Resins with the Ability to Bind Copper and Uranyl Ions

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ABSTRACT: Crosslinked poly(1-vinyl imidazole-*co*-acrylic acid) and crosslinked poly(1-vinylmidazole-*co*-2-acrylamido-2-methyl-1-propanesulfonic acid) were synthesized by radical polymerization and characterized by elemental analysis and FTIR spectroscopy. The polymerization yields were 79 and 99%, respectively. The metal ion binding properties for copper(II) and uranium(VI) were studied under noncompetitive and competitive conditions by Batch equilibrium procedure. The resin crosslinked poly(1-vinyl imidazole-*co*-acrylic acid) showed a higher dependence on pH than crosslinked poly(1-vinylmidazole-*co*-2-acrylamido-2-methyl-1-propanesulfonic acid). The retention of uranyl ions for the latter resin was close to 100% at pH 5.0. The higher maximum retention capacity was close to 0.8 mmol/g dry resin at pH 5.0. Regeneration of the resin was possible by treatment with basic eluent. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 706–711, 2006

Key words: resins; ion exchangers; metal ion; polymer–metal complexes

INTRODUCTION

Metal ion complexation behavior of polymer-supported ligands is critical for their use as analytical reagents and catalysis 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.[1–3] Therefore, such polymers continue to attract the attention of many researchers.[4–16]

The selective extraction of metal ions from industrial wastewater streams and from contaminated areas is a topic of great interest. Materials suited to perform this task should be highly selective, nonhydrophobic, and easy to regenerate. Selectivity of a chelating group for a certain metal ion can be obtained by applying multidentate ligands, and the utilization of functional polymers offers the possibility of immobilizing these ligands on a support.[17–19]

In view of the anticipated exhaustion of terresterial uranium reserves in the near future, further research has been directed to recovering uranium from nonconventional sources such as coal and natural waters (0.1–10 mg U/m^3), especially from sea water (2.8–3.3 mg U/m^3) during the past 3 decades. The recovery of uranium from contaminated water of flooded mines (0.1–15 mg U/m^3) also presents a very important environmental problem to be solved. Uranium is also associated with copper ions from the copper mines.

In the early 1980s the possible use of polymers for the treatment of nuclear wastes of low-level activity was outlined. In 1984 Westinghouse patented the electrochemical synthesis of poly(vinyl imidazole) (PVI) with the purpose of complexing uranium compounds from low activity and secondary liquid wastes.[20] This technique was progressive compared to the usual processes using polymer resins.[21–28]

The design of effective host molecules for uranyl ions is connected with the economic importance of selective extraction of uranium from sea water as well as the development of therapeutic agents for the removal of uranyl ions from human bodies. In addition, the unusual coordination structures of uranyl complexes having four, five, or six secondary coordinations in an equatorial plane perpendicular to the main U-O-U axis also attracted interest in the design of uranophiles.

This paper reports the synthesis of resins containing ligands able to bind uranyl ions. The uranyl ion affinity of these resins is studied under different experimental conditions and also from a mixture with copper(II) ions.

EXPERIMENTAL

Reagents

Acrylic acid (AA, Merck) and 1-vinyl imidazole (Vim, 99%, Aldrich) were purified by distillation. 2-Acrylamido-2-methyl-1-propanesulfonic acid (APSA, Aldrich), *N*,*N*'-methylene-bisacrylamide (MBA, 99%, Aldrich), and ammonium persulfate (AP, Aldrich) were used without further purification.

The metal salts used were copper(II) nitrate 2.5 hydrated (T. J. Baker) and uranyl acetate dihydrate (Merck p.a). The analytical grade, nitric acid, perchloric acid, and sodium hydroxide were purchased from Merck.

Synthesis of the resins

Synthesis of crosslinked poly(1-vinyl imidazole-*co*-acrylic acid) P(VIm-*co*-AA) was carried out in a polymerization flask to which 0.03 mol (2.7 mL) of VIm, 0.03 mol (2.5 mL) of AA, 2.0 mol % of MBA as crosslinking reagent, and 1.0 mol % of AP as initiator were added. The reaction was kept under nitrogen at 70 °C for 24 h. The resin was filtered and washed with abundant water and dried up to constant weight. Yield was 79%.

