Water-Insoluble Polymers with Ability to Remove Metal Ions

Bernabé L. Rivas, Sandra Villegas

Polymer Department, Faculty of Chemistry, University of Concepción, Casilla 160-C, Concepción, Chile

ABSTRACT: Crosslinked poly[3-(methacryloylamino)-propyl]dimethyl(3-sulfopropyl)ammonium hydroxide-*co*-2-acrylamido glycolic acid [P(MAAPDSA-*co*-AGCO)] was synthesized by radical polymerization and tested as an adsorbent under competitive and noncompetitive conditions for Cu(II), Cd(II), Hg(II), Zn(II), Pb(II), and Cr(III) by batch and column equilibrium procedures. The resin–metal ion equilibrium was achieved before 1 h. The resin showed a maximum retention capacity value for Hg(II) at pH 2 of 1.084 meq/g. The recovery of the resin was investigated at 20°C under different concentrations of HNO_3 and $HClO_4$. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 91: 3679–3685, 2004

Key words: adsorbents; metal ions; separation; crosslinking; maximum retention capacity

INTRODUCTION

The development of high-performance adsorbents for removing heavy metal ions from wastewater is considered a research priority in the environmental field.[1–18] Chelating resins have been successfully used for enriching and separating some metal ions from aqueous solutions. They are very useful because they have a higher selectivity and larger adsorbing capacities than those of other adsorbents (e.g., activated carbons and metal oxides) and they are also easily eluted and regenerated. Many researchers have prepared highly selective chelating resins for particular ions over the last two decades. For example, a new copper-selectivity chelating resin containing a salicylaldoxime group[19] was designed for the large-scale hydrometallurgical separation of copper ions from its ores. Egawa et al.[20] synthesized certain chelating resins containing mercapto functional groups. Matejka et al.[21] prepared poly(acrylamide) with oligo(ethyleneamine) moieties, and stated that the presence of alkaline earth-metal cations in the loading solution significantly improved the sorption capacities toward the chelated heavy metals. The large-scale commercial use of chelating resins is common with simple ion-exchange resins. Few of the chelating resins have been used chiefly in analytical applications, rather than for the recovery of toxic metal ions from wastewater because of the expensive cost. The commercially available chelating polymers are typically manufactured as porous microspheres.

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]

The use of polymer-bonded ligands in selective mercury removal has been subject of several studies.[2,13,17,23] Because of the high toxicity of all mercury compounds, the extraction of mercuric ions from aqueous wastes and drinking water is of special environmental importance. Two common ligand types, sulfur and amide, are currently being used in the design of polymer sorbents for selective binding of mercuric ions. The amide group has less of a tendency to bind with other metal ions under the same conditions because of the weak electron-donating nature of the amide group. As a result, the amide ligand is unique in its selective mercury uptake.

This article reports the metal ion retention properties of the resin poly[3-(methacryloylamino)propyl]-dimethyl(3-sulfopropyl)ammonium hydroxide-*co*-2-acrylamido glycolic acid [P(MAAPDSA-*co*-AGCO)], by using the batch and column equilibrium procedures. The metal ions were selected according to their environmental impact.

EXPERIMENTAL

Reagents

[3-(Methacryloylamino)propyl]dimethyl(3-sulfopropyl)ammonium hydroxide (MAAPDSA, 96%; Aldrich,

Milwaukee, WI), 2-acrylamido glycolic acid (AGCO, 99%; Aldrich), N,N'-methylene-bisacrylamide (MBA, 99%; Aldrich), and ammonium persulfate (AP; Aldrich) were used without further purification.

The metal salts (all from Merck, Darmstadt, Germany) used were cadmium (II), nitrate tetrahydrated; copper (II) nitrate, 2.5 hydrated; chromium (III) nitrate, nonahydrated; mercury (II) nitrate, monohydrated; lead (II) nitrate; and zinc (II) nitrate, hexahydrated. Analytical-grade nitric acid, perchloric acid, and sodium hydroxide were all purchased from Merck.

Synthesis of the resins

The synthesis of P(MAAPDSA-co-AGCO) was carried out in a polymerization flask to which 0.0613 mol of MAAPDSA, 0.0613 mol of AGCO, 2.0 mol % of MBA as crosslinking reagent, and 0.5 mol % of AP as initiator were added. The reaction was kept under nitrogen at 70°C for 4 h. The resin was filtered and washed with abundant water, and dried to a constant weight. Yield: 99%. Afterward, the resin was sized by screening, and the fraction with mesh size in the range of 180–250 μm (0.16–0.125 mm) was chosen.

