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ORIGINAL PAPER

Poly(*N*-hydroxymethyl acrylamide-*co*-acrylic acid) and poly(*N*-hydroxymethyl acrylamide-*co*-acrylamidoglycolic acid): synthesis, characterization, and metal ion removal properties

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Abstract Macroreticular chelating resins containing carboxylic groups, poly(*N*-hydroxymethyl acrylamide-*co*-acrylic acid) P(HMA-*co*-AA) and poly(*N*-hydroxymethyl acrylamide-*co*-2-acrylamido glycolic acid) P(HMA-*co*-AGA) were synthesized by solution radical polymerization with ammonium persulfate as initiator and *N*,*N*′-methylene-bis-acrylamide as cross-linking reagent. The polymerization yield was 98.9 and 91.9% for P(HMA-*co*-AA) and P(HMA-*co*-AGA), respectively. The retention properties were studied under competitive and noncompetitive conditions by batch equilibrium procedure for the following metal ions: Cd(II), Cr(III), Zn(II), Pb(II), and Hg(II). The effects of pH, time, temperature, and initial ion concentration on adsorption were investigated. The resins showed a significant ability to retain Pb(II), greater than 79%, at pH 5.

Keywords Resin · Adsorption · Metal–polymer complexes

Introduction

Even when heavy metals can be found in many useful applications in a variety of fields, they are very harmful when discharged into natural water resources and their toxicity has become a major concern due to its deleterious effects on human health and the environment. For example, the US Environmental Protection Agency (US EPA) has classified the heavy metals lead, mercury, and cadmium as priority

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pollutants [1]. The main effects of heavy metal poisoning are manifested as neurological and renal disturbances [2]. Heavy metals are classified as persistent environmental toxic substances because they cannot be rendered harmless by chemical or biological remediation processes [3].

Numerous research studies have been performed to develop methods to remove heavy metals ions, especially from wastewaters produced by hydrometallurgy and related industries, in order to reuse the water. The principal techniques are chemical precipitation, evaporation, ion exchange, solvent extraction, biological treatment, chemical and electrochemical techniques, and membrane separation [4–7].

Many researchers have studied metal ion recovery using chelating polymers because they are reusable, offer easy handling, and have higher adsorption capacities and efficiencies as well as high selectivity for some metal ions [8, 9]. In addition, synthetic or natural polymeric matrixes have been modified by functionalizing reactions to achieve chelating polymers. Basically, a chelating resin is an organic polymer containing donor atoms that can successfully interact with the metal ions through a coordinate bond and polymer backbone, making them more efficient by offering a large surface area [10–12]. In this context, we have reported in the last few years the synthesis of numerous adsorbents bearing amide, amine, ammonium, and carboxylic groups by radical polymerization [13–22]. When acrylic acid (AA) is copolymerized with monomers containing amine groups, our results show that the retention of metal ions, like Cd(II), Cr(III), Zn(II), Pb(II), and Hg(II), decreased at the low pH range as did the homopolymer with the amine groups with the exception of Hg(II) [18, 19]. On the other hand, the cross-linked homopolymers of AA and 2-acrylamido glycolic acid (AGA) have been studied at a higher pH range (6–8) for the retention of Ni(II), Pb(II), Cd(II), and Cu(II) at low concentrations, where the poly(AGA) presents a slightly better retention behavior than the poly(AA) [16].

The aim of this study is to report the metal ion adsorption behavior for Cd(II), Cr(III), Zn(II), Pb(II), and Hg(II) of the cross-linked poly(*N*-hydroxymethyl acrylamide-*co*-acrylic acid) P(HMA-*co*-AA) and poly(*N*-hydroxymethyl acrylamide-*co*-2-AGA) P(HMA-*co*-AGA) in order to evaluate the influence of the HMA on the ability of these two resins containing amide and carboxylic acid groups to recover metal ions with environmental impact using the batch equilibrium procedure.

Experimental

Materials

Acrylic acid supplied from Merck was purified by distillation. *N*-hydroxymethyl acrylamide (HMA, 48%, Aldrich) and 2-acrylamido glycolic acid (AGA, 98%, Aldrich) were used as received. *N*,*N*′-methylene-bis-acrylamide (MBA, 99%, Aldrich) and ammonium peroxide disulfate (AP, Fluka), as cross-linking and initiator reagents respectively, were used as received.