Crosslinked poly(1-vinylimidazole-*co*-2-acrylamido-2-methyl-1-propanesulfonic acid) P(VIm-*co*-APSA) was synthesized in a polymerization flask to which 0.016 mol (1.44 mL) of VIm, 0.016 mol (3.4 g) of APSA, 0.00064 mol (2.0 mol %) of MBA as crosslinking reagent, and 0.00032 mol (1.0 mol %) of AP as initiator were added. The reaction was kept under nitrogen at 70 °C for 24 h. The resin was filtered and washed with abundant water, and dried up to constant weight. Yield was 99%.

Afterward, both resins were sized by screening, and the fraction with mesh size in the range of 180–250 μm (0.16–0.125 mm) was chosen to carry out the metal ion binding studies.

Resin–metal ion uptake

Batch metal uptake experiments were performed using standard metal salt $Cu(NO_3)_2$ and $UO_2(CH_3COO)_2$ at pH range 1–5 depending on the metal ion. All experiments were performed in flasks mounted on a shaker at 25 °C. The capacities for Cu(II) and UO_2^{2+} under noncompetitive and competitive conditions were determined as a function of pH. Batches of 0.1 g resin were used, together with a mixture of 10 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 0.1 g resin were used together with a mixture of 10 mL of each metal solution (0.5 g/L). After being shaken for 1 h, the samples were further handled as described for noncompetitive experiments.

To obtain the maximum adsorption capacity for the metal ions, 50 mL of an aqueous solution, 1 g/L, was shaken with 0.1 g of the resin for 1 h at 25 °C. The mixture in the flask was filtered and washed with water, and the filtered solution was transferred into a calibrated flask. The process was repeated three times, the volume was made up to 250 mL, and then the metal ion was determined by colorimetry by atomic absorption spectrometry.

In the regeneration experiments (1 and 4*M*) HNO_3 and $HClO_4$ and (025–1*M*) Na_2CO_3 were tested for their stripping potential. Batches of 1.0 g resin were loaded with metal ion solution (50 mL of the metal solution 1.0 g/L) at pH 5 under shaking for a period of 1 h. The loaded resin was washed with water and the filtrates were collected. This procedure was repeated three times.

Measurements

A Julabo air-batch shaker was used for shaking the solution at a desired temperature. The pH was measured with a digital H. Jürgens pH meter. A Unicam Solaar 5M series atomic absorption spectrometer was used for the determination of single and mixed metal ions. Uranyl ions were determined by colorimetry by the spectrophotometer CADAS 100. The FTIR spectra of the sample were recorded with a Magna Nicolet 550 spectrophotometer. The thermograms of the loaded and unloaded resins were recorded on a STA-625 thermoanalyzer (Polymer Laboratories). Approximately 5 mg of the dry sample were heated at 10 °C/min heating rate under dynamic nitrogen atmosphere.

