

Resins Containing Amino and Carboxylic Acid Groups. Synthesis, Characterization, and Metal Ion Retention Properties

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ABSTRACT: The crosslinked poly[3-(methacryloylamino)propyl]dimethyl(3-sulfopropyl)ammonium hydroxide], P(MAPDSA), and poly[3-(methacryloylamino)propyl]dimethyl(3-sulfopropyl)ammonium hydroxide-co-acrylic acid], P(MAPDSA-co-AA), were synthesized by radical polymerization. The resins were completely insoluble in water. Due to the lower metal ion retention of P(MAPDSA), the metal ions investigated under competitive and noncompetitive conditions for Cu(II), Cd(II), Hg(II), Zn(II), Pb(II), and Cr(III) ions by batch and column equilibrium procedures were carried out only for P(MAPDA-co-AA), particularly for

Hg(II). The resin-Hg(II) ion equilibrium was achieved before 15 min. The resin showed a maximum retention capacity value for Hg(II) at pH 2 of 1.89 meq/g. The resin showed a high selectivity to Hg(II) ions. The recovery of the resin was investigated at 25°C with different concentrations of HNO₃ and HClO₄. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 525–530, 2005

Key words: resin; radical polymerization; metal-polymer complex

INTRODUCTION

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

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 process. The ion-exchange reaction is an extremely versatile reaction and one that is well suited to the complexation 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 a 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 fourfold²¹: (1) high capacity for the metal(s) of interest; (2) high selectivity; (3) fast kinetics—rapid equilibration with metal-containing solutions; and (4) high mechanical strength and toughness of the exchanger particles. Unfortunately, the last two are competitive. That means that if a soft gel is obtained, the ligand–metal equilibrium should be achieved faster than that with a very hard polymeric material, but it should be not adequate as adsorbent material, particularly for the study by column method. On the contrary, a non-gel-type material should be more adequate for study by the column method, but it is important to consider that the ligand–metal ion equilibrium will need a longer time. Therefore, it is necessary to achieve a compromise between both properties.

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 the subject of several papers^{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 envi-

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ronmental importance. Two common ligand types, sulfur and amide, are being used currently in the design of polymer sorbents for binding mercuric ion selectivity. Many sulfur-containing chelators display strong affinities for certain transition and heavy metals, e.g., Cd(II), Pb(II), and Hg(II), as well as for some of the organometallic derivatives of these metals. Dithiocarbamates are known to form complexes of very high thermodynamic stability with several heavy metal ions, especially with Hg(II). 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 paper reports the metal ion retention properties of the resins poly[3-(methacryloylamino)propyl]dimethyl(3-sulfopropyl)ammonium hydroxide] and poly[3-(methacryloylamino)propyl]dimethyl(3-sulfopropyl)ammonium hydroxide-*co*-acrylic acid] 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 96% (Aldrich) (MAPDSA), acrylic acid 99% (AA, Merck), *N,N'*-methylenebisacrylamide (MBA 99%, Aldrich), and ammonium persulfate (AP, Aldrich), were used without further purification.

The metal salts 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 (all from Merck). The analytical grade, nitric acid, perchloric acid, and sodium hydroxide were purchased from Merck.

Synthesis of the resins

The synthesis of the resins poly[3-(methacryloylamino)propyl]dimethyl(3-sulfopropyl)ammonium hydroxide], P(MAPDSA) and poly[3-(methacryloylamino)propyl]dimethyl(3-sulfopropyl)ammonium hydroxide-*co*-acrylic acid] P(MAPDSA-*co*-AA) was carried out in a polymerization flask. As an example the polymerization of P(MAPDSA-*co*-AA) was carried out as follows: 0.034 mol of MAPDSA, 0.034 mol of AA, 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 up to 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.

Elemental analysis of P(MAPDSA-*co*-AA): Theoretical (exp) values (%): C: 47.06 (47.28); H: 7.84 (7.97); N: 7.32 (7.22); S: 8.37 (8.31).