Resin–metal ion uptake

The batch metal uptake experiments were performed using standard metal salt $Cu(NO_3)_2$, $CdCl_2$, $HgCl_2$, $Zn(NO_3)_2$, $Pb(NO_3)_2$, and $Cr(NO_3)_3$ at pH range 1–5 depending on the metal ion. All experiments were performed in flasks mounted on a shaker at 20°C. The capacities for Cu(II), Cd(II), Zn(II), Hg(II), Pb(II), and Cr(III), under noncompetitive and competitive conditions, were determined as a function of the pH. Batch metal-uptake experiments under competitive conditions were performed with the following metal ion mixtures. Batches of 0.05 g resin were used, together with a mixture of 5 mL of metal ion solution. After a shaking time of 1 h, the samples were filtered, washed with water, and dried under vacuum at 50°C. The resin : metal ion ratio (in mol) was 20 : 1.0. After a shaking time of 1 h, the samples were further handled as described for the noncompetitive experiments. For the column method 0.2 g resin was used together with a mixture of 20 mL of each metal solution. The flux time was 40 min. The solution was collected in a 100-mL flask and completed to volume.

To obtain the maximum adsorption capacity for mercury ions the column method was used. The column was packed with 0.5 g of resin and 25 mL of an aqueous solution (1 g/L) was passed through the column for 1 h. The mixture in the flask was filtered and washed with water, and the solution transferred into calibrated 100-mL flasks. The metal ion was determined colorimetrically by atomic absorption spectrometry.
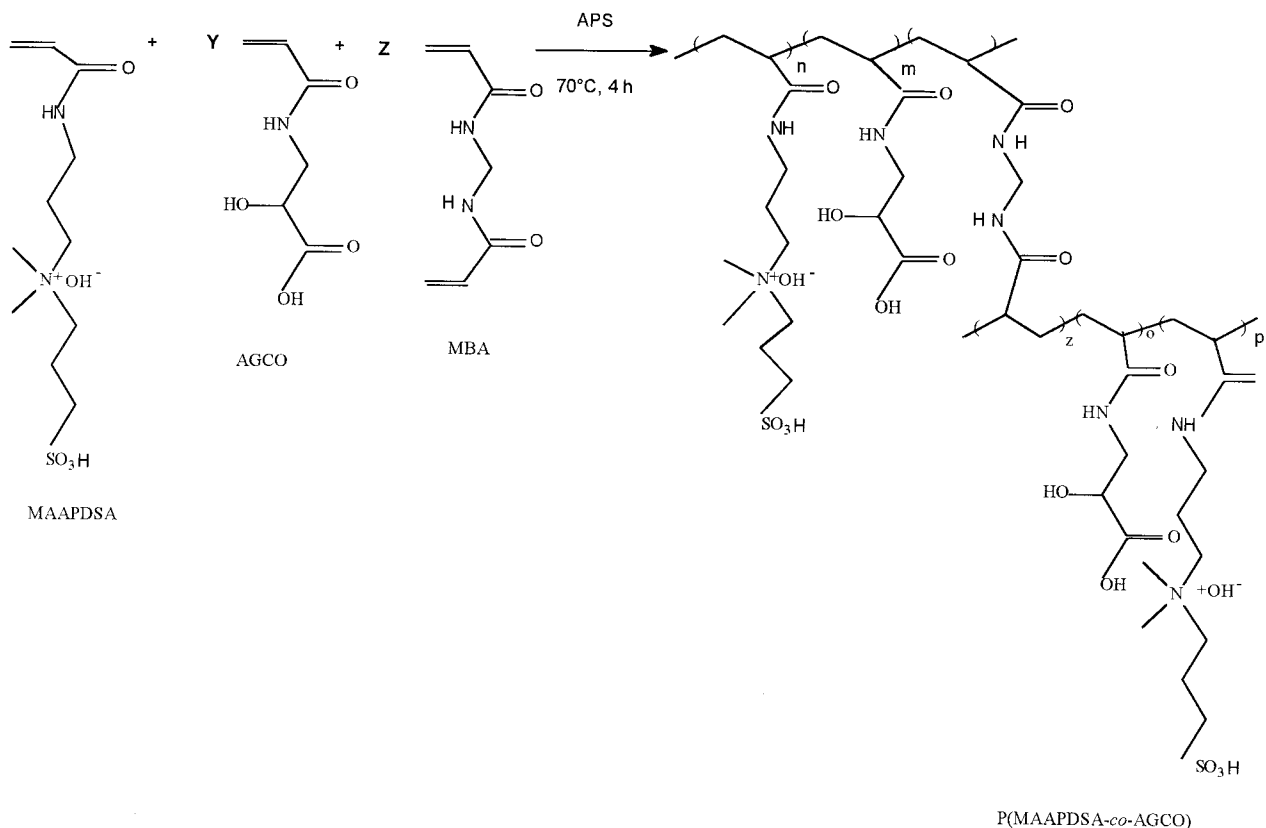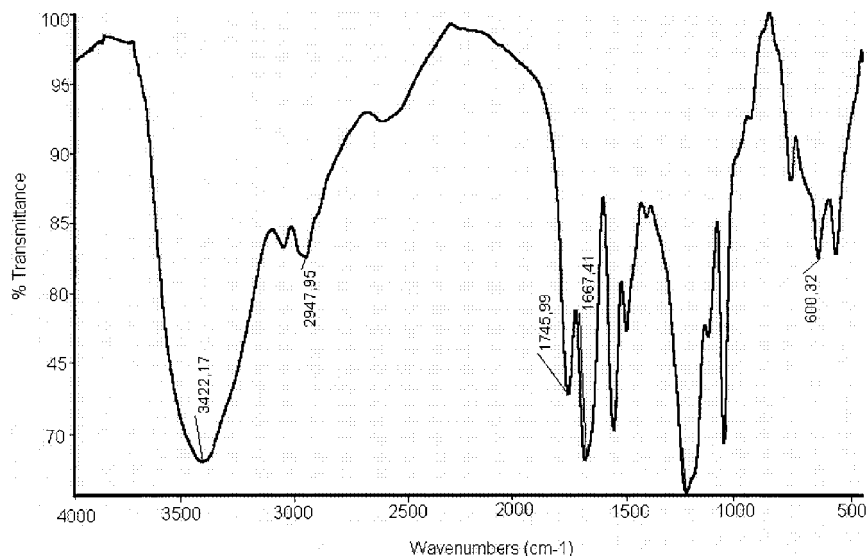

