Preparation and Metal Ion Adsorption Properties of the Resin Containing Sulfonic Acid Groups

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ABSTRACT: In this study, we explored a new ion exchange material synthesized by radical polymerization of styrene and 2-acrylamido-2-methyl-1-propane sulfonic acid by using 2,2'-azo-isobutyronitrile (1 mol %) and divinylbenzene (0.5 mol %) as initiator and crosslinking reagents, respectively. The resin was obtained from a large excess (90%) of styrene in the feed. The yield was 72.3%. The resin was completely insoluble in water and characterized by elemental analysis, FTIR spectroscopy, scanning electron microscopy, and thermal analysis. The metal ion retention capability was investigated for Ag(I), Hg(II), Cd(II), Zn(II), Pb(II), and Cr(III). The effect of pH, time, and resin/metal ion mol ratio on the metal ion retention was studied. Selectivity of the resins from a mixture of metal ions and the maximum retention capacity at optimum pH were also determined. The recovery of the resin by using 1 and 4 M $HClO_4$ and HNO_3 demonstrated that it is possible to recover the resin above 80%. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 1230–1235, 2003

Key words: ion exchange resin; metal ions; adsorption; regeneration

INTRODUCTION

Reactive polymeric materials for waste water treatment and metal ion recovery have received much attention. Many studies have been done in the field of preparation and characterization of these polymeric materials containing complexing and/or ion exchanger groups. This field is of particular importance in polymer chemistry since such materials are being used as very convenient and selective ion exchange/coordination resins.[1–4] Resins with metal ions attached to them, either by ion exchange or coordination bonds, are used as catalysts in inorganic chemistry and separation media in biotechnology.

Since a wide range of materials and methods of synthesis are possible, it is not surprising that the exchanger's physical form may vary from rock-hard material to soft gel. The desirable properties of chelating exchangers are of high capacity for the metal(s) of interest, high selectivity, fast kinetics, and high mechanical strength and toughness of the exchanger particles.[5] Unfortunately, the last two are competitive.

The separation of metal ions present as contaminants in water is complicated due to the number of variables that must be considered, including the solution composition, pH, and the presence of organic substances.[6] It is well known, for example, that heavy metal ions like Pb(II) and Hg(II), which are toxic to most organisms, have found their way into the water from different processes.

Polymers with low molecular substances attached in their structure have been extensively studied.[7–20] However, most of them are either weak acids or weak bases and the useful pH range is limited. To overcome this problem, new polymers with more acidic ligands have been synthesized.[21,22]

In the present work, we describe the synthesis of a resin containing sulfonic acid groups and the study by batch procedure of its ability to bind metal ions. Because poly(APSA) is a hydrogel with a high water absorption capacity, it is very difficult to be used as an ion exchanger; the strategy carried out to prepare the resin was through the copolymerization with styrene and crosslinked with divinylbenzene.

EXPERIMENTAL

Reagents

Styrene (Sty; Aldrich, Milwaukee, WI) and divinylbenzene (DVB; Aldrich) were purified by distillation. 2,2'-Azo-isobutyronitrile (AIBN; Merck, Darmstadt, Germany) was purified by recrystallization from chloroform. 2-Acrylamido-2-methyl-1-propane sulfonic acid (APSA; Aldrich) was used without further purification.

