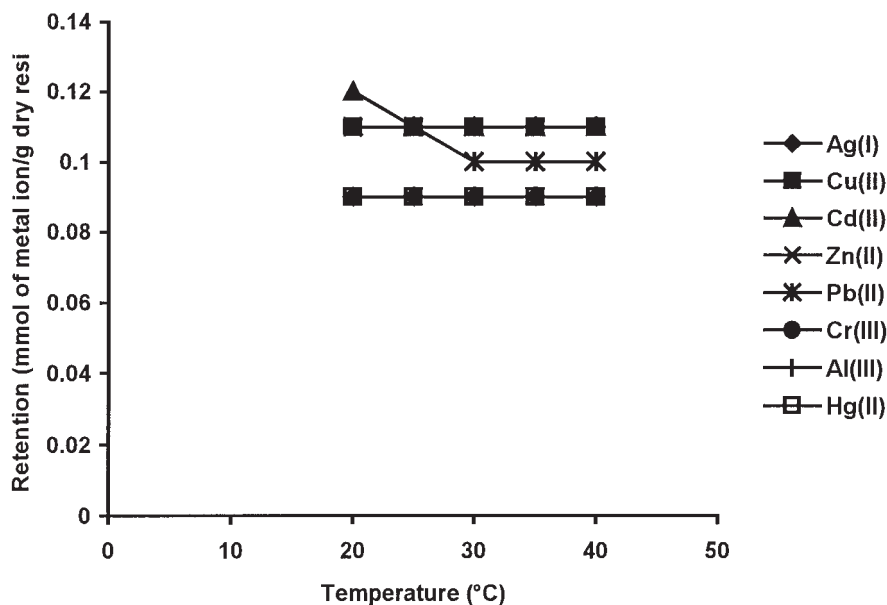


Figure 7 Effect of the temperature on the retention (mmol of metal ion/g of dry resin) for the resin P(AMo-co-APSA). Ag(I), Cu(II), Cd(II), Zn(II), Pb(II), Cr(III), and Al(III) were studied at pH 5, and Hg(II) was studied at pH 2.

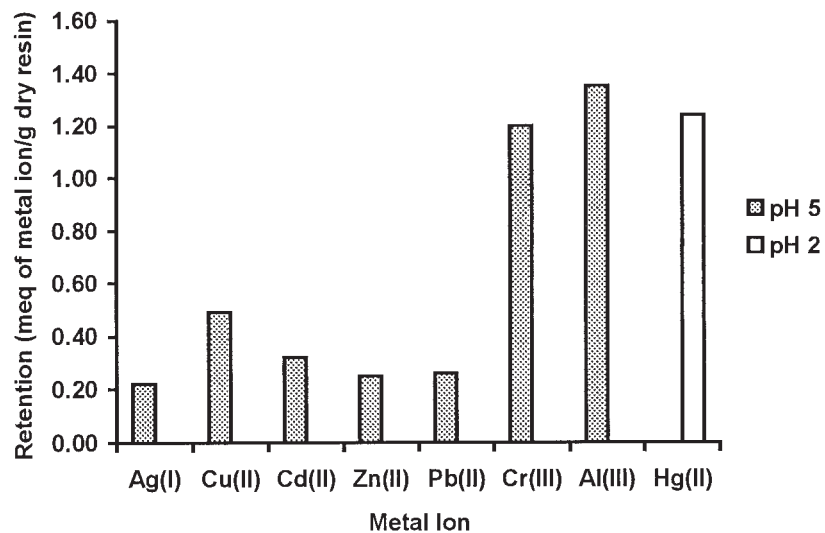


Figure 8 MRL (mequiv of metal ion/g of dry resin) versus the metal ion for the resin P(AMo-co-AA). Ag(I), Cu(II), Cd(II), Zn(II), Pb(II), Cr(III), and Al(III) were studied at pH 5, and Hg(II) was studied at pH 2.

