Synthesis and Metal Ion Adsorption Properties of Poly(4-sodium styrene sulfonate-*co*-acrylic acid)

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ABSTRACT: The water-insoluble resin poly(sodium 4-styrene sulfonate-*co*-acrylic acid) was synthesized through a solution radical polymerization with ammonium persulfate as an initiator and *N*,*N*′-methylene-bis-acrylamide as a crosslinking reagent (CR) at different amounts (2, 4, 6, and 8 mol %). The polymerization yield ranged from 75 to 91%. The metal ion retention properties were studied by batch and column equilibrium procedures for: Cd(II), Cr(III), Zn(II), Al(III), Pb(II), and Hg(II). These properties were investigated under competitive and noncompetitive conditions. The effect of pH, particle size, time, temperature, and initial metal ion concentration on metal ion adsorption was investigated. The resins showed a high retention ability for Hg(II) ions over 85% at pH 2 and for Cd(II), Cr(III), Zn(II), and Pb(II) over 96% at pH 5. The maximum adsorption performance for Pb(II) was achieved as 148.5 mg/g at an optimum pH. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 1587–1592, 2009

Key words: adsorption; ion exchanger; metal polymer complexes

INTRODUCTION

Purification of large amount of wastewater within a reasonable time is increasingly required.[1] The effective treatment of metal ions from aqueous solutions has received much attention because of their toxicity even at low concentration and their tendency to bioaccumulate.[2] The ability of several methods, such as ion exchange, adsorption, reverse osmosis, and precipitation to remove metal ions from polluted liquids, has been extensively studied in the literature.[3,4] Ion exchangers and chelating resins are widely used in hydrometallurgy, especially for the recovery of precious metals from leaching solutions. Chelating polymers are able to form complexes with metal ions[5–10] in the presence of reactive functional groups containing O, N, P, and S donor atoms. Ion exchange resins are very important for metal ion complexation reactions because of their hydrophilicity, accessibility, and capacity. In addition, the synthesis of a polymer with a high degree of selectivity is of great importance for different applications.[11]

Adsorption properties depend on the resin's physical and chemical properties, such as type and structure of the functional group introduced into the polymer matrix, the cross linking degree, as well as swelling and sorption conditions that include the solution's pH, resin quality, contact time, metal ion concentration, and the type and presence of interfering ions.

The reaction between the functional group and the metal ion as well as the diffusion of the metal ions into the resin's interior plays a key role in determining chelating resins capacity to adsorb metal ions.[12]

There are two ways to synthesize functional polymers for preconcentration and removal of metal ions. In the first approach, a monomer with active and specific ligand for the target metal ions is polymerized. In the second approach, after the polymerization, polymeric materials are modified by the active and specific ligand to one or more different metal ions.[13] For the extraction, determination, preconcentration, and removal of some heavy metal ions, a variety of new types of functional resins have been very intensively studied.[14–18]

The aim of this article is to report the metal ion retention properties of the poly(sodium 4-styrene sulfonate-*co*-acrylic acid) [P(StyS-*co*-AA)] resin using the batch and column equilibrium methods. The metal ions were selected according to their environmental impact.

EXPERIMENTAL PART

Materials

Acrylic acid (AA) supplied from Aldrich was purified by distillation. Sodium 4-styrene sulfonate (StyS, 96%, Aldrich) was used as obtained. *N*,*N*′-