RESULTS AND DISCUSSION

Two types of resins containing weak and strong acid groups by radical polymerization were synthesized. Crosslinked poly(1-vinyl imidazole-*co*-acrylic acid)
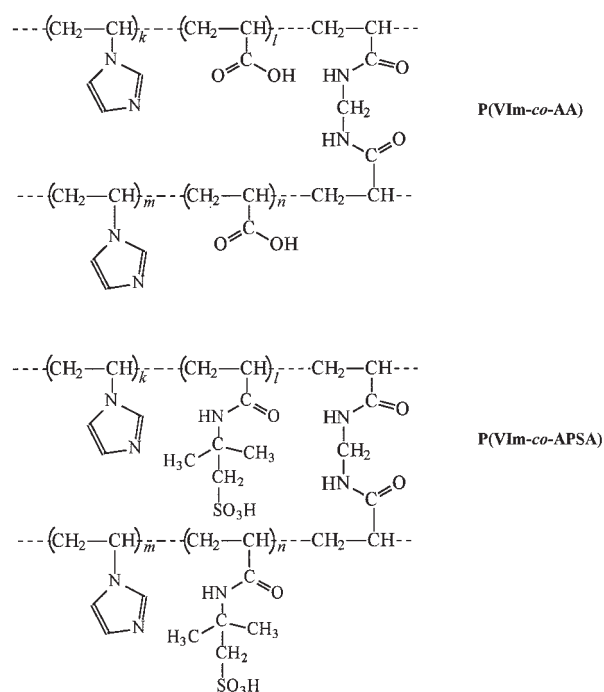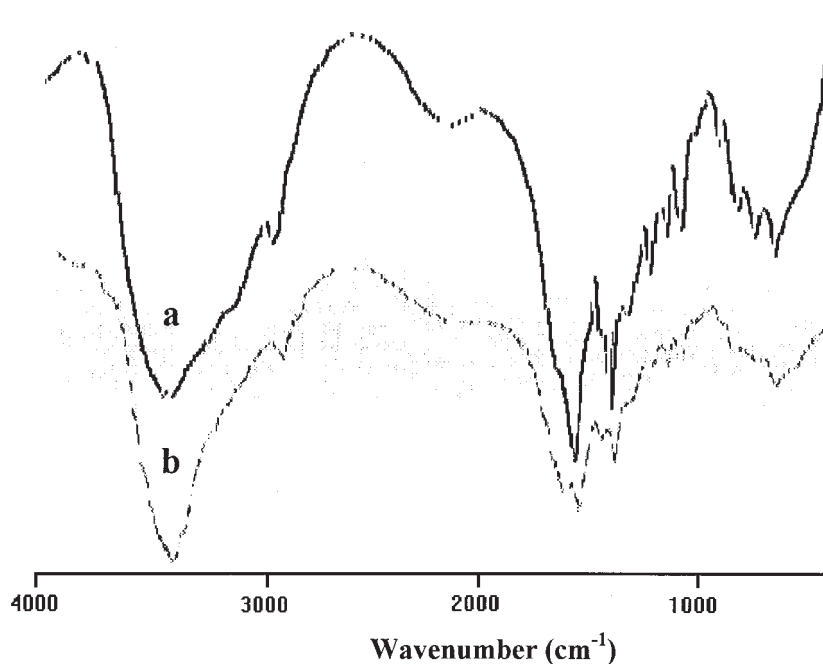

Scheme 1
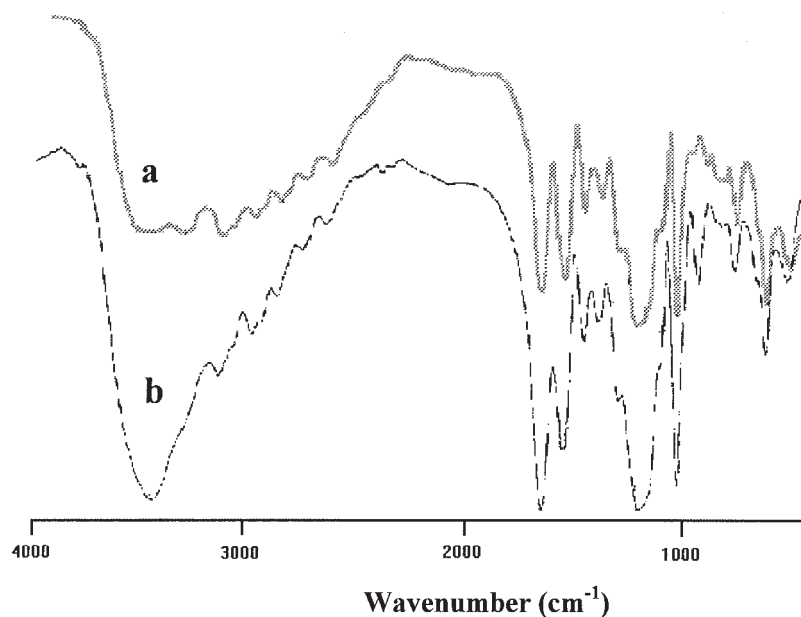
Figure 1   FTIR of crosslinked poly(1-vinylimidazole-co-2-acrylamido-2-methyl-1-propane sulfonic acid) P(VIm-co-APSA): (a) unloaded resin and (b) loaded resin with uranium (KBr pellets).