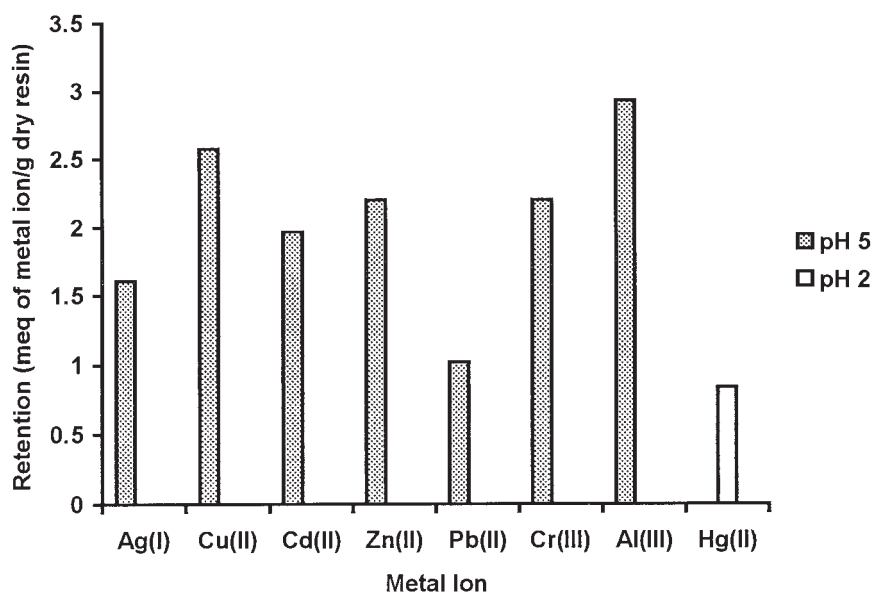


Figure 9 MRL (mequiv of metal ion/g of dry resin) versus the metal ion for the resin P(AMo-co-APSA). Ag(I), Cu(II), Cd(II), Zn(II), Pb(II), Cr(III), and Al(III) were studied at pH 5, and Hg(II) was studied at pH 2.

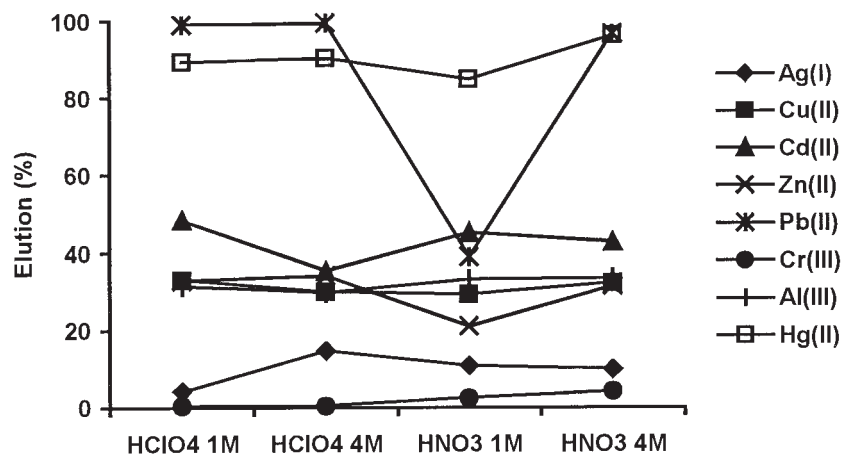


Figure 10 Elution (%) of the metal ion for the loaded resin P(AMo-co-AA) with Ag(I), Cu(II), Cd(II), Zn(II), Pb(II), Cr(III), and Al(III) at pH 5 and Hg(II) at pH 2.