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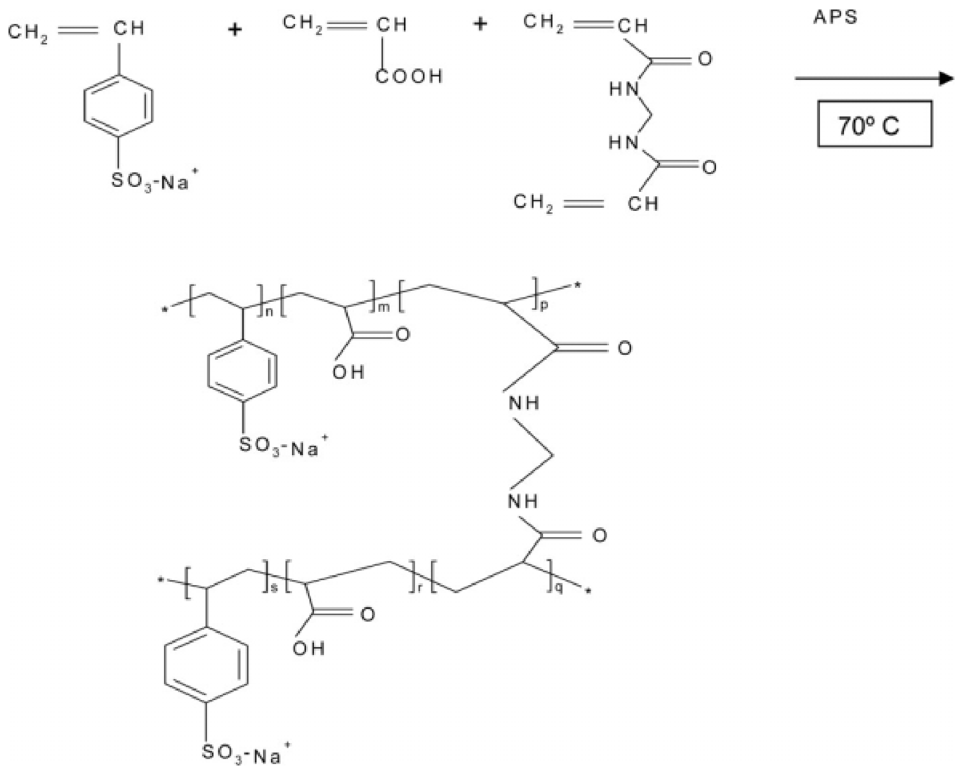

Scheme 1 Synthesis of the resin poly(sodium 4-styrene sulfonate-*co*-acrylic acid).

methylene-bis-acrylamide (MBA, 99%, Aldrich) and ammonium peroxide disulfate (AP, Fluka) were used as obtained as crosslinking and initiator reagents, respectively.

For adsorption studies, the metal salts used were $CdCl_2$, $Cr(NO_3)_3$, $Hg(NO_3)_2$, $Pb(NO_3)_2$, $Al(NO_3)_3$, and $Zn(NO_3)_2$. Metal salts were purchased from Merck. The analytical grade HNO_3, $HClO_4$, H_2SO_4, and HCl were purchased from Fisher.

Synthesis of the resins

The synthesis of the resin P(StyS-*co*-AA) was carried out in a polymerization flask as follows: 0.01456 mol of StyS (3 g), 0.01456 mol of AA (1.048 g), 5.825 $\times$ 10^{-4} mol of AP (0.1328 g), and an equivalent amount of MBA to 2–8 mol % were dissolved in 20 mL of twice-distilled water and then added to a polymerization flask. The system was kept under N_2 at 70°C for 4 h. Subsequently, the resin was filtered and washed with distilled water and dried up to a 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 metal ion binding ability of the synthesized adsorbents. All experiments were performed in a flask mounted on a shaker. The adsorption equilibrium experiments were performed to study the effects of pH, metal ion concentration, contact time, temperature, and particle size. Additionally, the retention ability for di- and trivalent cations, Cd(II), Zn(II), Hg(II), Pb(II), Cr(III), and Al(III) under competitive conditions was studied.

Then, 0.05 g of dried resin and 5 mL of metal ion solution were shaken for 1 h at 20°C. After shaking, the resin samples were filtered and washed with water at the same pH. The concentrations of metal ions in the filtrate were determined by atomic absorption spectroscopy. Batch metal uptake experiments under competitive conditions were performed with the following divalent metal ion mixtures: Cd-Zn-Hg-Pb at pH 2 and to Cd-Zn-Pb at pH 5. For this test, 0.15 g of resin and 15 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.

In the regeneration experiments, HNO_3, HCl, H_2SO_4, and $HClO_4$ at various concentrations were studied as potential stripping reagents by using the batch method. A 0.05 g of resin loaded with Hg(II), Cd(II), Zn(II), Cr(III), and Pb(II) ions was eluted with 5 mL of eluent for 1 h.