Synthesis of resin

The resin was synthesized by radical polymerization of 2-acrylamido-2-methyl-1-propane sulfonic acid with styrene in a mol ratio of 0.1:0.9, which would
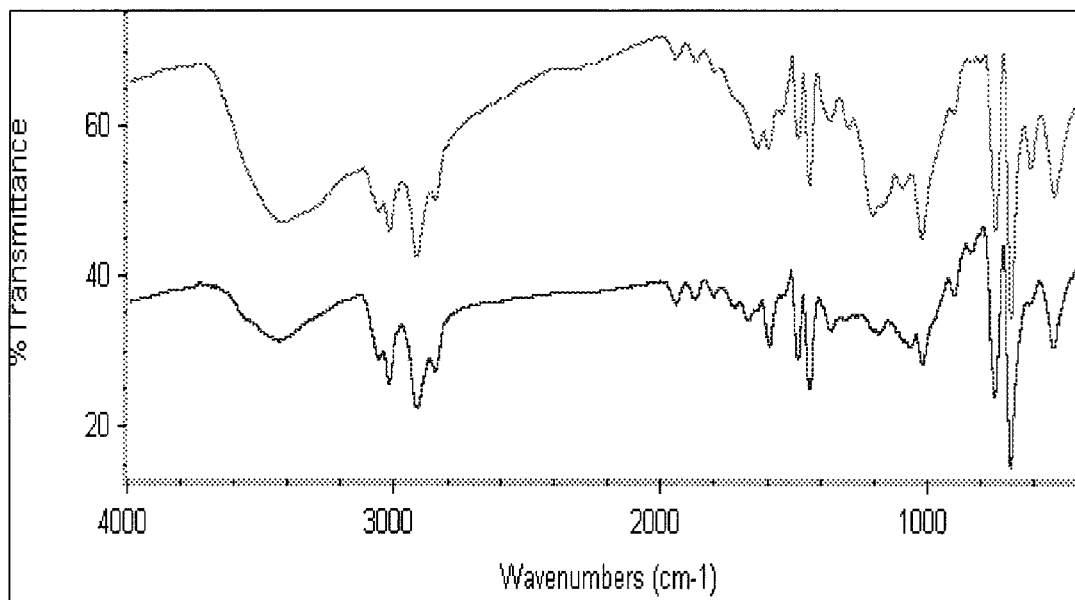
Figure 1 FTIR spectra of the (top) unloaded P(Sty-*co*-APSA) resin and (bottom) P(Sty-*co*-APSA) resin with Ag(I) ions at pH 5.

yield a most useful material. 2,2′-Azo-bis-isobutyronitrile (1 mol %) and divinylbenzene (0.5 mol %) were used as initiator and crosslinking reagents, respectively. The flask was kept under stirring at 70°C for 10 h. The resin was filtered, washed with abundant distilled water, and dried under vacuum at 40°C until

constant weight. The resin was completely insoluble in water. The yield was 72.3%. The resin was ground to obtain a fraction with particle size of 250–500 μm.

Swelling percentage

A weighed amount of dry resin (0.5 g) was immersed in 250 mL of water (1 S cm^{-1}, pH 5.6, 25°C) in a beaker for 24 h. The percentage of swelling (S) was determined gravimetrically by the following equation: S (%) = [($M_t - M_o)/M_o$] × 100, where M_o is the initial weight and M_t is the weight of the swollen gel at time t.

TABLE I
Metal Ion Retention of P (Sty-*co*-APSA) Resin at Different pH and Resin/Metal Ion Mol Ratios

Metal ion	pH	Resin/metal ion (in mol)	Retention (%)	C (mmol/g dry resin)
Hg(II)	1	20/1	88.9	0.12
	2	20/1	91.4	0.14
	2	10/1	93.5	0.33
Cd(II)	1	20/1	92.0	0.23
	3	20/1	92.0	0.25
	5	20/1	92.8	0.22
	5	10/1	91.9	0.47
Ag(I)	1	20/1	92.8	0.24
	3	20/1	92.3	0.32
	5	20/1	92.8	0.24
	5	10/1	90.9	0.46
Zn(II)	1	20/1	89.1	0.21
	3	20/1	91.9	0.23
	5	20/1	92.4	0.26
	5	10/1	92.0	0.44
Pb(II)	1	20/1	91.2	0.19
	3	20/1	92.5	0.23
	5	20/1	92.9	0.24
	5	10/1	92.9	0.36
Cr(III)	1	20/1	88.7	0.27
	3	20/1	89.7	0.27
	5	20/1	93.1	0.28
	5	10/1	93.0	0.44

Particle size: 250–500 μm.