Scheme 1

Figure 1 FTIR spectrum of the resin P(MAAPDSA-*co*-AGCO).

In the regeneration experiments, (1, 2, and 4*M*) HNO_3 and (1, 2, and 4*M*) $HClO_4$ were tested for their stripping potential, studied by the batch method. Batches of 0.05 g resin-loaded mercury ions with metal ion solution at pH 2 were stirred for a period of 1 h. The loaded resin was washed with water and the filtrates were collected.

Measurements

A Julabo air-batch shaker (Germany) was used for shaking the solution at a desired temperature. The pH was measured with a digital pH meter (H. Jurgens and Co., Germany). A Unicam Solaar 5M series atomic absorption spectrometer (UK) was used for the determination of single and mixed metal ions. The FTIR spectra of the sample were recorded with a Magna Nicolet 550 spectrophotometer (Nicolet Analytical Instruments, Madison, WI). The thermograms of the loaded and unloaded resins were recorded on an STA-625 thermoanalyzer (Polymer Laboratories, UK). Approximately 5 mg of the dry sample was heated at 10°C/min heating rate under dynamic nitrogen atmosphere.

RESULTS AND DISCUSSION

The water-insoluble resin P(MAAPDSA-*co*-AGCO) was synthesized through radical polymerization solution by using AP and MBA as initiator and crosslinking reagent, respectively. The general polymerization reaction is shown as follows in Scheme 1.

The yield is 99.% with a particle size $> 1000 \ \mu$m but it does not depend on the crosslinking ratio. The resin also shows a high thermal stability up to 200°C with a weight loss lower than 10%. At 300°C the weight loss is 30%.