For the column experiments, 0.2 g of resin was placed into a column with 15 cm length and 1 cm diameter. In all runs, a 20-mL metal salt solution

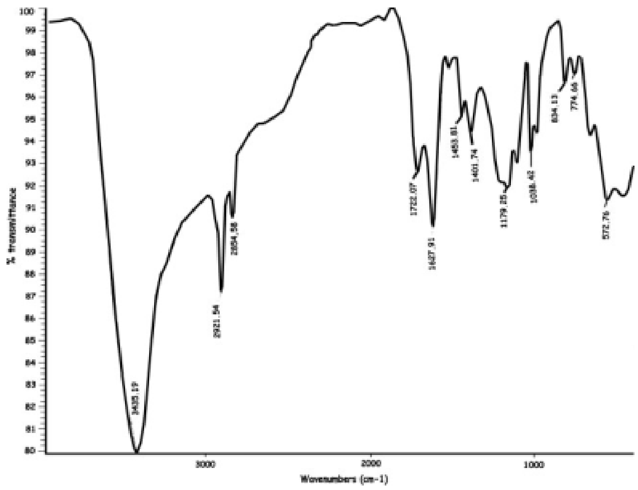

Figure 1 FTIR (KBr) of the resin P(StyS-*co*-AA).

passed through the column. The fractions were collected and analyzed for the metal ion concentration.

Measurements

A Julabo air-batch shaker was used for shaking the solution at a desired temperature. The pH was measured with a digital pH meter. Atomic absorption spectrometer (H. Jürgens and Co. A Unicam Solar M series) was used for the determination of metal ions. The FTIR spectra of the samples 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 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 4-sodium styrene sulfonate with AA. AP was used as an initiator and MBA as a crosslinking reagent (CR) at different mol percentages (2, 4, 6, and 8 mol %). The yields for these resins were as follows: 76, 86, 86, and 91%, respectively. The general polymerization reaction is shown in Scheme 1.

The FTIR spectrum of P(StyS-*co*-AA) shows the most characteristic absorption signals (in cm^{-1}) as 1179.25 (S=O), 1722.07 (C=O) among the absorption bands (see Fig. 1).

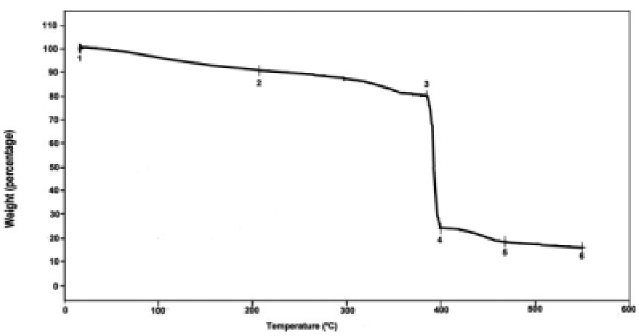

Figure 2 Thermogravimetric analysis (TGA) of the resin P(StyS-*co*-AA) under nitrogen at a heating rate of 20°C/min.