For adsorption studies, the metal salts used were $Cd(NO_3)_2$, $Cr(NO_3)_3$, $Hg(NO_3)_2$, $Pb(NO_3)_2$, and $Zn(NO_3)_2$. Metal salts were purchased from Merck. The analytical grade HNO_3, $HClO_4$, CH_3COOH, and HCl were purchased from Fisher.

Resin synthesis

The resins P(HMA-*co*-AA) and P(HMA-*co*-AGA) were synthesized in a polymerization flask as follows: monomers, cross-linking, and initiator (see Table 1) were dissolved in 50 mL of bi-distilled water. The system was kept under N_2 at 70 °C for 4 h. Then, the resin was filtered and washed with distilled water and dried up to constant weight at 40 °C. The resin was screened, and a particle size fraction in the range of 180–250 μm was chosen for all experiments.

Metal ion adsorption

A batch equilibrium procedure was applied to determine the synthesized adsorbent's metal ion binding ability. All experiments were performed in a flask mounted on shaker. The sorption equilibrium experiments were performed to study the effects of pH, metal ion concentration, contact time, and temperature. In addition, the retention ability for Cd(II), Zn(II), Hg(II), Pb(II), and Cr(III) was studied under competitive conditions. A total of 0.05 g ± 0.1 mg of dried resin in 5.0 mL of metal ion solution was shaken for 1 h at 20 °C. After shaking, the resin samples were filtered and washed with distilled water at the same pH. The concentration of metal ions in the filtrate was determined by atomic absorption spectroscopy (AAS).

Batch metal uptake experiments under competitive conditions were performed with the following divalent metal ion mixtures: Pb–Hg at pH 2.0 and Cd–Zn–Hg–Pb at pH 2.0. For the first run, 0.10 g ± 0.1 mg of resin and 10.0 mL of metal ion solution were used; for the second test, 0.200 g ± 0.1 mg of resin and 20.0 mL of metal ion solution were used. The resin–metal ion ratio in the mixture (in mol) was 20:1. After shaking for 1 h, the resin samples were further handled as described for the noncompetitive experiments.

To determine the maximum sorption capacity for Pb(II) and Hg(II), the following runs were carried out: 25.0 mL of an aqueous solution of each metal ion (1.000 g/L) was shaken with 0.500 g ± 0.1 mg of dry resin for 1 h at 20 °C. The process was repeated three times, and the metal ions in the supernatant were determined by AAS.

Table 1 Conditions of polymerization of the resins P(HMA-*co*-AA) and P(HMA-*co*-AGA). Temperature: 60 °C. Time: 4 h

Resin	HMA		AA or AGA		MBA		AP	
	Weight (g)	Mole	Weight (g)	Mole	Weight (g)	Mole	Weight (g)	Mole
P(HMA-*co*-AA)	20.83	0.103	7.13	0.1059	0.61	0.005	0.45	0.002
P(HMA-*co*-AGA)	20.83	0.103	16.21	0.099	0.61	0.005	0.45	0.002

In the regeneration experiments, HNO_3, HCl, CH_3COOH, and $HClO_4$ at various concentrations were studied as potential stripping reagents using the batch method. A total of 0.050 g ± 0.1 mg of resin loaded with Hg(II) and Pb(II) ions was eluted with 5.0 mL of eluent for 1 h.

Measurements

A Julabo air-batch shaker was used to shake the solution at the desired temperature. The pH was measured with a digital pH meter (H. Jürgens and Co.). An atomic absorption spectrometer (Unicam Solaar 5 M series) was used to identify the metal ions. The samples' FT–IR spectra were recorded with a Magna Nicolet 550 spectrophotometer. The thermograms of the loaded and unloaded resins were recorded on an STA-625 thermoanalyzer. Approximately 5.0 mg of the dry sample was heated at a heating rate of 20 °C/min under a dynamic nitrogen atmosphere.

Results and discussion

Water-insoluble resins were obtained by copolymerization of an equivalent mole ratio of HMA with AA and HMA with AGA. AP was used as an initiator and MBA as a cross-linking reagent (CR). The resin yields were: 98.9 and 91.9%, respectively. The resin's structures are shown in the Scheme 1.

The resins presented high thermal stability under N_2 atmosphere up to 200 °C with a weight loss lower that 15% for P(HMA-*co*-AA) and lower than 6% for P(HMA-*co*-AGA). At temperatures below 100 °C, the weight loss is attributable to water at the surface; at temperatures above 100 °C, it is attributable to the occluded water. In both resins, the weight loss increased at higher temperatures, basically due to the evolution of CO_2.