TABLE II
Effect of Time on Ag(I), Hg(II), Cd(II), and Zn(II) Ion Retention of P(Sty-*co*-APSA) Resin at Optimum pH

Metal ion	pH	Time (min)	Retention (%)	C (mmol/g dry resin)
Ag(I)	5	5	92.7	0.23
		15	92.6	0.24
		30	92.8	0.24
		60	92.8	0.24
Hg(II)	2	5	93.2	0.15
		15	93.0	0.15
		30	93.7	0.16
		60	91.4	0.14
Cd(II)	5	5	93.5	0.24
		15	92.6	0.22
		30	93.1	0.23
		60	92.0	0.22
Zn(II)	5	5	94.6	0.44
		15	94.0	0.45
		30	93.3	0.43
		60	92.4	0.29

TABLE III
Distribution Coefficients for Ternary (0.015 mmol of Each One) and Quaternary (0.087 mmol of Each One) Mixture of Metal Ions at pH 2

Metal ion	K_d	$\log K_d$
Ag(I)	50.2	1.7
Cd(II)	377.4	2.6
Hg(II)	61.8	1.8
Zn(II)	62.1	1.8
Cd(II)	290.9	2.5
Hg(II)	42.6	1.6
Pb(II)	43.3	1.6

Electron micrographs

The surface of each unloaded and loaded resin was coated with gold for 3 min to obtain a 150 Å thickness using an Edwards Model S 150 sputter coater.

Batch metal uptake experiments

Batch metal ion uptake was carried out using standard metal solutions in absence of a buffer solution. All the experiments were performed in flask at around 20°C. The capacities for Ag(I), Hg(II), Cd(II), Zn(II), Pb(II), and Cr(III) under noncompetitive conditions were determined as a function of pH (range, 1.0–5.0, depending on the metal ion solubility). Batches of 0.05 g of the resin were soaked and stirred in a solution formed by mixing with 5 mL of a metal nitrate solution. The polymer was washed with water and then dried up to constant weight under vacuum at 40°C. To determine the maximum load capacity, a 250 mL glass beaker containing dry resin (0.1 g) and metal ion salt solution (5 mL; equivalent to 1.0 g metal ion/L) were placed in a thermostatically controlled bath at 20°C. The mixture was shaken for 1 h. The aqueous solution was separated by decanting and filtration and washed with distilled water. This process was repeated three times using the same resin. Metal ions were determined by atomic absorption spectrometry as above, and the metal ion fixed in the resin was determined by the difference.

Desorption of metal ions

Regeneration of the resin attached with the metal ion adsorbed was performed in a batch system. The resin loaded with the metal ion (0.025 g) was placed in the desorption medium containing 2.5 mL of 1 and 4 M $HClO_4$, 1 and 4 M HNO_3. After 1 h, the loaded sorbent

was filtered off and washed with distilled water. The combined filtrates were analyzed for indirect determination of the amount of sorbed ion.

Loading–stripping cycles

Batches of 50 mg of the metal ion-loaded resin were stripped with 5 mL of an aqueous solution of 1 M HNO_3. This procedure was repeated four times with fresh metal ion solution and a solution of the most effective stripping reagents.

Measurements

The pH was measured with an H. Jürgens pH meter. The metal ion content was analyzed using a Unicam Solaar 5 M atomic absorption spectrophotometer (AAS). The metal ion content of all these solutions was measured by AAS spectroscopy using a linear calibration curve. FTIR spectra were recorded with a Magna Nicolet 550 spectrophotometer. The thermograms of the resin and the loaded resin were recorded with a thermoanalyzer STA 625 from Polymer Laboratories under N_2 with a heating rate of 10°C/min. Electron micrographs were recorded with a scanning electron microscope (Model Autoscan 1, Etec).