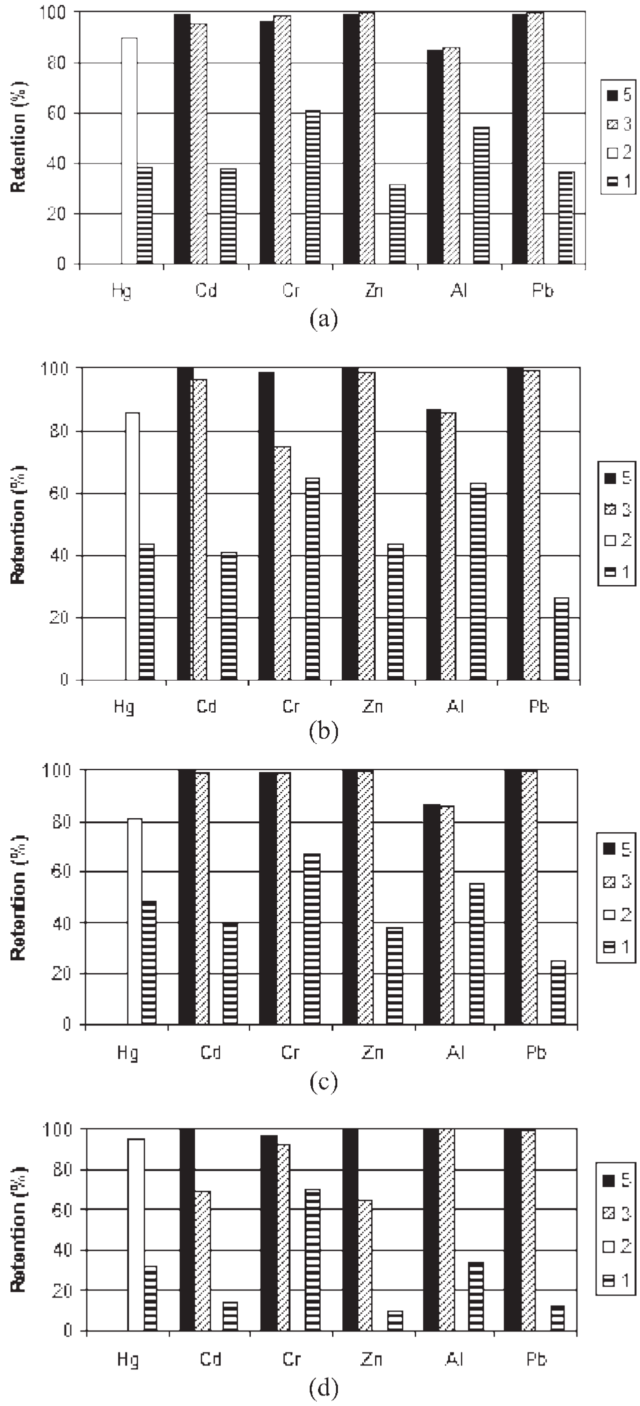

Figure 3 Effect of the pH and crosslinking reagent amount on the metal retention capacity of P(StyS-*co*-AA). Particle size 180–250 μm, resin–metal ion ratio 20 : 1, contact time 1 h. (a) 2 mol % MBA, (b) 4 mol % MBA, (c) 6 mol % MBA, and (d) 8 mol % MBA.

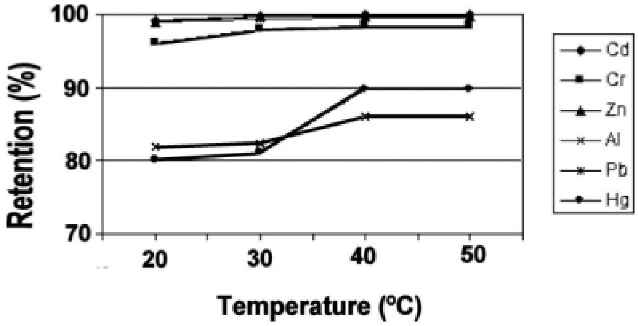

Figure 4 Effect of temperature on the metal ion retention capacity of P(StyS-*co*-AA) at an optimum pH (5 for Cd(II), Cr(III), Zn(II), Al(III), and Pb(II) and 2 for Hg(II)), particle size 180–250 μm, resin–metal ion ratio 20 : 1.

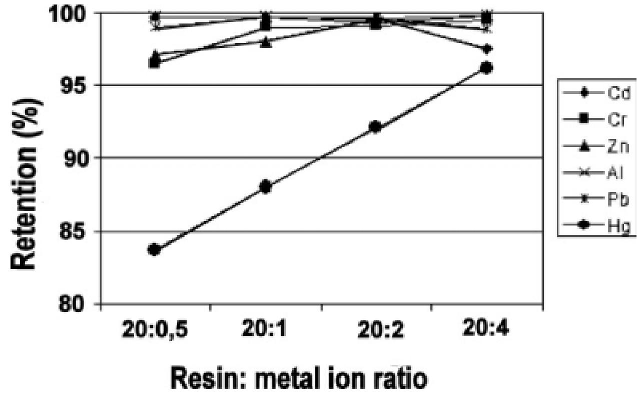

Figure 5 Effect of the initial metal ion concentration on metal ion retention capacity of P(StyS-*co*-AA) at an optimum pH (pH 5 for Cd(II), Cr(III), Zn(II), Al(III), and Pb(II) and pH 2 for Hg(II)), particle size 180–250 μm.