The FTIR spectrum of P(MAAPDSA-*co*-AGCO) shows among the absorption bands the most charac-

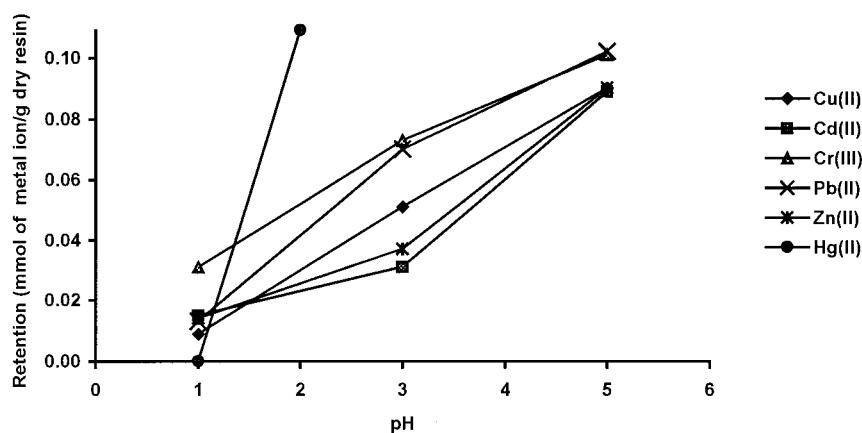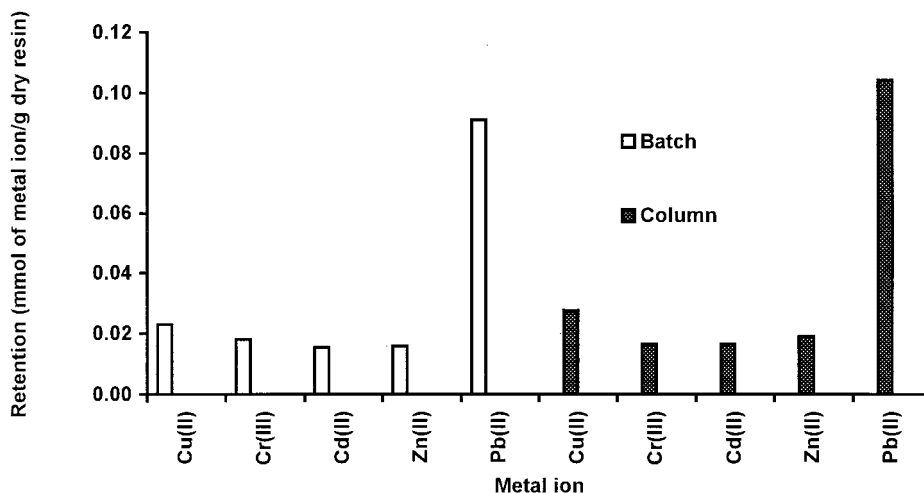**Figure 2** Effect of pH on metal ion retention. Contact time: 1 h, temperature: 20°C.

Figure 3 Metal ion retention at pH 5 by batch and column procedures. Flux rate: 30 mL/h, temperature: 20°C.

teristic ones (in cm^{-1}): 600.3 (weak) (C—S st.); at 1667.4 (C=O st. of a secondary amide); at 1745.9 (C=O st of carboxylic acid); at 2947.9 (C—H aliphatic st.); and at 3422.2 (N—H st. of a secondary amide) (see Fig. 1).

The copolymer composition was determined by comparing the intensity of the characteristic absorption signals of MAAPDSA and AGCO counits at 1667.4 and 1745.9 cm^{-1}, respectively. The coplymer composition corresponds to a 1 : 1 ratio, confirmed by elemental analysis through the sulfur content.

Metal ion–retention properties

Figure 2 shows the effect of the pH on the metal ion retention for the cations Cu(II), Cd(II), Hg(II), Pb(II), Zn(II), and Cr(III) by the batch procedure equilibrium. The resin/metal ion mol ratio studied was 20/1 to ensure a great excess of the ligand sites. The initial

amount of each metal ion was 0.10 mmol/g dry resin. The results demonstrated a strong dependency on the pH. The higher retention values were observed at pH = 5, which is near 80%. At pH = 2.0 the resin has a great affinity (99%) with the mercury ions, whereas for the other metal ions it was lower than 25%. Figure 3 shows the retention behavior at pH = 5. There is a high retention and selectivity for Pb(II) ions. No important difference between both equilibrium methods was observed.