P(VIm-*co*-AA) and crosslinked poly(1-vinyl imidazole-*co*-2-acrylamido-2-methyl-1-propane sulfonic acid) P(VIm-*co*-APSA), at determined pH, behave as polyanions; therefore, they would bind preferably metal cations like UO_2^{2+} The general structure of the resins is shown in Scheme 1.

The crosslinked polymers are completely insoluble in water and in common organic solvents such as methanol, chloroform, acetone, dichloromethane, dimethylformamide, and dimethylsulfoxide.

The resins were characterized by FTIR spectroscopy (see Figs. 1 and 2).

The FTIR spectrum of crosslinked poly(1-vinyl-imidazole-*co*-2-acrylamido-2-methyl-1-propane acid) shows a broad signal at 3457.18 cm^{-1} corresponding to OH and NH coming from the carboxylic acid and amide groups, respectively, at 1664.86 cm^{-1} C = O (from amide), at 1547.08 cm^{-1} (C = N) corresponding to imidazole, and at 1296.16 cm^{-1} stretching S-O (from sulfonic acid).

Figure 2   FTIR of crosslinked poly(1-vinylimidazole-*co*-accrylic acid) P(VIm-*co*-AA): (a) unloaded resin and (b) loaded resin with uranium (KBr pellets).

TABLE I
Thermal Stability Behavior of the Resins under N_2
Atmosphere (Heating rate, 10 °C/min)

Resin	Weight loss at different temperatures (°C)				
	100	200	300	400	500
P(VIm-co-AA)	0.4	6.4	8.6	55.5	37.5
P(VIm-co-APSA)	2.5	10.4	17.5	34.1	56.2

The copolymer composition (1 : 1) was determined by quantitative FTIR spectra.

Figure 2 shows the FTIR spectrum of crosslinked poly(1-vinyl imidazole-co-acrylic acid). It presents characteristic absorption bands at 3427.94 cm^{-1} corresponding to OH (carboxylic acid), at 3135 cm^{-1} (C = C-H aromatic of imidazole), at 1712.08cm^{-1} (stretching of C = O, carboxylic acid), at 1575.34 cm^{-1} (C = N), and at 1228.26 cm^{-1} (stretching C-N). The copolymer composition 1 : 1 was determined by elemental analysis.

The thermal stability behavior of the resins was studied under dynamic conditions. The results are summarized in Table I. The resin P(PVIm-co-APSA) shows a higher thermal stability than that of crosslinked P(VIm-co-AA), probably due to the easier loss of CO_2.

The resin metal ion binding properties were studied under different experimental conditions.

The complexing properties of crosslinked poly(1-vinyl imidazole), crosslinked poly(acrylic acid), and crosslinked poly(2-acrylamido-2-methyl-1-propane sulfonic acid) are very well known.

Figure 3 shows that the uranyl ion retention ability increases as pH increases. At pH 3 the comparison of the resins corresponding to the crosslinked homopolymers P(VIm) and P(AA) demonstrates that P(AA) shows a lower affinity, but at pH 5 no important difference was observed. This is due to the fact that at pH 3 most of the ligand groups are carboxylic acid
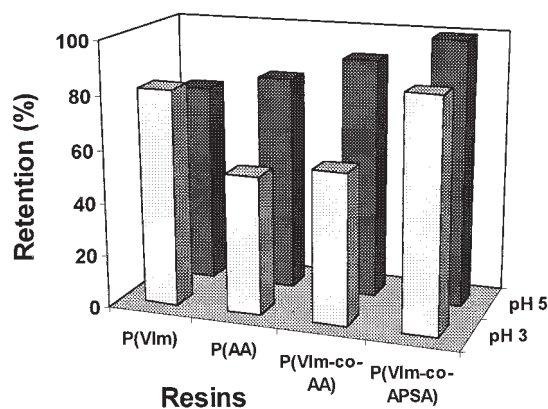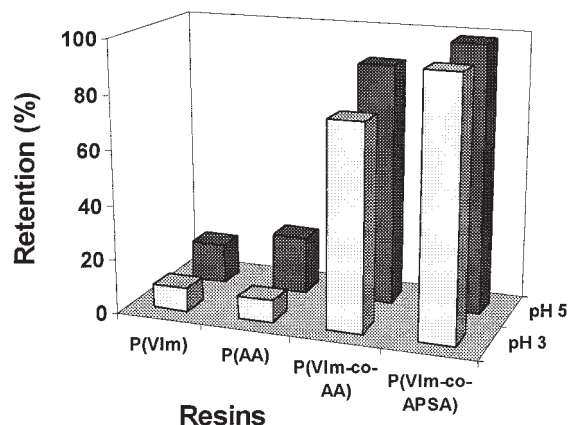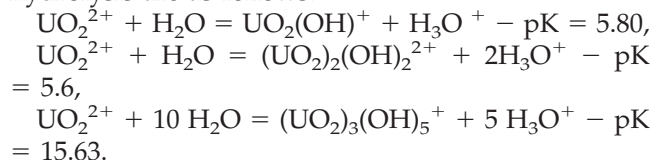