The copolymer composition of the resin was calculated from FTIR spectrum by comparison of the absorption band intensity of characteristic signals coming from both monomers. Thus, those stretching bands C=O (1627 cm^{-1}) from AA and S=O (1038 cm^{-1}) from StyS were used. According to that, the ratio of AA/StyS was 2 : 1.

The resins showed a high thermal stability up to 300°C with a weight loss below 15%. Weight loss increased up to 76% at 400°C. It was considered that the resin losses the carboxylic moiety in the form of CO_2 (see Fig. 2).

Because metal ion retention is usually a diffusion-controlled process, it is very important to determine the resin's swelling capacity. For the resin studied, the water adsorption capacity (WAC) was determined by gravimetry. The highest value, 88.5 g of water/g of resin, was obtained by the resin with the lowest CR (2 mol %). The other WAC values are the following: 44.7 (4 mol %), 41.4 (6 mol %), and 24.2 (8 mol %). These results suggest that the resin could be a hydrogel.

Metal ion retention properties

The nature of the adsorption depends on several factors: the adsorbent (ionic charge), the pH of the solution, and the metal ion's chemistry (e.g., ionic charge, ability of the resin to be hydrolyzed and to form polynuclear species).

The resin's affinity for the metal ions was studied by batch and column equilibrium methods using a resin with a particle size of 180–250 μm and resin–metal ion mole ratio 20 : 1. This ratio ensures the metal ion's access to ligand sites.

Effect of pH

The uptake of Cd(II), Cr(III), Zn(II), Al(III), Pb(II), and Hg(II) ions as a function of pH by batch equilibrium method was examined at a pH range of 1–5. The resin showed a high dependence on the pH, because the metal's ionic species and the ligand groups' change with the pH. The metal ion sorption was favored at higher pH because the ligand groups are deprotonated and are free to exchange or complex the metal ion. In general, the crosslinking degree does not affect the retention properties. For the resin with 8 mol % of MBA, the highest retention values were obtained at pH 5 for Cd(II), 99.2%, 2.6 mg/g; Zn(II) 99.2%, 12.3 mg/g; Al(III), 99.0%, 5.1 mg/g; and Pb(II), 99.0%, 40 mg/g. The optimum pH was 2 for Hg(II) and 5 for the other metal ions. Therefore, this value was chosen for further experiments. Figure 3(a–d) shows experimental results obtained at pH 1 and 5 for the resins obtained by batch procedure with different amount of MBA (2–8 mol %).

Because of the metal ion retention behavior of P(StyS-*co*-AA) depends on functionalities in the polymer rather than other properties, it was determined considering a comonomer ratio AA/StyS 2 : 1, and that in each contact with the metal ion, 0.05 g of the resin, it is obtained 0.445 mmol of functional group per 0.05 g of resin or 8.9 mmol/g of resin.

TABLE I
Selectivity Behavior of the Resin P(StyS-*co*-AA), 8 mol % at pH 2 from the Quaternary Metal Ion Mixture Cd(II)-Pb(II)-Zn(II)-Hg(II)

Metal ion	Retention[a] (%)	Retention[b] (%)
Cd(II)	90.0	24.4
Pb(II)	92.6	52.9
Zn(II)	90.0	18.3
Hg(II)	7.9	4.5

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

TABLE II
Selectivity Behavior of the Resin P(StyS-*co*-AA), 8 mol % at pH 5 from the Ternary Metal Ion Mixture Cd(II)-Zn(II)-Pb(II)

Metal ion	Retention[a] (%)	Retention[b] (%)
Cd(II)	98.8	31.3
Pb(II)	99.5	35.3
Zn(II)	99.0	33.5

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

Effect of temperature

The effect of the temperature on the metal ion retention was studied in the range of 20–50°C. It was observed that only the metal uptake for Al(III) and Hg(II) was slightly influenced. For all the other metal ions, there was not observed effect on the metal ion retention behavior as shown in Figure 4.