Figure 4 shows that at pH 2 the highest retention corresponds to Hg(II) ions near 100%, and Zn(II) ions lower than 55%. There is only a difference for Zn(II) depending on the equilibrium procedure.

The resin has carboxylic acid, sulfonic acid, and ammonium as potential ion exchange/complexing groups. The retention of mercury ions could be explained by the complex formation of Hg(CH$_3$COO)$_2$ with the carboxylate groups coming from 2-acryl-
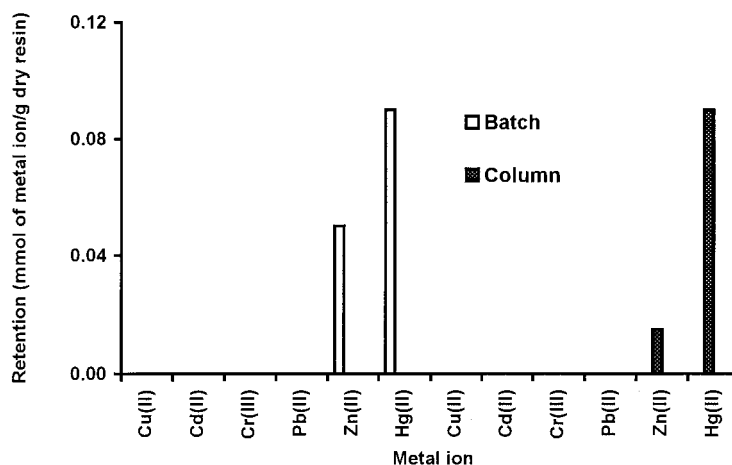

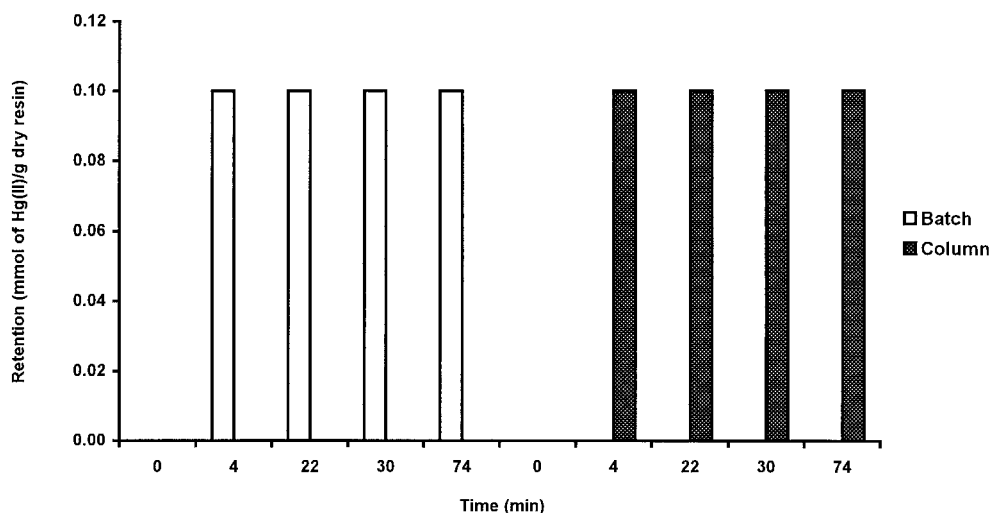**Figure 4** Metal ion retention at pH 2 by batch and column procedures. Flux rate: 30 mL/h, temperature: 20°C.

Figure 5 Effect of time on metal ion retention at pH 2. Temperature: 20°C.

amido glicoylc acid[24] and by electrostatic interactions with the sulfonic groups from the MAAPDSA unit.

According to these results the other runs were carried out considering the mercury ions as the central interest. The batch and column equilibrium procedures were tested.

At pH = 2 the resin showed a high selectivity for Hg(II) and the kinetics of the metal uptake was measured for the resin. Figure 5 shows that the resin removes the Hg(II) ions and the uptake is fast with 100% of cations sorbed within 4 min.

To explore the applications of the resin, it is very important to obtain knowledge on the sorption capacity of the resin toward Hg(II) ions and, according to that, the maximum retention of load of P(MAAPDSA-

co-AGCO) was determined at pH = 2.0. The value obtained corresponds to 1.084 meq (0.524 mmol)/g of dry resin.