Figure 4 Copper(II) ions sorption under noncompetitive conditions for resins at pH 3 and 5.

groups and the VIm would be protonated and the uranyl ions could remove the protons to coordinate with the imidazole group.

The highest retention capacity (99.7%, 0.108 mmol/g dry resin) for uranyl ions is crosslinked P(VIm-co-APSA). There is no important effect of pH.

Uranyl ion species are easily hydrolyzed into various forms previously described.[29] The equilibriums of hydrolysis are as follows:

$$UO_2^{2+} + H_2O = UO_2(OH)^+ + H_3O^+ - pK = 5.80,$$
$$UO_2^{2+} + H_2O = (UO_2)_2(OH)_2^{2+} + 2H_3O^+ - pK = 5.6,$$
$$UO_2^{2+} + 10 H_2O = (UO_2)_3(OH)_5^+ + 5 H_3O^+ - pK = 15.63.$$

Consequently, the pH at which the hydrolyzed forms appear decreases as the metal concentration increases. The major form of hydrolyzed uranyl species is the $(UO_2)_3(OH)_5^+$ form, the ionic size of which is much greater than the free form.

In an adsorption process there are several parameters that determine the adsorption, such as the agitation rate in the aqueous phase, amount of sorbent, structural properties, and metal ion properties (i.e., hydrated ionic radius, initial concentration of metal ion, etc.). Therefore, this result was expected only for the selected experiment conditions.

The interaction of the uranyl ions with functional groups is corroborated by FTIR spectroscopy due to the presence of the signal at 932 cm^{-1} attributed to the UO_2^{2+} [see Figs. 1(b) and 2(b)].

Figure 4 shows that both crosslinked homopolymers, P(VIm) and P(AA), have a very poor affinity for Cu(II) ions but both copolymers show an affinity higher than 70%, particularly P(VIm-co-APSA), and there is not a strong effect of pH.

Moreover, the maximum load capacity (MLC) for copper(II) and uranyl ions was determined at pH 5, demonstrating that after three contacts with an aqueous solution, the ligand sites were practically saturated. The MLC values for P(VIm-co-AA) for Cu(II)

Figure 3 Uranyl ion sorption under noncompetitive conditions for resins at pH 3 and 5.

TABLE II
Selectivity and Distribution Constant for Competitive Retention of Uranyl and Copper Ions

Resin	Distribution constant K_d (log)		Selectivity	
	Cu(II)	U(VI)	U(VI)-Cu(II)	Cu(II)-U(VI)
P(VIm-co-AA)	1.6	2.0	0.4	—
P(VIm-co-APSA)	4.6	3.9	—	0.7

and U(VI) are 0.49 and 027 mmol/g dry resin, respectively, and for P(VIm-co-APSA) are 0.75 and 0.40 mmol/g dry resin, respectively. The MLC for copper(II) was higher than that for uranyl ions. This is due to the fact that it was determined after three contacts, and in the experiment to study the effect of pH it was determined after only after one contact.

Therefore, it could be assumed that this process, whose diffusion is controlled, can depend on the concentration and the time.