RESULTS AND DISCUSSION

The resin was synthesized by radical polymerization of 2-acrylamido-2-methyl-1-propane sulfonic acid with styrene in a feed mol ratio of 0.1:0.9, which yielded a useful material to bind metal ions through the batch equilibrium procedure. The yield was 72.3%. The particle size of the resin immediately after the polymerization was higher than 500 μm. Subsequently, the resin was ground to yield a material with particle size of 250–500 μm. This fraction was used to investigate the metal ion binding capacity. The copolymer composition of Sty:APSA (0.84:0.16) was determined by elemental analysis.

Important effect exists between the swelling of a crosslinked polymer and the availability of the complexing or ion exchange site to interact with the metal ions. Therefore, the swelling was determined for the resin yielding a high value: 665%. FTIR shows the most important signals (in cm^{-1}) placed at 3,025 (st arC—H), 2,920 (st alC—H), 1,596 (st arC—C), 1,489 (st arC—C), 1,446 (δ CH_2 as), 755 (arC—H), 3,240–3,090 (st N—H and O—H), 1,647 (amide I; 1,552 amide II).

TABLE IV
Selectivity of Cd(II) With Ions Respect to Ag(I), Hg(II), Zn(II), and Pb(II) Ions

Metal ion mixture	Selectivity		
Ag(I)–Cd(II)–Hg(II)	0.9 Cd(II)/Ag(I)	0.8 Cd(II)/Hg(II)	
Zn(II)–Cd(II)–Hg(II)–Pb(II)	0.7 Cd(II)/Zn(II)	0.9 Cd(II)/Hg(II)	0.9 Cd(II)/Pb(II)
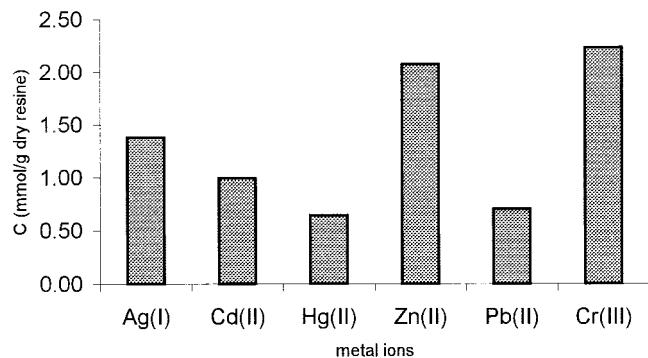
Figure 2 Maximum retention capacity of P(Sty-*co*-APSA) resin of metal ions at optimum pH: pH 5 for Ag(I), Zn(II), Pb(II), and Cr(III); pH 3 for Cd(II), and pH 2 for Hg(II) ions.

The bands due to the presence of sulfonic acid groups were in the range of 1,224–1,153 cm^{-1} (Fig. 1).[23]

The weight capacity (*C*), which is defined as the total amount of adsorbed metal divided by the initial weight of dry resin[12] for the resin to adsorb Ag(I), Hg(II), Cd(II), Zn(II), Pb(II), and Cr(III), was determined by varying the pH, resin/metal ion ratio, and the time to achieve the equilibrium (Table I): *C* = (mmol adsorbed metal ion)/(g of dry resin).

By using a resin/metal ion ratio (in mol) of 20:1, for all the cations the capacity was higher than 88.9%, varying from 0.12 mmol/g of dry resin for Hg(II) at pH 1 to 0.32 mmol/g of dry resin for Ag(I) at pH 5. Decreasing the resin/metal ion ratio to 10 : 1.0 similar retention values (in percentage) and an increase of the capacity, *C* was observed. Only for Pb(II) and Cr(III) cation were the C values lower than those expected.

Only 5 min was the time required to achieve a metal ion retention above 90% (Table II). Up to 60 min, there was no important observed change in the retention values. This is very important considering that the reaction occurs in a heterogeneous medium.

To determine the selectivity of the resin, 10 mL of metal ion of the same concentration were contacted with the resin (100 mg) and the suspension was shaken by 1 h. The adsorbed metal ions were monitored to determine the remaining content of the solution by AAS. The distribution coefficient (*D*) is described as $D = [(mmol\ M^{n+})/(g\ of\ dry\ resin)]/[(mmol\ M^{n+})/(cm^3\ of\ solution)]$.

