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Poly(4-sodium styrene sulfonate-*co*-4-acryloylmorpholine). Synthesis, Characterization, and Metal Ion Retention Properties

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Abstract: A novel resin poly(sodium 4-styrene sulfonate-*co*-4-acryloyl morpholine) was synthesized through a radical solution polymerization in solution and studied as an adsorbent under uncompetitive and competitive conditions by batch and column equilibrium procedures for the following divalent metal ions Cd(II), Zn(II), Pb(II), and Hg(II), and trivalent Cr(III). For all metal ions, the adsorption was strongly influenced by the pH. The maximum retention capacity, 3.29 mmol of metal ion/g, was obtained for Zn(II) at pH 5 by batch equilibrium procedure. For both the batch and column procedures, the retention behavior was similar for Cd(II), Cr(III), Zn(II), and Pb(II).

Keywords: batch procedure, metal ions, removal, resin

INTRODUCTION

The hazardous effect of heavy elements in the environment has considerably limited their use in various industries (1). With an ever increasing population and rapid industrial growth, industrial discharge contains these metals, making environmental contamination inevitable. Indeed, heavy metal ions are among the most important pollutants of aqueous samples because these ions are not biodegradable and tend to accumulate

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in living organisms, causing several diseases and disorders. As a result, heavy metal ion concentration levels are of great importance.

However, the concentration level of metal ions is lower than that method detection limit for processes as liquid-liquid extraction, sorption, precipitation, ion exchangers, among others, etc., and metal usually exists in very complex matrix environments.

The separation and enrichment of hazardous metal ions in aqueous solutions play an important role for their removal from municipal and industrial waste water.

The most commonly used pre-concentration and separation methods for geological, biological, environmental, and industrial fluids are liquid-liquid extraction, sorption, precipitation, ion exchangers, among others (2).

It is well known that the chelating resins with covalent bonded functional groups containing nitrogen and sulfur atoms possess excellent adsorption and selectivity properties for metal ions (3–8). Several coordination polymers have been prepared from aromatic and aliphatic polymers containing pendant functional groups, which act as a chelating group in binding polyvalent metal ions (9). Accordingly, various chelating resins have been synthesized based on Pearson's hard and soft acids and bases (HSAB) approach and have been applied to various fields such as trace element analysis (10), wastewater treatment, and precious metal recovery (11–19).

For these reasons, the current work develops a resin that contains active groups able to act as a chelating or exchanger for several metal ions. The resin poly(sodium 4-styrene sulfonate-*co*-4-acryloylmorpholine), contains the sulfonic group which can act as an ion exchanger and the nitrogen from the morpholinic group would act as a chelating reagent. The combination of both groups would make a more specific resin for the same metal ion.

EXPERIMENTAL PART

Materials

4-acryloylmorpholine (AM) supplied from Aldrich and sodium 4-styrene sulfonate (StyS, 96%, Aldrich) were used as obtained. N,N′-methylene-bis-acrylamide (MBA, 99%, Aldrich) and ammonium peroxide disulfate (AP, Fluka) were used as obtained as cross-linking 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 $Zn(NO_3)_2$. It was not available the

$Cd(NO_3)_2$. All metal salts are 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 poly(sodium 4-styrene sulfonate-*co*-4-acryloylmorpholine) was performed in a polymerization flask as follows: 0.01456 mol of StyS (3.00 g), 0.01456 mol of AM (2.0534 g), 5.825×10^{-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 placed in a polymerization flask. The polymerization mixture was kept under N_2 at 70°C for 4 hours. Then, the resin was filtered and washed with distilled water and dried up to constant weight at 40°C. The polymerization yields for these resins with 2, 4, 6, and 8 mol% of MBA were: 97%, 86%, 92%, and 96%, respectively. The resins were crushed, and then screened, and a particle size fraction in the range of 180–250 μm was chosen for all experiments.