To determine the metal ion retention under competitive conditions 50 mg of the resin was put in contact with 5 mL of an aqueous solution (at pH = 2.0 for 1 h) containing the same concentration of each metal ion. At pH 2 the resin showed a high selectivity for Hg(II) (99.9%) with respect to the other metal ions Cu(II), Cr(III), Pb(II), and Cd(II), which were not retained (0%), and Zn(II) (18%) (see Fig. 4).

Figure 6 shows that the resin adsorbed Hg(II) ions according to the feed concentration between the range 0.058 and 0.944 mmol but at a higher concentration the retention decreased up to about 25% at 0.944 mmol.
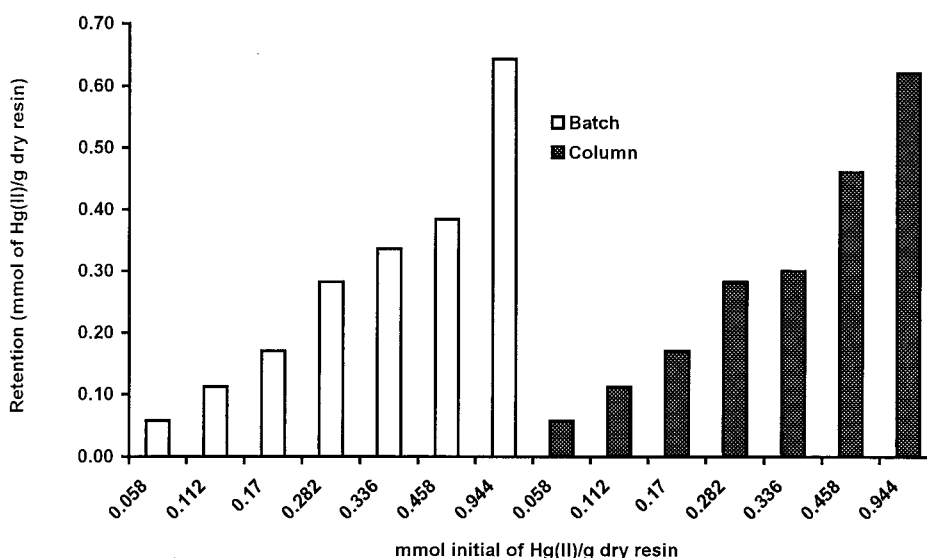

Figure 6 Effect of feed concentration of Hg(II) ions on retention at pH 2. Flux rate: 30 mL/h (column), contact time: 40 min (batch), temperature: 20°C.
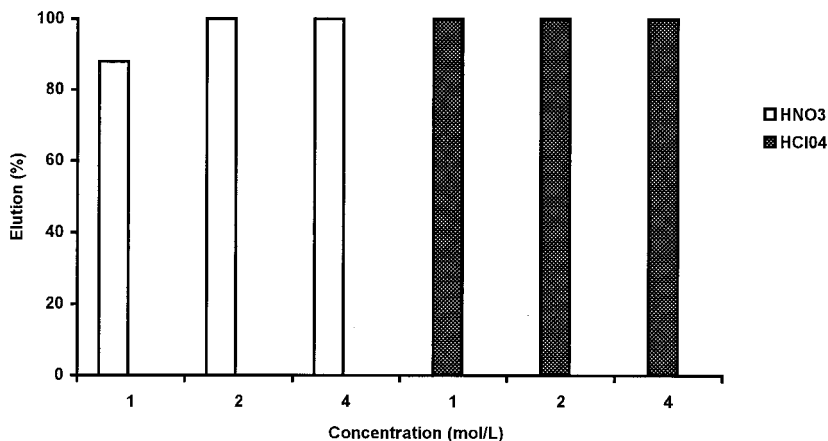
Figure 7   Elution of Hg(II) ions by HNO_3 and $HClO_4$ acids as eluents. Contact time: 30 min, temperature: 20°C.

That means that the active sites are saturated, particularly those placed at the surface considering that the ligand–metal ion interaction is basically diffusion controlled.

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 carried out by loading samples of the resin exclusively with Hg(II) followed by the treatment with an excess of the extracting reagent. Two extractants were chosen: $HClO_4$ and HNO_3. Both reagents would act in a similar way.