Selectivity is obtained from the following general equation: selectivity = log K_d metal 1 − log K_d metal 2, where K_d is [weight (mg) of metal ion for g of resin]/[weight (mg) of metal ion for mL of solution].

The corresponding values for the distribution coefficients are summarized in Table III and the selectivity in Table IV. The selectivity for Cd(II) at pH 2 with respect to all the other metal ions is low for both ternary and quaternary metal ion mixtures. The values ranged from 0.7 to 0.9, which means that the active groups show a similar affinity for the metal ions under noncompetitive and competitive conditions.

TABLE V
**Effect of Eluent on Recovery of P(Sty-*co*-APSA) Resin**

Metal ion	pH	Eluent	Retention (%)
Hg(II)	2	HNO$_3$, 1 M	87.7
		HNO$_3$, 4 M	81.9
		HClO$_4$, 1 M	83.3
		HClO$_4$, 4 M	86.6
Cd(II)	3	HNO$_3$, 1 M	91.3
		HNO$_3$, 4 M	95.7
		HClO$_4$, 1 M	91.0
		HClO$_4$, 4 M	91.0
Zn(II)	5	HNO$_3$, 1 M	98.6
		HNO$_3$, 4 M	98.8
		HClO$_4$, 1 M	98.5
		HClO$_4$, 4 M	98.8
Pb(II)	5	HNO$_3$, 1 M	95.9
		HNO$_3$, 4 M	95.9
		HClO$_4$, 1 M	96.9
		HClO$_4$, 4 M	96.8
Cr(III)	5	HNO$_3$, 1 M	99.4
		HNO$_3$, 4 M	99.3
		HClO$_4$, 1 M	99.4
		HClO$_4$, 4 M	99.6
Ag(I)	5	HNO$_3$, 1 M	85.9
		HNO$_3$, 4 M	85.9
		HClO$_4$, 1 M	86.9
		HClO$_4$, 4 M	86.8

The maximum retention capacity of load for Ag(I), Hg(II), Cd(II), Zn(II), Pb(II), and Cr(III) after three batch contacts of 1 g of dry resin with an aqueous solution containing 1 g/L in each metal ion is shown in Figure 2. The highest values of 2.07 and 2.23 mmol/g dry resin were observed for Zn(II) and Cr(III), respectively, and the lowest values of 0.64 and 0.70 mmol/g dry resin correspond to Hg(II) and Pb(II), respectively.