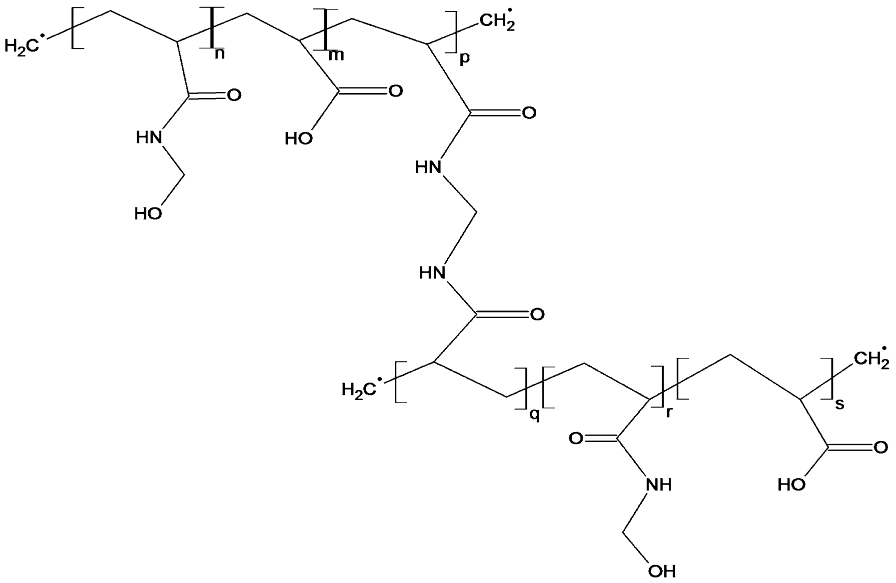
The FT–IR spectrum of P(HMA-*co*-AA) shows the following most characteristic absorption signals (in cm^{-1}): 3428.90 (N–H) and 1723.21 (C=O). The FT–IR spectrum of P(HMA-*co*-AGA) shows the following most characteristic absorption bands (in cm^{-1}): 3426.71 (N–H) and 1741.61 (C=O) (see Fig. 1).

Since metal ion retention is usually a diffusion-controlled process, the resin's swelling capacity should be determined. For the resins studied, the water-adsorption capacity was gravimetrically determined. The highest value of 2.7 g of water/g of resin was obtained for the resin P(HMA-*co*-AGA) and the lowest value was 1.0 g of water/g of resin.

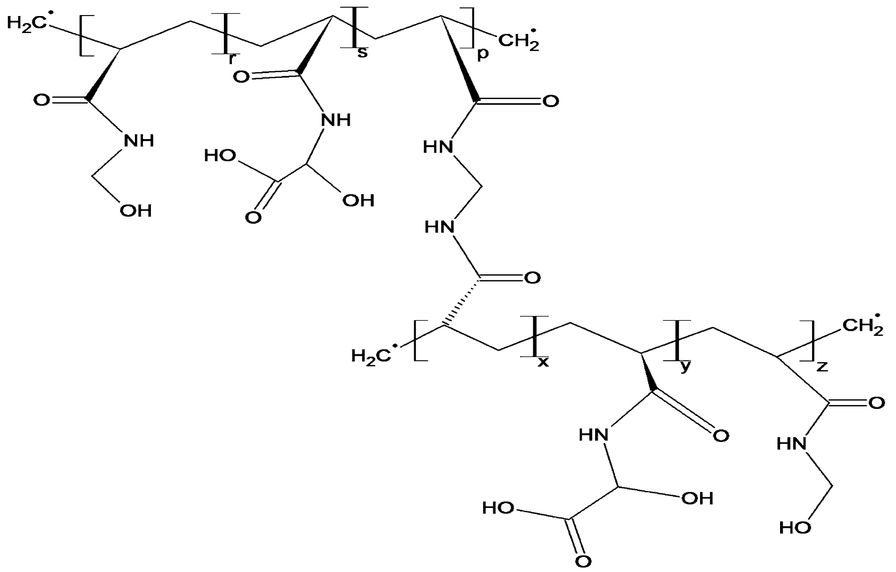
Metal ion retention properties

Effect of pH

Metal ion sorption on chelating adsorbents is pH dependent. In the absence of metal-chelating groups, metal ion precipitation is affected by the soluble metal species' concentration and form. The solubility is governed by hydroxide or



(a) P(HMA-*co*-AA)



(b) P(HMA-*co*-AGA)

Scheme 1 Structure of the adsorbents

carbonate concentration. Metal ion precipitation becomes significant at approximately pH 7.0 for almost all metal ions under study; it also depends on the concentration of metal ions in the medium.