For all the experiments, the elution was higher than 99% with a treatment with $1M$ $HClO_4$ for 30 min. Moreover, the sorbent was able to withstand the strong acidic conditions and its metal ion–binding ability was retained after repeated acid treatments.

The resin was able to displace anionic metal complexes being ionically sorbed onto cationic functional groups. The results of the desorption are shown in Figure 7. Regarding the data of elution, it is evident that both eluent reagents show a similar behavior. This result supports the assumption that the retention of Hg(II) is caused not exclusively by ion pairing but also by a coordinative bonding between this metal and the complexing functionalities.

Hence, to obtain the reusability of the resin, the sorption–desorption cycle was repeated four times using the same sorbent. Initial amounts of Hg(II) were used to load the resin. In each cycle the desorption was carried out at pH 2 for 1 h. No important decrease on the metal ion retention affinity was found (see Fig. 8).

To apply this resin it is important to maintain the metal ion capacity after the treatment with the eluent reagent. The ability of the resin to remove Hg(II) ions was tested under dynamic conditions by passing a solution of Hg(II) at pH = 2.0 through a column. The packing of the column was carried out with 200 mg of the resin at 20°C. The time of flux was 13 min.
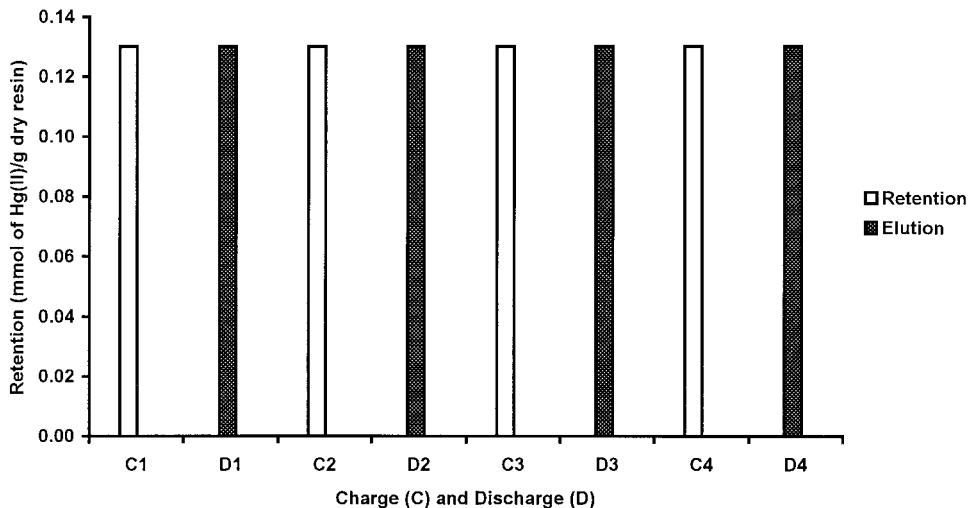

Figure 8   Charge (C) and discharge (D) cycles % of Hg(II) ions by batch equilibrium procedure.
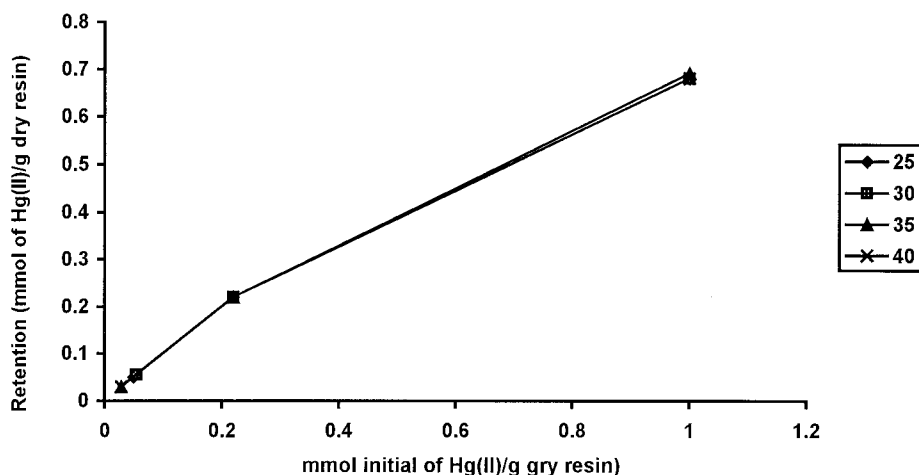
Figure 9 Effect of temperature (in °C) on retention of Hg(II) ions by column procedure. pH 2, time: 90 min.