Resin-metal ion uptake

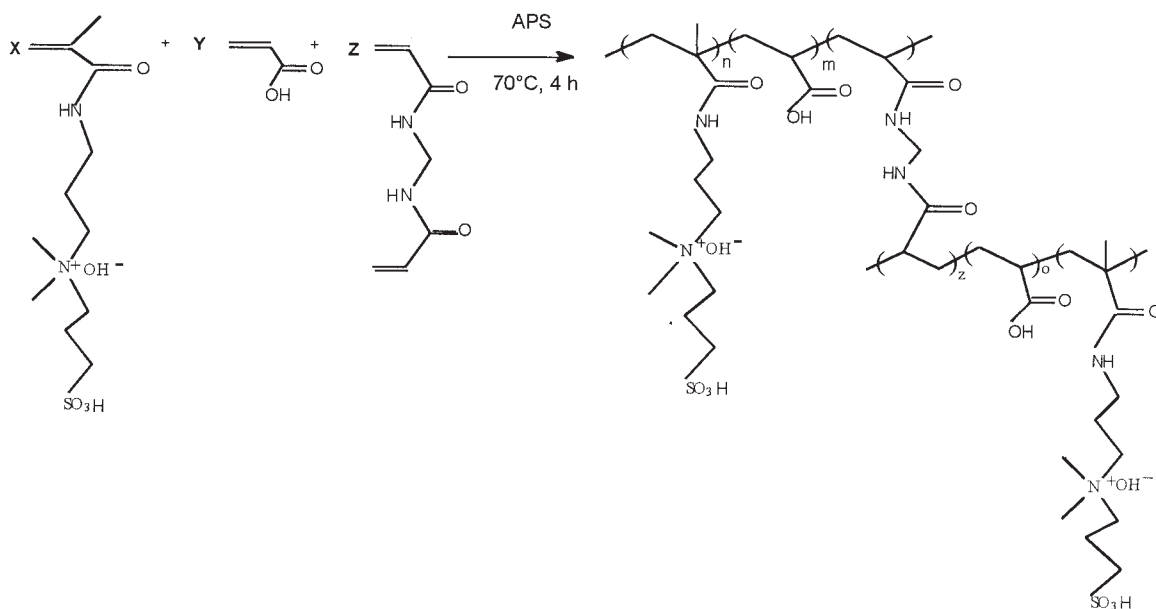
The batch metal uptake experiments were performed using standard metal salt $\text{Cu}(\text{NO}_3)_2$, $\text{Cd}(\text{NO}_3)_2$, $\text{Hg}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$, and $\text{Cr}(\text{NO}_3)_3$ at pH range 1–5 depending on the metal ion. All experiments were performed in flasks mounted on a shaker at 20°C. The retention ability for Cu(II), Cd(II), Zn(II), Hg(II), Pb(II), and Cr(III), under noncompetitive and competitive conditions, was determined as a function of the pH. 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. Batch metal-uptake experiments under competitive conditions were performed with the following metal ion mixtures. Batches of 0.2 g resin were used together with a mixture of 20 mL of each metal solution. The resin:metal ion ratio (in mol) is 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, the flux time was 45 min. The solution was collected in a flask of 100 mL 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 during 37 min. 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.

In the regeneration experiments, (1, 2, and 4M) HNO_3 and (1, 2, and 4M) HClO_4 were tested for their stripping potential. It was studied by the batch method. Batches of 0.05 g resin loaded mercury ions were used. The loaded resin was washed with water and the filtrates were collected.

Measurements

A Julabo air-batch shaker was used for shaking the solution at a desired temperature. The pH was measured with a Jenco Electronics 1671 pH meter (Jenco Instruments, CA). A Unicam Solaar 5M series atomic absorption spectrometer (Unicam, 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 Ana-



Scheme 1

lytical Instruments, Madison, WI). The thermograms of the loaded and unloaded resins were recorded on a STA-625 thermoanalyzer (Polymer Laboratories, Amherst, UK). Approximately 5 mg of the dry sample was heated at 10°C/min heating rate under nitrogen atmosphere.