The metal ion retention behavior under competitive conditions (from mixtures Cu(II)-U(VI) shows a dif-

ferent behavior. The resin P(VIm-co-APSA) shows a higher selectivity for copper ions, but P(VIm-co-AA) shows a higher affinity for uranyl ions. This means that the moiety containing carboxylic/carboxylate groups forms more stable complexes with uranyl ions than that containing sulfonic/sulfonate groups where the interactions with copper ions would be favored (see Table II).

Figure 5 shows the most probable polymer ligand–uranyl interactions, including that involving complex formation.

To repeatedly reuse the resin for the recovery of uranium, uranium adsorbed on the resin must be easily eluted with a certain kind of eluent. The elution was investigated by batch method. The results are shown in Figures 6 and 7. Uranium(VI) adsorbed on the crosslinked P(VIm.-co-AA) shows a higher elution in acidic and in basic media than that of the crosslinked P(VIm-co-APSA).

Uranium(VI) adsorbed in the resins was eluted close to 90% by nitric acid and 95% by sodium carbonate. Meanwhile, there was no important effect of the eluent type and of the concentration on uranium(VI) desorption [see Fig. 6(a)]. Uranyl ions in basic
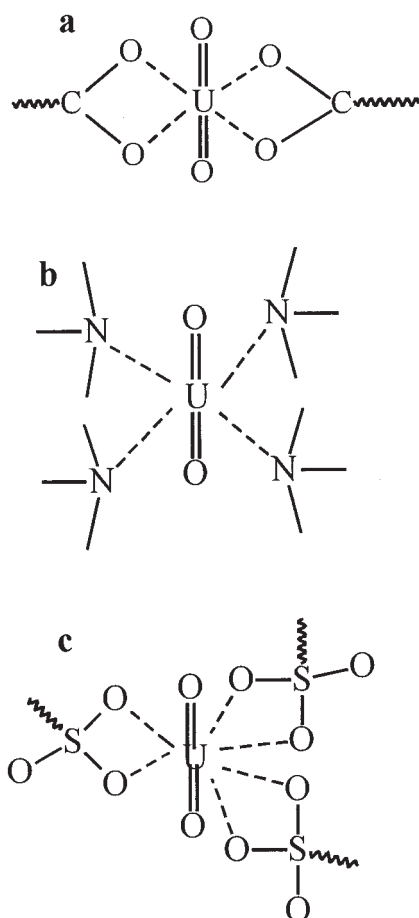
Figure 5   Proposed uranyl interaction with (a) oxygen from carboxylic group, (b) nitrogen from amines or amides, and (c) oxygen from sulfonic acid groups.
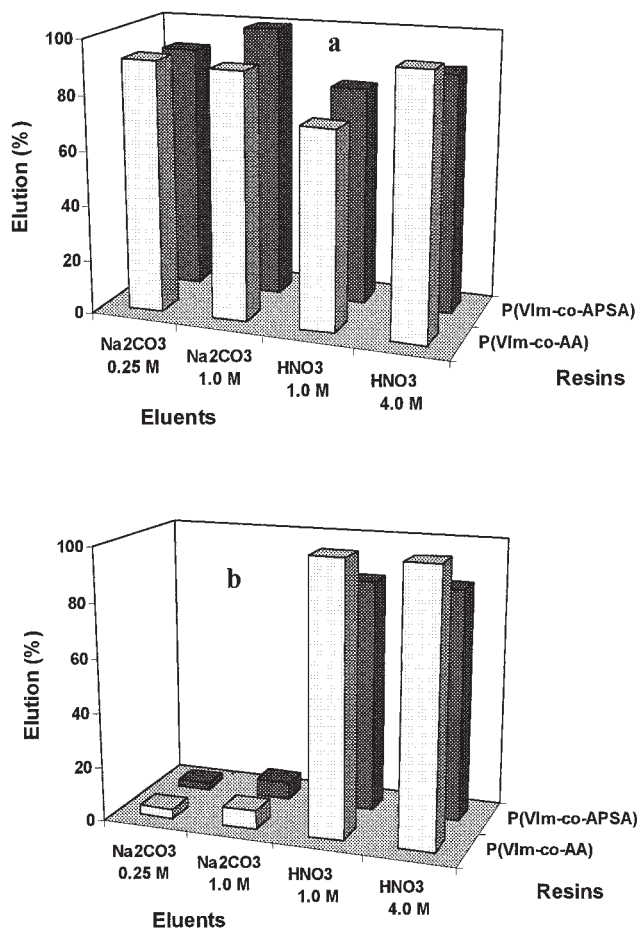
Figure 6   Elution of (a) uranyl and (b) copper ions by different eluents.
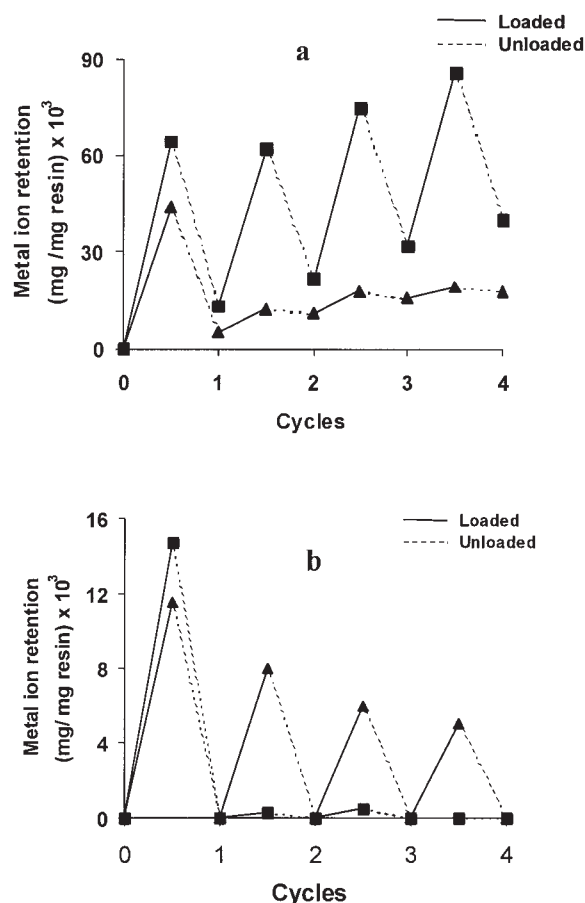
Figure 7 Loading-elution cycles of (a) uranyl ions and (b) copper ions on (-■-) crosslinked P(VIm-*co*-AA) and (-▲-) crosslinked P(VIm-*co*-APSA) resin.