Figure 9 shows that there is no effect of the temperature on the mercury ion retention by using the column equilibrium procedure. No important effect of the temperature on the mercury ion retention was observed.

CONCLUSIONS

The crosslinked P(MAAPDSA-co-AGCO), synthesized by solution radical polymerization, showed great promise in the removal of mercury ions from aqueous solution, particularly at pH = 2.0. The two most common equilibrium procedures, batch and column, were tested without important differences between the results. The adsorption equilibrium for Hg(II) ions was reached within 4 min. The adsorption capacity at pH 2.0 was 1.084 meq/g dry resin. No important effect of the temperature on the mercury ion retention was observed. An elution over 88% was obtained by using 1–4M HClO$_4$ and HNO$_3$. Consecutive adsorption and desorption showed the feasibility of this resin for Hg(II) ion adsorption.

References

1. Sigel, H., Ed. Metal Ion in Biological Systems, Vol. 2; Marcel Dekker: New York, 1973.
2. Sahni, S. K.; Reedjik, J. Coord Chem Rev 1984, 59, 1.
3. von Zelewsky, K.; Barbosa, L.; Schlapfer, C. W. Coord Chem Rev 1993, 123, 229.
4. Warshawsky, A. Angew Makromol Chem 1982, 109/110, 171.
5. Das, D.; Das, A. K.; Sinha, Ch. Talanta 1999, 48, 1013.
6. Montembault, V.; Soutif, J. C.; Brosse, J. C.; Grote, M. React Polym 1999, 39, 253.
7. Rivas, B. L.; Pooley, S. A.; Maturana, H. A.; Villegas, S. A. J Appl Polym Sci 2001, 80, 253.
8. Rivas, B. L. In: Polymeric Encyclopedia Materials. Synthesis, Properties, and Applications; Salamone, J. C., Ed.; CRC Press: Boca Raton, FL, 1996; Vol. 6, p. 4137.
9. Pearson, R. G. J Am Chem Soc 1963, 85, 3533.
10. Bradshaw, J. S.; Izatt, R. M. Acc Chem Res 1997, 30, 338.
11. Izatt, R. M.; Pawlak, K.; Bradshaw, J. S.; Bruening, J. L. Chem Rev 1995, 95, 2529.
12. Wu, G.; Jiang, W.; Lamb, J. D.; Bradshaw, J. S.; Izatt, R. M. J Am Chem Soc 1991, 113, 6538.
13. Rivas, B. L.; Geckeler, K. E. Adv Polym Sci 1992, 102, 171.
14. Rivas, B. L.; Pooley, S. A.; Maturana, H. A.; Villegas, S. Macromol Phys 2001, 202, 443.
15. Rivas, B. L.; Pereira, E. D. Bol Soc Chil Quim 2000, 45, 165.
16. Rivas, B. L.; Pooley, S. A.; Maturana, H. A.; Villegas, S. J Appl Polym Sci 2001, 80, 2123.
17. Rivas, B. L.; Maturana, H. A.; Luna, M. J Appl Polym Sci 1999, 74, 1557.
18. Rivas, B. L.; Peric, I. M.; Maturana, H. A.; Fuentes, L. Polym Bull 1999, 42, 337.
19. Ebraheem, K. A. K; Hamdi, S. T. React Funct Polym 1997, 34, 5.
20. Egawa, H.; Nonaka, T.; Maeda, H. Sep Sci Tecnnol 1985, 20, 653.
21. Matejka, Z.; Zitkova, Z. React Funct Polym 1997, 35, 81.
22. Kaliyappan, T.; Kannan, P. Prog Polym Sci 2000, 25, 343.
23. Filho, N. L.; Gushikem, Y. Sep Sci Technol 1997, 32, 2535.
24. Yatsimirskii, K. B; Vasil'ev, V. P. Instability Constants of Complex Compounds; Chernyaev, I. I., Ed.; Originally published by Academy of Sciences USSR Press: Moscow, 1959; p. 151 [Consultants Bureau Enterprises: New York, 1960].