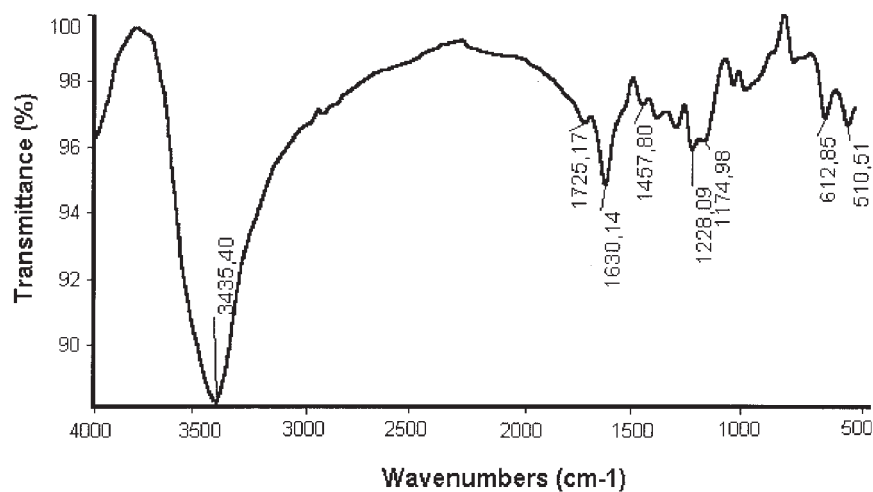
RESULTS AND DISCUSSION

The water-insoluble resins P(MAPDSA) and P(MAPDSA-*co*-AA) were synthesized through radical polymerization solution using AP and MBA as initiator and crosslinking reagents, respectively. The general scheme of polymerization reaction is shown below (Scheme 1).

The yield is 99% with a particle size > 1000 μm but it does not depend on the crosslinking reagent concentration.

The FTIR of the resin P(MAPDSA) shows the following characteristic absorption bands (in cm^{-1}): 606.18 (weak, C-S st.); 1481.39 (strong, ammonium salt); 1641.74 (strong, C = O, amide); 3437, 63 (strong, N-H, secondary amide).

The FTIR spectrum of the resin P(MAPDSA-*co*-AA) shows among the absorption bands the most characteristic ones (in cm^{-1}): 612.85 (weak) (C-S st.); at 1037.78 (weak) (S = O, sulfonic acid); 1630.14 (C = O st. of a secondary amide); at 1725.17 (C = O st. of carboxylic acid); at 2947.9 (C-H aliphatic st.); and at 3435.40 (N-H st. of a secondary amide) (see Fig. 1).

Figure 1 FTIR spectrum of the resin P(MAPDSA-*co*-AA).

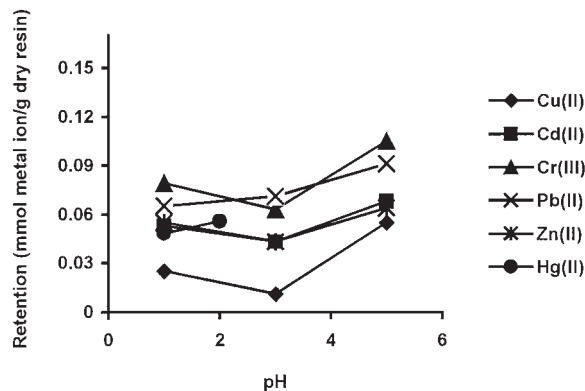


Figure 2 Effect of pH on the metal ion retention of the resin P(MAPDSA). Contact time: 1 h. Temperature: 20°C.

The resin P(MADPSA-*co*-AA) also shows a high thermal stability up to 200°C with a weight loss lower than 10%. At 300°C the weight loss is 25%, and it increases significantly at 400°C (70%).

The copolymer composition was determined by comparing the intensity of the characteristic absorption signals of MAPDSA and AA counts at 1630.14 and 1725.17 cm^{-1} , respectively. The copolymer composition corresponds to a 1:1 ratio. It was corroborated by elemental analysis through the sulfur content.

Metal ion retention properties

Figure 2 shows the effect of the pH on the metal ion retention of the resin P(MAPDSA) for the Cu(II), Cd(II), Hg(II), Pb(II), Zn(II), and Cr(III) cations by the batch procedure equilibrium. The resin/metal ion mol ratio studied was 20/1 to assure a great excess of the ligand sites. The initial amount of each metal ion was 0.17 mmol/g dry resin. The results demonstrated a low metal ion retention ability. The highest retention value was observed at pH 5 for Cr(III), which is near 60% (0.105 mmol/g dry resin).

Figure 3 shows the metal ion retention behavior of the resin P(MADPSA-*co*-AA) at different pH. There is a high retention and selectivity for Hg(II) ions at pH 2. All the other metal ions were retained with values lower than 0.09 mmol/g. No important difference between both equilibrium methods was observed. Only at pH 5 did the retention of all other metal ions increase up to values that ranged between 0.06 and 0.09 mmol/g dry resin. For this resin, the carboxylate groups should be the most active ligand groups.