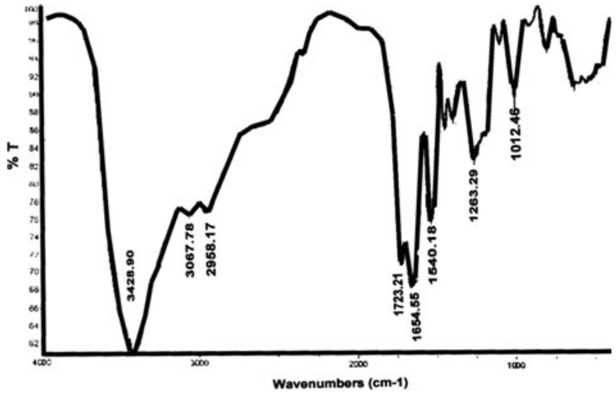


Fig. 1 FT–IR spectrum of the resin P(HMA-*co*-AA)

The uptake of the ions by batch equilibrium method as a function of pH was examined in a pH range of 1–5 for Cd(II), Cr(III), Zn(II), and Pb(II) and in a pH range 1–2 for Hg(II). Resins showed a high dependence on the pH since metals' ionic species and the ligand groups change with pH. The metal ion sorption was favored at higher pH because the ligand groups are deprotonated, and the groups are free to exchange or complex the metal ion.

Table 2 shows that the highest retention for the resin P(HMA-*co*-AGA) was obtained at pH 2 for Hg(II) and at pH 5 for the other metal ions. On the other hand, the highest retention for the resin P(HMA-*co*-AA) was obtained at pH 5 for Pb(II) with 60% (79.6 mg/g) and at pH 2 for Hg(II) with 65% (78.2 mg/g) as shown in Table 3. Therefore, pH 5 was chosen for further experiments. All these results are related with the initial metal ion concentration expressed in ppm. In comparison

Table 2 Effect of the pH on retention behavior for the resin P(HMA-*co*-AGA); contact time: 1 h, particle size: 180–250 μm, resin:metal ion ratio: 20:1

Metal ion	pH	Initial concentration (ppm)	Retention (%)	Retention (mg/g)
Pb(II)	1	828	8	7.3
	3	804	60	49.2
	5	1060	82	92.6
Cd(II)	1	340	18	6.5
	3	320	38	12.0
	5	356	66	24.2
Cr(III)	1	258	41	11.3
	3	234	47	11.1
	5	192	48	9.7
Zn(II)	1	236	0	0
	3	240	42	10.2
	5	300	47	14.1
Hg(II)	1	805	59	48.3
	2	925	70	65.5

Table 3 Effect of the pH on the metal ion retention behavior for the resin P(HMA-*co*-AA); contact time: 1 h, particle size: 180–250 µm, resin:metal ion ratio: 20:1

Metal ion	pH	Initial concentration (ppm)	Retention (%)	Retention (mg/g)
Pb(II)	1	1580	20	35.5
	3	1700	25	42.2
	5	1540	60	79.6
Cd(II)	1	720	22	16.5
	3	700	20	14.7
	5	700	50	2.8
Cr(III)	1	332	1	0.2
	3	312	10	3.2
	5	384	55	17.6
Zn(II)	1	450	11	5.2
	3	450	11	5.0
	5	430	26	10.0
Hg(II)	1	1324	50	66.6
	2	1283	65	78.2

with an earlier study [16], these results show a remarkable decrease in retention for Cd(II), Cr(III), and Zn(II) although retention for Pb(II) and Hg(II) are significant at optimum pH. In this context, the HMA moieties contribute with hydrophilicity, while hindering the interactions between metal ions and the carboxylate chelating groups.

In order to evaluate the resins' applications, the maximum retention capacity (MRC) was determined for Hg(II) and Pb(II). These values are shown in Table 4.