Effect of metal concentration

For practical reasons, the metal ion retention capacity should be maintained when the metal ion concentration in the solution changes. The effect of the metal concentration on metal ion recovery was studied using different mole ratios of resin–metal ion. The mole ratio of resin to metal ion was varied from 20 : 0.5 to 20 : 4. For all resins, metal ion retention increased when the resin in metal ion ratio increased. This result means that the resin still has active places to retain the metal ions (see Fig. 5).

Selectivity behavior

To determine metal ion retention under competitive conditions, several tests were conducted. First, 200 mg of dry resin was placed in contact at pH 2 for 1 h with 20 mL of an aqueous solution containing the same concentration for each metal ions (Cd(II), Zn(II), Pb(II), and Hg(II)). The resin showed a high retention for Pb(II), Cd(II), and Zn(II), but very low retention for Hg(II) (7.9%) (see Table I). Second, 150 mg of the resin was placed in contact for 1 h at pH 5 with 15 mL of an aqueous solution containing the same concentration for each metal ions (Cd(II), Zn(II), and Pb(II)). The three metals studied were retained over 98% (see Table II). The resin did not

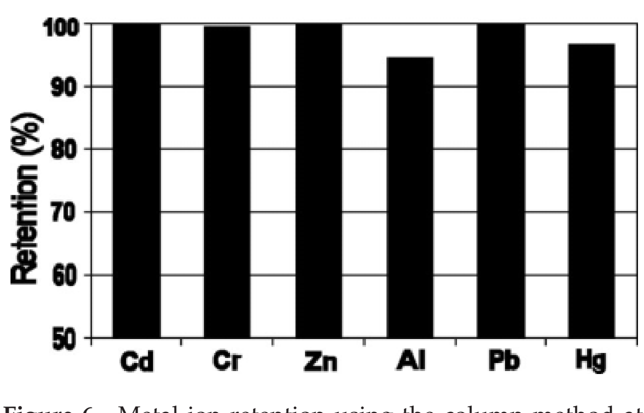

Figure 6 Metal ion retention using the column method at an optimum pH (pH 5 for Cd(II), Cr(III), Zn(II), Al(III), and Pb(II) and pH 2 for Hg(II)).