medium could form a stable carbonate complex, $[UO_2(CO_3)_3]^{4-}$. Moreover, the desorption of Cu(II) is not possible by 0.25 and 1.0M Na$_2$CO$_3$, but in acid medium it was possible to recover both resins. The desorption behavior shows no effect on the eluent concentration. With 1M HNO$_3$ the elution for the crosslinked polymers P(VIm-*co*-AA) and P(VIm-*co*-APSA) is 95 and 97%, respectively.

The behavior during the load-discharge cycles is shown in Figure 7. Resin P(VIm-*co*-AA) shows a better behavior than resin P(VIm-*co*-APSA), particularly for uranyl ions. For both resins, the load capacity for copper(II) ions decreases strongly after the first cycle. For uranyl ions, the crosslinked P(VIm-*co*-APSA) significantly decreases the retention after the first cycle, which is different for resin P(VIm-*co*-APSA).

CONCLUSIONS

Resins containing carboxylic acid, imidazole, and sulfonic acid groups showed affinity for copper and uranyl ions. The metal ion retention affinity was higher than that corresponding to both homopolymers. At pH 5 higher retention values were observed.

The FTIR spectra of the loaded resins showed the characteristic absorption band at 932 cm^{-1}, which is attributed to linear uranyl. The uranyl ions were desorbed from the loaded resins by treatment with nitric acid and sodium carbonate.

Crosslinked P(VIm-*co*-APSA) showed an adequate behavior to reuse the resin after four cycles of load-discharge. Nevertheless, during the retention process the metal ion affinity of the ligand sites decreases.

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