Effect of ion concentration

Since, for practical use, it is important to maintain the metal ion's retention capacity with the change of the metal ion's concentration in the solution, the effect of the metal concentration on metal ion uptake was studied using different resin:metal ion ratios (in mol) for Pb(II) and Hg(II). The resin:metal ion ratio was varied from 20:1 to 20:4. This ratio was calculated considering the resin's mass and the resin's

Table 4 Maximum retention capacity (MRC) of the resins P(HMA-*co*-AGA) and P(HMA-*co*-AA) 8 mol% of CR

Resin	Metal ion	MRC[a]	MRC[b]
P(HMA-*co*-AGA)	Pb(II)	126.3	0.61
	Hg(II)	73.0	0.36
P(HMA-*co*-AA)	Pb(II)	64.8	0.31
	Hg(II)	92.9	0.46

[a] mg of metal ion/g dry resin

[b] mmol of metal ion/g dry resin, at optimum pH (5 for Pb(II) and 2 for Hg(II))

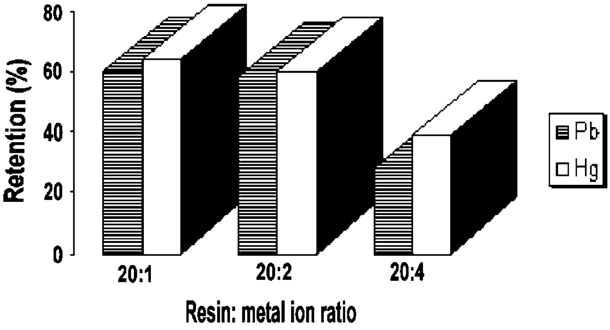


Fig. 2 Effect of the initial metal ion concentration on metal ion retention capacity of P(HMA-*co*-AA) at optimum pH 5 for Pb(II) and pH 2 for Hg(II), particle size 180–250 μm

repeating unit. In both resins, metal ion retention decreased with the increasing resin: metal ion ratio. The greatest decrease was obtained with the P(HMA-*co*-AA) resin. In this context, the Pb(II) retention was 60% at the 20:1 ratio and was 28% at the 20:4 ratio. On the other hand, the resin P(HMA-*co*-AGA) showed the smallest decrease. Accordingly, the Pb(II) retention was 82% at the 20:1 ratio and 54% at the 20:4 ratio (see Figs. 2, 3). These results can be attributed to the great flexibility of the AGA moiety's pendant chain, which favors the polymer ligand–metal ion interaction.

Effect of the contact time

Experiments were performed to determine the time that the metal removal process needed, to reach equilibrium. For Pb(II) and Hg(II), the resin P(HMA-*co*-AA) showed a similar retention percentage in all the experiments (see Fig. 4), while the resin P(HMA-*co*-AGA) presents an increase in the retention percentage over time. These results are presented in Fig. 5, where the polymer ligand–metal ion equilibrium was achieved at around 1 h, which is adequate considering that it takes place in a heterogeneous medium.

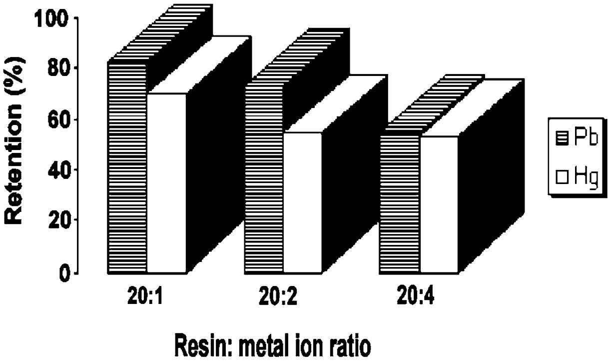


Fig. 3 Effect of the initial metal ion concentration on metal ion retention capacity of P(HMA-*co*-AGA) at optimum pH 5 for Pb(II) and pH 2 for Hg(II), particle size 180–250 μm

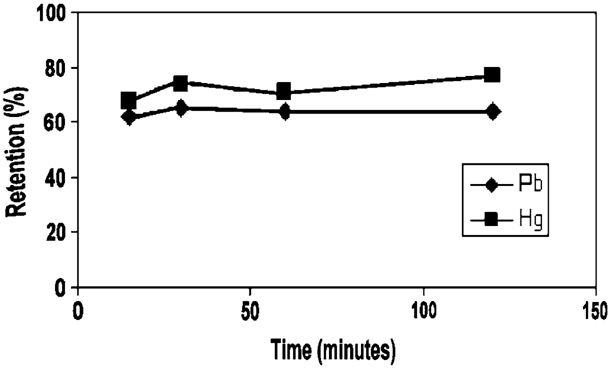


Fig. 4 Effect of the contact time on metal ion retention capacity of P(HMA-*co*-AA) at optimum pH 5 for Pb(II) and pH2 for Hg(II), particle size 180–250 μm