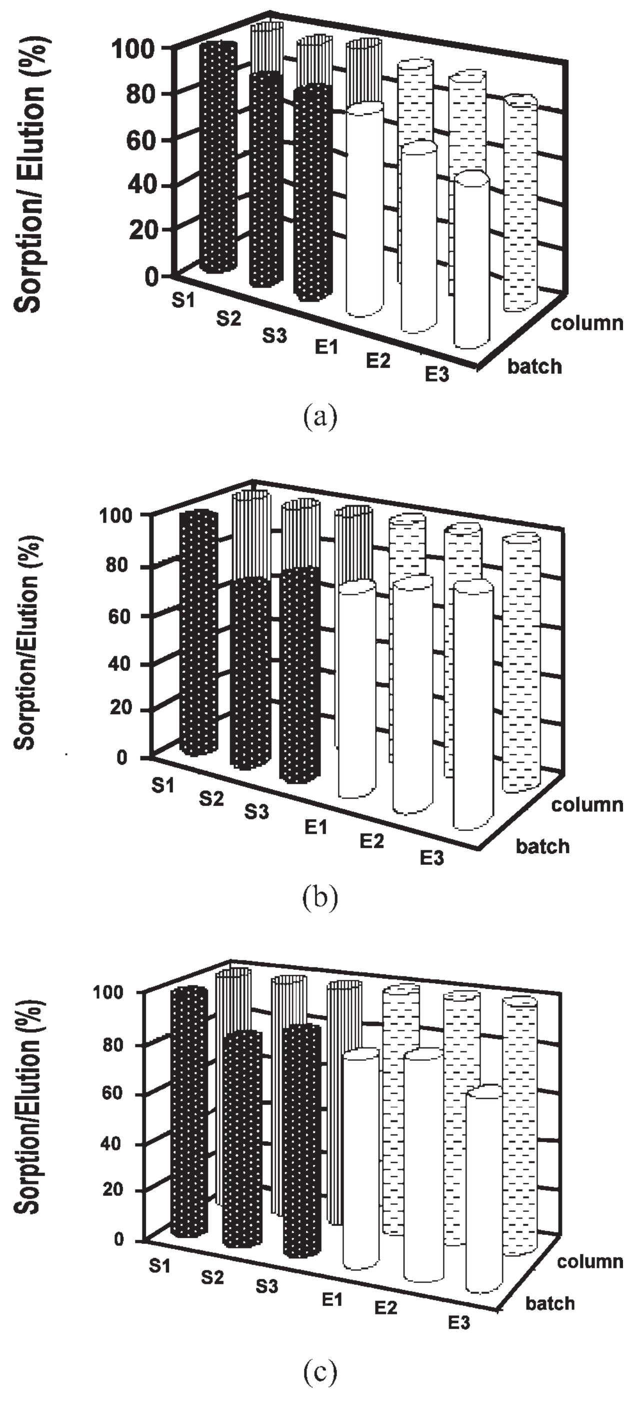

Figure 7 Reusability of the resin. (a) Cd(II), eluent 1*M* HCl, (b) Zn(II), eluent 1*M* $HClO_4$, and (c) Pb(II), eluent 1*M* HCl. (S, sorption; E, elution).

present selectivity behavior for any specific metal ion, which means that the retention does not depend on the metal ion's size even though the metal ions have different ionic radii, Zn(II) 0.074 nm and Pb(II) 0.120 nm. Metal ion retention can be produced by electrostatic interaction between the sulfonic group or the carboxylate group and the metal ions.

Retention by column equilibrium procedure

It is important for the resin to maintain the similar retention behavior in a continuously operated process as obtained during a batch process. The retentions obtained for each metal ion using the optimum pH were over 94%. The column equilibrium procedure results are shown in Figure 6. This retention behavior demonstrated that the equilibrium between the active site and the metal ion was achieved in a short time period because the contact time was shorter in column method in comparison with the batch method.

Reusability of the resin

To use this resin in a continuously operated process, it is very important to maintain the metal ion capacity after the treatment with an eluent reagent. The metal ion adsorbed by the resin should be easily released under appropriate conditions. The batch desorption studies were performed using four different stripping acid solutions (HCl, $HClO_4$, HNO_3, and H_2SO_4). For resin reusability, the sorption–desorption cycle was repeated three times with the same adsorbent in batch and column processes. The results are shown in Figure 7(a–c). In case of Figure 7(a), the resin was loaded with Cd(II) and the desorption was performed with 1*M* HCl. Under these experimental conditions, the resin was able to maintain its retention capacity in the three cycles, and it is possible to produce desorption at a high percentage after three cycles. In the second experiment [Fig. 7(b)], the resin was loaded with Zn(II) and the desorption was produced with 1*M* $HClO_4$. In the third experiment [see Fig. 7(c)], the resin was contacted with a Pb(II) solution and the desorption was performed with 1*M* HCl. During the three sorption–elution cycles, the resin could be loaded and regenerated without any loss in its metal ion retention capacity. Thus, this resin could be used in a continuously operated process to remove the undesirable metal ions.

CONCLUSIONS

The crosslinked P(StyS-*co*-AA) resins were synthesized by radical solution polymerization using different crosslinking degree. The resins showed a high retention for Cd(II), Cr(III), Zn(II), Al(III), and Pb(II) at pH 5 and Hg(II) at pH 2. Particle size, temperature, or contact time did not significantly affect the metal ion retention behavior. Consecutive adsorption and desorption test showed that this resin has a potential for recycled use with Cd(II), Zn(II), and Pb(II).

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