According to these results all other runs were carried out at pH 2 considering the mercury ions 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 4 shows that the resin

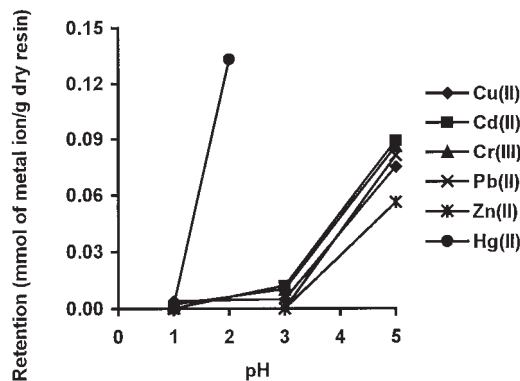


Figure 3 Metal ion retention behavior at different pH of the resin P(MAPDSA-*co*-AA). Time: 1 h. Batch procedure at 20°C.

removes the Hg(II) ions from an aqueous solution and the uptake is fast with 100% of cations sorbed within 5 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 the resin P(MAPDSA-*co*-AA) was determined at pH 2. The value obtained corresponds to 1.89 meq (0.524 mmol)/g of dry resin.

To determine the metal ion retention under competitive conditions 50 mg of the resin were contacted at pH 2 during 1 h with 5 mL of an aqueous solution containing the same concentration of each metal ion. 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. 5).

In terms of Pearson's concept of hard and soft acids and bases⁹, carboxylate groups are soft bases and Hg(II) is a soft acid. As a general rule, hard acids coordinate better with hard bases, and soft acids co-

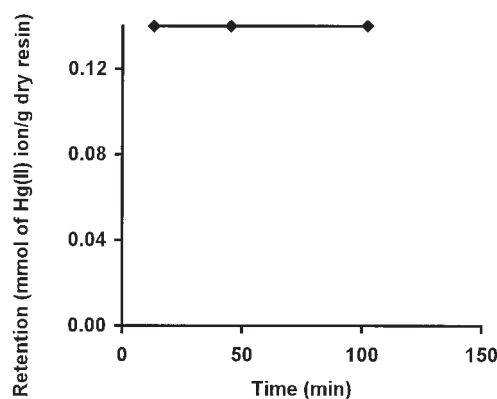


Figure 4 Effect of time on metal ion retention at pH 2. Temperature: 20°C.

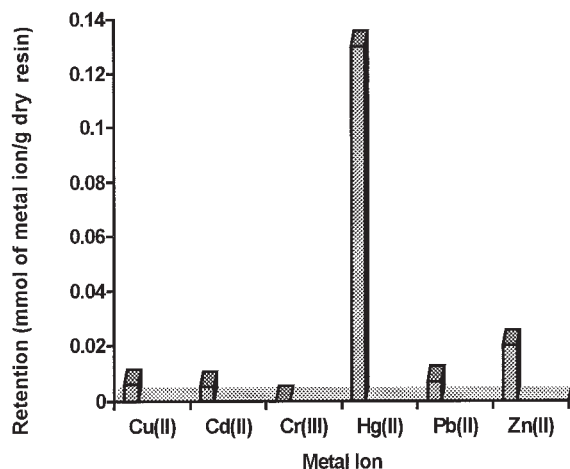


Figure 5 Metal ion retention of Hg(II) ions under competitive conditions at pH 2 by column procedure. Flux rate: 20 mL/h. Temperature: 20°C.

ordinate better with soft bases. The hard-base/hard-acid interaction is a charge-controlled one, resulting mostly from a favorable electrostatic interaction between a donor and an acceptor, respectively, with high and low orbital electronegativity. However, the interaction between a soft acid and a soft base normally leads to the covalent coordination of a donor with low orbital electronegativity and an acceptor with high electronegativity. Therefore, a strong interaction between Hg(II) and P(MADPSA-co-AA) was expected to be found because of their high ability to form coordination bonds.

Figure 6 shows that there is not an effect of the size resin particle on the Hg(II) ions retention in the range of 100 and 500 μm , and it decreases slightly at higher sizes. This could suggest that the interaction is not strongly diffusion controlled.

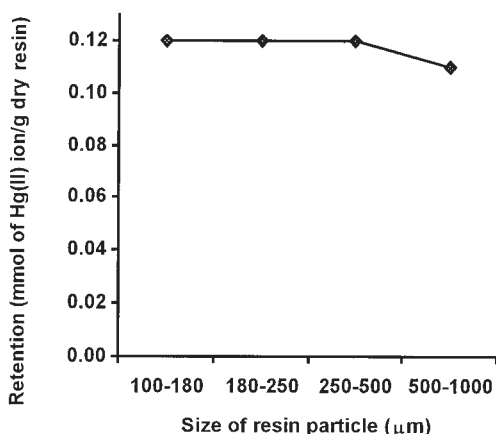


Figure 6 Effect of resin particle size on Hg(II) ion retention at pH 2. Flux rate: 30 mL/h. Initial concentration of Hg(II): 0.14 mmol/g dry resin.