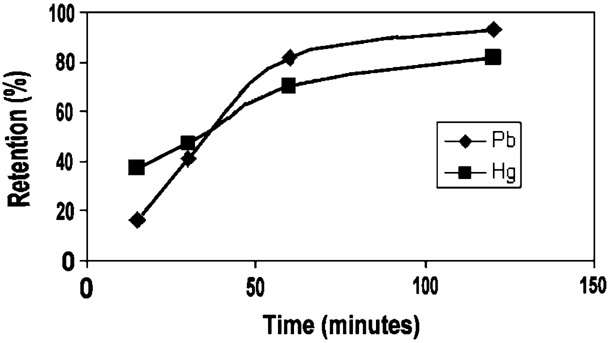


Fig. 5 Effect of the contact time on metal ion retention capacity of P(HMA-*co*-AGA) at optimum pH 5 for Pb(II) and pH 2 for Hg(II), particle size 180–250 μm

Selectivity behavior

The effect of a metal ion mixture on a polymer matrix is extremely complex and depends on the polymer type, number of metals competing for binding sites, metal combination, metal concentration levels, residence time, and experimental conditions.

To determine selectivity and the distribution coefficients, the following expressions were used [23]:

$$S = \log K_{\mathrm{d(M1)}} - \log \sum K_{\mathrm{d(Mi)}}$$

where S is the selectivity for the metal ion and K_d is the distribution constant of the metal ions inside the mix.

$$K_\mathrm{d} = \frac{\text{mg of ion per gram resin}}{\text{mg of ion per mL of solution}}$$

To determine metal ion retention under competitive conditions, several tests were performed. First, 0.10 g ± 0.1 mg of dry resin was contacted with 10.0 mL of an aqueous solution containing the same concentration of each metal ion (Pb(II) and Hg(II)) at pH 2 for 1 h. The resin P(HMA-*co*-AGA) showed high retention for Hg(II) (81 and 63%, respectively) (see Table 5). Considering their K_d, we can conclude that both polymers prefer Hg(II). This result was also corroborated with the *S* value: 0.6 for Hg(II) with the P(HMA-*co*-AGA) resin and 0.4 for Hg(II) with the P(HMA-*co*-AA) resin. Second, 0.20 g ± 0.1 mg of the resin was contacted for 1 h at pH 2 with 20.0 mL of an aqueous solution containing the same concentration of each metal ion (Cd(II), Zn(II), Hg(II), and Pb(II)). The retention of Pb(II) and Hg(II) was similar, around 50%; P(HMA-*co*-AGA) did not retain Zn(II) and Cd(II). The *S* value shows the same preference for Pb(II) and Hg(II) ($S_{Hg} = 0.60$, $S_{Pb} = 0.61$); and P(HMA-*co*-AA) retained a similar percentage of Hg(II) and Pb(II), while Zn(II) and Cd(II) ions were retained in a lower amount (see Table 6). The resin P(HMA-*co*-AA) did not show selectivity behavior for a specific metal ion (as observed in *S* values: $S_{Pb} = -0.37$, $S_{Cd} = -0.31$, $S_{Hg} = -0.31$, and $S_{Zn} = -1.35$).

Table 5 Selectivity behavior of the resin P(HMA-*co*-AA) and P(HMA-*co*-AGA), 8 mol% of CR at pH 2 from the binary metal ion mixture Hg(II)–Pb(II)

Resin	Metal ion	Retention (%)[a]	Retention (%)[b]	K_d
P(HMA-*co*-AA)	Hg(II)	43	63	74.1
	Pb(II)	24	38	31.1
P(HMA-*co*-AGA)	Hg(II)	50	81	102.6
	Pb(II)	21	19	25.8

[a] Respect to the initial quantity (in mol) of each metal ion

[b] Respect to the initial quantity (in mol) of all metal ions

Table 6 Selectivity behavior of the resin P(HMA-*co*-AA) and P(HMA-*co*-AGA), 8 mol% of CR at pH 2 from the quaternary metal ion mixture Hg(II)–Pb(II)–Cd(II)–Zn(II)