The sulfonic groups could interact electrostatically with the ions. These resin active sites–metal ion interactions depend strongly on the pH. At low pH, the contribution of the electrostatic effect is very important.
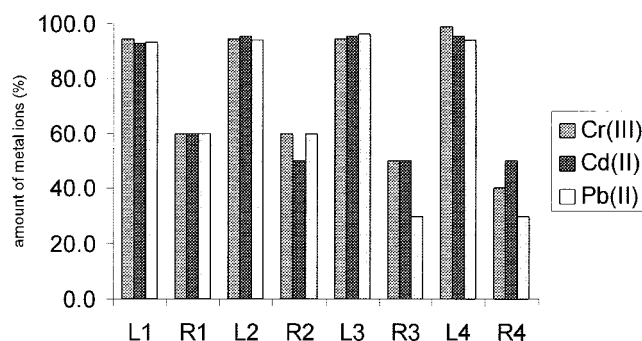
Figure 3 Amounts of Cr(III), Cd(II), and Pb(II) ions on the P(Sty-*co*-APSA) resin after four cycles of loading (*L*) and regeneration (*R*) with 1 M HNO$_3$. Initial amount of Cr(III), Cd(II), and Pb(II) are 127, 114, and 372 mg/L, respectively.
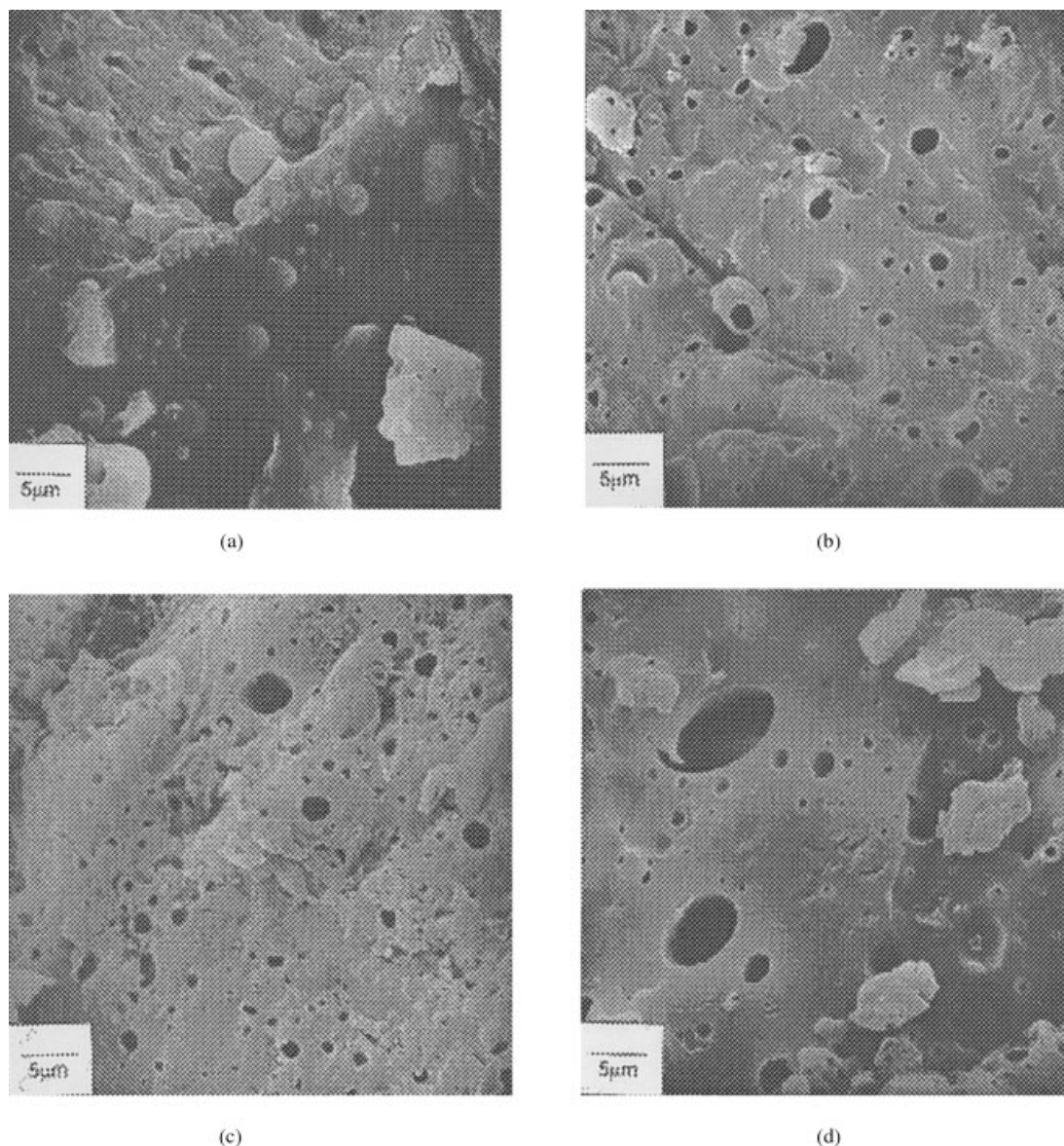
Figure 4 Scanning electron micrographs of the (a) unloaded P(Sty-*co*-APSA) resin P(Sty-*co*-APSA) resin with different metal ions: (b) Hg(II); (c) Zn(II), and (d) Ag(I). Magnification: ×2,000.