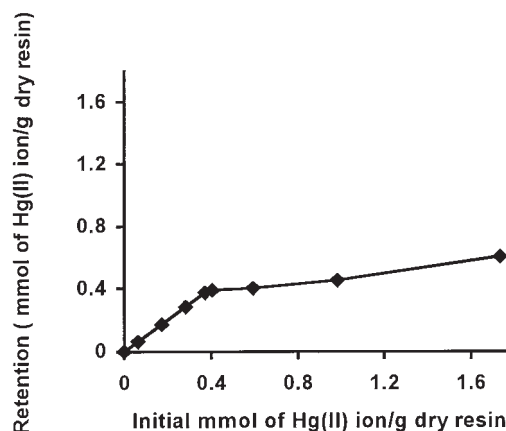


Figure 7 Effect of feed concentration of Hg(II) ions on retention at pH 2. Flux rate: 20 mL/h (column). Temperature: 20°C.

Figure 7 shows that the resin adsorbs Hg(II) ions according to the feed concentration between the range 0.025 and 0.04 mmol, but at a higher concentration the retention decreases up to about 50% at 1.8 mmol. That means that the active sites are saturated, particularly those placed at the surface.

Figure 8 shows that there is not an effect of temperature in the range of 25 and 40°C on mercury ion retention by using the column equilibrium procedure. This could be attributed to the fact that the chemical adsorption process is the most relevant.

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 have been chosen: HClO_4 and HNO_3 . For all the experiments, the elution was higher than 98% with treatment with 1M HClO_4 during 30 min.

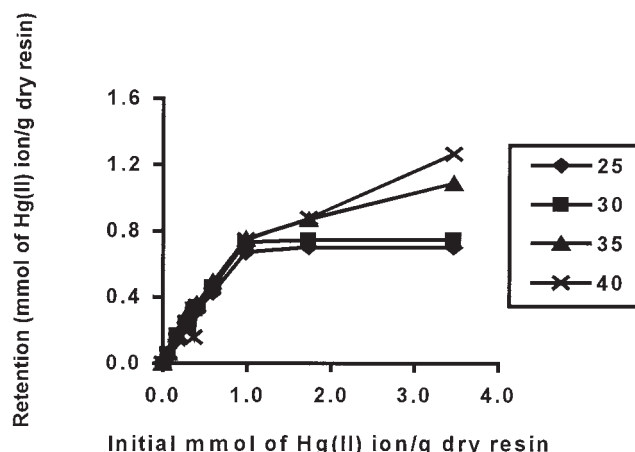


Figure 8 Effect of temperature (in °C) on Hg(II) ion retention by batch procedure. pH 2. Time: 72 h.

The resin is able to displace anionic metal complexes being ionically sorbed onto cationic functional groups. The results of the desorption are shown in Figure 9. Regarding the data of elution, 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 employed to load the resin. In each cycle the desorption was carried out at pH 2 for 1 h. No important decrease in metal ion retention affinity was found (see Fig. 10).

To apply this resin it is important to maintain the metal ion capacity after 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 resin at 20°C. The time of flux was 60 min.

CONCLUSIONS

The crosslinked P(MAAPDSA-co-AA) that was synthesized by solution radical polymerization showed great affinity in the removal of mercury ions from aqueous solution at pH 2. 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 5 min. The adsorption capacity at pH 2 was 1.89 meq/g dry resin. An elution over 90% was obtained using 1–4M HClO₄ and HNO₃. Consecutive

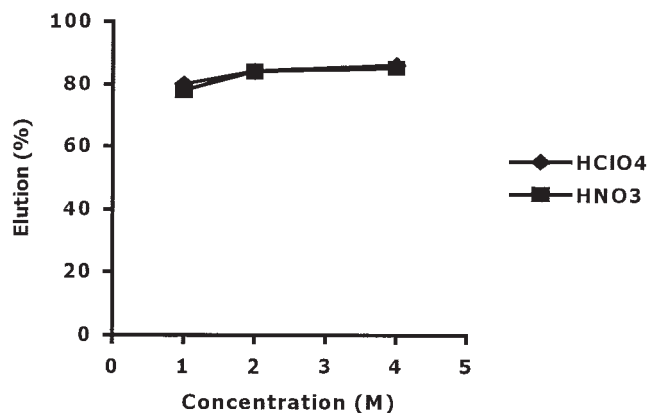


Figure 9 Elution of Hg(II) ions by HNO₃ and HClO₄ acids as eluents. Contact time: 60 min. Temperature: 20°C.