Resin	Metal ion	Retention (%)[a]	Retention (%)[b]	K_d
P(HMA-*co*-AA)	Hg(II)	19	39	23.2
	Cd(II)	19	19	23.3
	Zn(II)	3	2	3.03
	Pb(II)	16	40	21.1
P(HMA-*co*-AGA)	Hg(II)	21	51	21.2
	Cd(II)	0	0	–
	Zn(II)	0	0	–
	Pb(II)	24	49	31.8

[a] Respect to the initial quantity (in mol) of each metal ion

[b] Respect to the initial quantity (in mol) of all metal ions

However, large-size metal ions showed similar retention (Pb(II): 1.20 Å and Hg(II): 1.10 Å), while the medium size Cd(II) showed medium retention and the smallest metal ion showed the lowest retention. These results indicate that retention is not dependent on the specific characteristics of each metal ion. Consequently, it is possible that the interaction between the active groups and the metal ions might be due only to the electrostatic nature rather than to a specific chelating process.

Since the nitrogen atom of the *N*-hydroxymethylamide group does not have a sufficient electron donating character due to the adjacent electron-withdrawing carbonyl group, the most active ligand group is the carboxylate group of the AA and AGA moieties. Thus, in both resins, the polymer–metal ion interaction is strongly related with the dissociation degree of the carboxylic acid. At higher pH, most of the active sites are as carboxylate groups. Therefore, these carboxylate groups form polymer–metal complexes. In this context, the experimental evidence shows that HMA moieties hinder the metal ions interaction with the carboxylate groups allowing the interactions only with the large-size metal ions Pb(II) and Hg(II), enhancing selectivity toward these metal ions.

Resin reusability

To use these resins in a continuous process, the resin's metal ion capacity should remain constant after treatment with an eluent reagent and the adsorbed metal ion should be easily released under appropriate conditions. The batch desorption studies were carried out with the loaded resin samples. The four stripping reagents studied (HCl, $HClO_4$, HNO_3, and CH_3COOH) were selected because they should be able to displace the metal ions. However, sorption–elution was very poor with HCl, $HClO_4$, and CH_3COOH. Therefore, for resin reusability, the sorption–desorption cycle was repeated in triplicate with the same adsorbent throughout the batch process. The resin P(HMA-*co*-AGA) was charged with Pb(II) at pH 5 and desorption was performed in 4 M HNO_3. The resin maintained its retention capacity (around the 80%) in the three cycles, while the elution percentages of Pb(II) were lower and gradually decreased between the cycles (see Fig. 6).

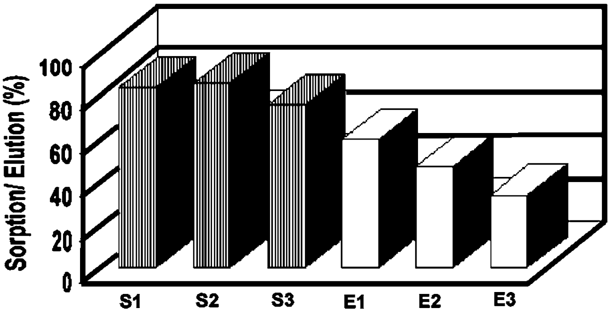


Fig. 6 Reusability of the resin P(HMA-*co*-AGA). Loaded resin with Pb(II), eluent 4 M HNO_3. Sorption (*S*)–Elution (*E*) cycles

Conclusions

The cross-linked P(HMA-*co*-AA) and P(HMA-*co*-AGA) were synthesized by radical solution polymerization. The resins showed significant retention for Pb(II) at pH 5 and Hg(II) at pH 2. When the resin:metal ratio was increased, the resin's retention capacity decreased. The contact time did not produce a change in the retention behavior for the resin P(HMA-*co*-AA), although it did significantly increased the retention capability for the resin P(HMA-*co*-AGA).

Temperature did not influence Hg(II) retention behavior of P(HMA-*co*-AGA). Both resins showed selective retention of Hg(II) in a mixture that contained just Hg(II) and Pb(II). In a quaternary mixture, only the P(HMA-*co*-AGA) resin showed a remarkable retention selectivity toward the large-size metal ions Pb(II) and Hg(II).

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