Desorption of metal ions from the loaded resin was studied with 1–4 M $HClO_4$ and 1 and 4 M HNO_3 solutions at 25°C with about 1 h of shaking time. The final amount of metal ion was determined by AAS.

In order to reuse the adsorbent material, the metal ion adsorbed by the resin should be easily released under the presence of an appropriate eluent medium. The effect of the different eluents on the desorption Hg(II), Zn(II), Pb(II), Cr(III), and Ag(I) is summarized in Table V. No important concentration of the eluent was observed. There is a difference, lower than 10%, between both concentrations. These media are efficient to destroy the sulfonic/sulfonate–metal ion interaction. The elution for Cd(II), Pb(II), and Cr(III) was higher than 96% and for Ag(I) and Hg(II) higher than 80%. Therefore, both nitric (1 and 4 M) and perchloric

acids (1–4 M) emerge as effective eluents for all the metal ions.

To obtain the reusability of the P(Sty–APSA) resin, the sorption–desorption cycle was repeated four times using the same sorbent. Initial amounts of 127, 114, and 372 mg/L of Cr(III), Cd(II), and Pb(II), respectively, were employed to load the resin. In each cycle, the adsorption was performed at pH 3 and the regeneration with 1 M HNO_3 (Fig. 3). Loading for all three metal ions is similar. Loading capacity is close to 90% and no important effect after the four cycles was observed. Up to two cycles the regeneration of the three metal ions is very similar, but at the third and fourth cycles the regeneration of Pb(II) is smaller than Cd(II) and Cr(III). This could be due to the stronger and more stable interactions between the sulfonic acid

Resin	pH	Weight loss at different temperatures					
		100	200	300	400	500	550
P(Sty-*co*-AMPS)		100.0	92.2	81.5	63.3	10.6	10.2
P(Sty-*co*-AMPS)–Hg(II)	2	100.0	93.9	85.5	57.9	9.2	8.6
P(Sty-*co*-AMPS)–Cr(III)	5	100.0	96.4	85.1	54.0	7.5	3.4
P(Sty-*co*-AMPS)–Pb(II)	5	100.0	97.9	86.8	58.4	9.0	7.9
P(Sty-*co*-AMPS)–Ag(I)	5	100.0	95.8	86.4	61.3	7.0	6.8
P(Sty-*co*-AMPS)–Zn(II)	5	100.0	97.2	86.1	51.2	8.2	7.0
P(Sty-*co*-AMPS)–Cd(II)	5	100.0	97.5	88.3	66.4	8.4	8.1

Heating rate 20°C/min under N_2.

groups and Pb(II) ions. It is relevant that the metal ion retention capability did not decrease significantly.

The morphology with a magnification of ×2,000 of the charged and uncharged resins is shown in Figure 4. The surface of the resin is smooth and with small holes [Fig. 4(a)], but the loaded metal ion resin shows a surface with more holes [Fig. 4(b–d)].

Thermogravimetric analysis under N_2 shows similar values between the resin and the loaded resin with the metal ion (Table VI). It could suggesting a resin–metal ion interaction involving active sites from the same polymer chain.

CONCLUSIONS

The present investigation has shown that the radical copolymerization of 2-acrylamido-2-methyl-1-propane sulfonic acid with styrene has a yield of 72.3%. The resin showed a high affinity for metal ions but not a selectivity. The metal ion retention properties depended on the pH. The resin–metal ion equilibrium was achieved at about 5 min, which is considered fast for a heterogeneous reaction. Adsorbed metal ions Ag(I), Hg(II), Cd(II), Zn(II), Pb(II), and Cr(III) were relatively easily desorbed by using 1 and 4 M HNO_3 and $HClO_4$. Consecutive adsorption and desorption showed the feasibility of this resin for Cd(II), Pb(II), and Cr(III). No important change between the thermal behavior of the unloaded and loaded metal ion resin was observed. The intrachain resin–metal ion should be the most probable active site–metal ion interaction. No important change during the metal ion adsorption on the morphology of the resin was observed.

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