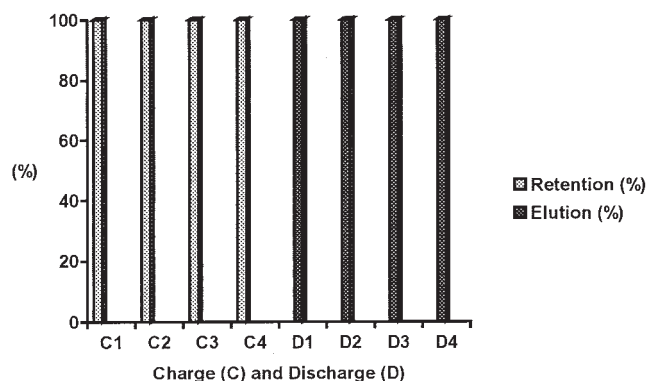


Figure 10 Charge (C) and discharge (D) cycles % of Hg(II) ions by batch equilibrium procedure.

adsorption and desorption showed the feasibility of this resin for Hg(II) ion adsorption.

References

- Sigel, H. (Ed.) Metal Ion in Biological Systems; Dekker: New York, 1973, p 2.
- Sahni, S. K.; Reedjik, J. Coord Chem Rev 1984, 59, 1.
- von Zelewsky, K.; Barbosa, L.; Schlapfer, C. W. Coord Chem Rev 1993, 123, 229.
- Warshawsky, A. Angew Makromol Chem 1982, 109/110, 171.
- Das, D.; Das, A. K.; Sinha, Ch. Talanta 1999, 48, 1013.
- Montebault, V.; Soutif, J. C.; Brosse, J. C.; Grote, M. React Polym 1999, 39, 253.
- Rivas, B. L.; Pooley, S. A.; Maturana, H. A.; Villegas, S. A. J Appl Polym Sci 2001, 80, 253.
- Rivas, B. L. In Polymeric Encyclopedia Materials. Synthesis, Properties, and Applications; Salamone, J. C., Ed.; CRC Press: Boca Raton, FL, 1996; p 4137, Vol 6.
- Pearson, R. G. J Am Chem Soc 1963, 85, 3533.
- Bradshaw, J. S.; Izatt, R. M. Acc Chem Res 1997, 30, 338.
- Izatt, R. M.; Pawlak, K.; Bradshaw, J. S.; Bruening, J. L. Chem Rev 1995, 95, 2529.
- Wu, G.; Jiang, W.; Lamb, J. D.; Bradshaw, J. S.; Izatt, R.M. J Am Chem Soc 1991, 113, 6538.
- Rivas, B. L.; Geckeler, K. E. Adv Polym Sci 1992, 102, 171.
- Rivas, B. L.; Pooley, S. A.; Maturana, H. A.; Villegas, S. Macromol Phys 2001, 202, 443.
- Rivas, B. L.; Schiappacasse, N.; Pereira, E. D.; Moreno-Villoslada, I. J Chil Chem Soc 2004, 49, 345.
- Rivas, B. L.; Pooley, S. A.; Maturana, H. A.; Villegas, S. J Appl Polym Sci 2001, 80, 2123.
- Rivas, B. L.; Maturana, H. A.; Luna, M. J Appl Polym Sci 1999, 74, 1557.
- Rivas, B. L.; Peric, I. M.; Maturana, H. A.; Fuentes, L. Polym Bull 1999, 42, 337.
- Ebraheem, K. A. K; Hamdi, S. T. React Funct Polym 1997, 34, 5.
- Egawa, H.; Nonaka, T.; Maeda, H. Sep Sci Technol 1985, 20, 653.
- Vernon, F. Chem Ind 1977, 635.
- Kaliyappan, T.; Kannan, P. Prog Polym Sci 2000, 25, 343.
- Filho, N. L.; Gushikem, Y. Sep Sci Technol 1997, 32, 2535.
- Bullock, J. L.; Tuck, D. J. J Chem Soc 1967, 1877.