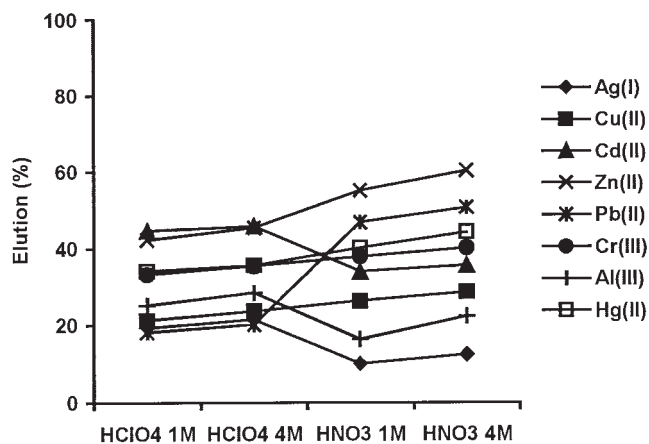


Figure 11 Elution (%) of the metal ion for the loaded resin P(AMo-co-APSA) with Ag(I), Cu(II), Cd(II), Zn(II), Pb(II), Cr(III), and Al(III) at pH 5 and Hg(II) at pH 2.

In general, there was not an important effect of the eluent concentration on the elution. For metal-ion-loaded P(AMo-co-AA), almost complete recovery was possible only when it was loaded with Pb(II) and Hg(II) ions. This result supports the assumption that the retention of Hg(II) is caused not exclusively by ion pairing but also by coordinative bonding between this metal and the complexing functionalities.

According to the previous results, to achieve reusability of the resin, the sorption-desorption cycles for Hg(II) were repeated four times with the same sorbent. Initial amounts of Hg(II) were employed to load the resin. In each cycle, the desorption was carried out at pH 2 for 1 h. A decrease close to 20% for the metal-ion-retention affinity was found (see Fig. 12).

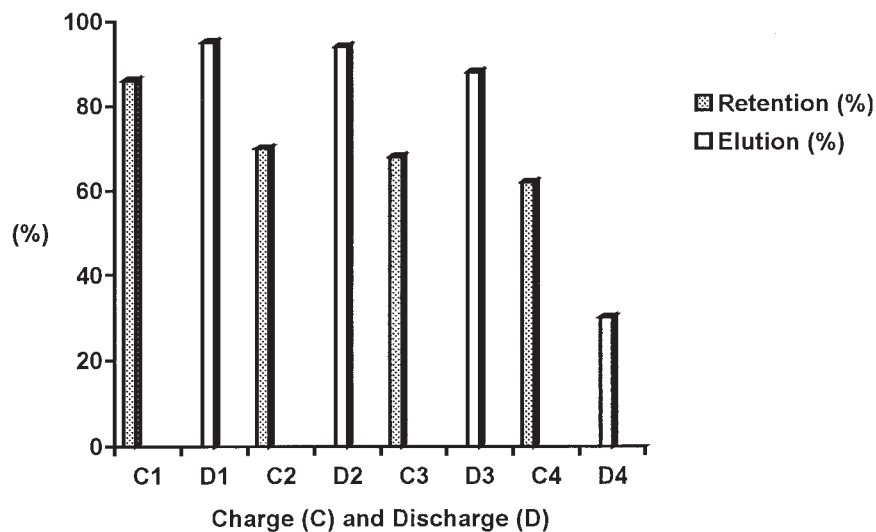


Figure 12 Charge and discharge cycles for P(AMo-co-AA) loaded with Hg(II). The eluent was 4M HNO₃.

CONCLUSIONS

The crosslinked resins P(AMo), P(AMo-co-AA), and P(AMo-co-APSA) were synthesized by solution radical polymerization. P(AMo), which contained tertiary amine groups, showed very poor affinity for the metal ions because of the steric hindrance of the cycle. P(AMo-co-AA) and P(AMo-co-APSA) with other functional groups (carboxylic acid and sulfonic acid, respectively) showed higher metal-ion capability than P(AMo). There was observed an effect of the pH but not of the temperature on the cation retention. The metal-ion retention showed a great affinity for the removal of mercury ions from an aqueous solution at pH 2. The adsorption equilibrium for the metal ions was reached within 5 min. An elution over 90% Hg(II) was obtained with 1–4M HClO₄ or HNO₃ as an eluent. Consecutive adsorption and desorption showed the feasibility of this resin for Hg(II)-ion adsorption.

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