Uptake Studies

All experiments were performed in a flask mounted on a shaker. The batch equilibrium procedure was used to study the effect of pH and metal ion concentration.

Additionally, the retention ability for di- and trivalent cations, Cd(II), Zn(II), Hg(II), Pb(II), and Cr(III), under competitive conditions was studied. For this test, 0.05 g of dried resin in 5 mL of metal ion solution (metal ion solution concentration 20:1 in mol between functional group of the resin and metal ion) was shaken for 1 hour at 20°C. To that, it is considered the amount mol corresponding to the polymer repeat unit. After shaking, the 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, AAS.

Batch metal uptake experiments under competitive conditions were performed with the divalent metal ion mixture Cd-Zn-Pb-Cr at pH 5. For this test, 0.2 g of resin was mixed with 20 mL of metal ion solution. The resin-metal ion ratio (in mol) is 20:1. After a shaking time of 1 hour, the samples are further handled as described for the non-competitive experiments.

To determine the maximum sorption capacity for Cd(II), Zn(II), Pb(II), Cr(III), and Hg(II), the following runs were carried out: 25 mL of an aqueous solution (1 g/L) was shaken with 0.5 g of dry resin for 1 hour at 20°C. The mixture in the flask was filtered, washed with distilled

water, and transferred into a calibrated 50 mL flask and completed to the volume. The process was repeated three times, and the metal ions in the supernatant were determined by AAS.

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 Cd(II), Cr(III), Zn(II), Pb(II), and Hg(II) ions were eluted with 5 mL of eluent for 1 hour. The loaded resin is washed with twice distilled water and the filtrates were collected.

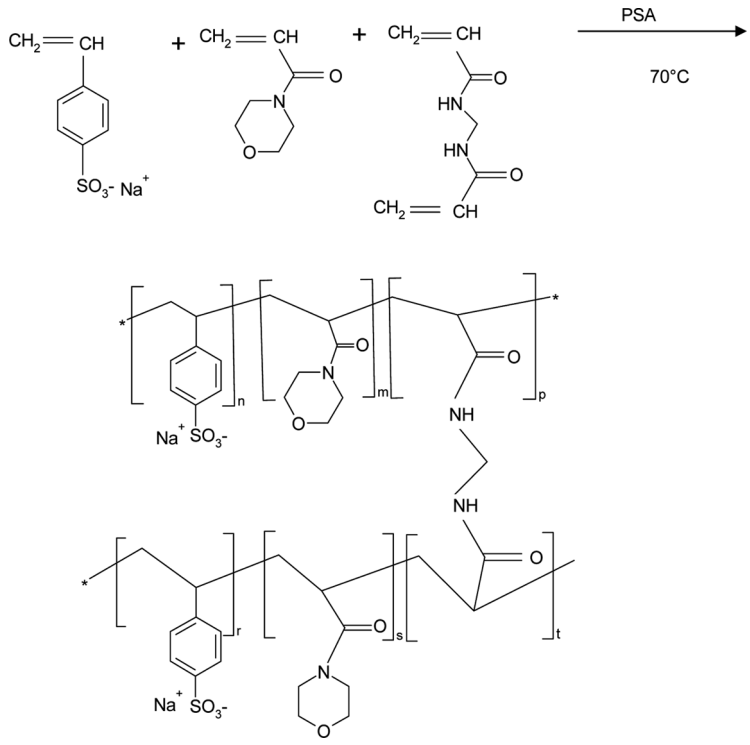
For the column experiments, 0.2 g of resin was placed in a column (15 cm length and 1 cm in diameter). To ensure an adequate metal ion retention behavior during all the preliminary experiments, this column was used only with 0.2 g of the resin. For resin packing, water at the same pH was used. In all runs, 20 mL metal salt solution passed through the column. The fractions were collected and analyzed the metal ion concentration by AAS.

Measurements

A Julabo air-batch shaker is used to shake the solution at a desired temperature. The pH was measured with a digital pH meter (H. Jürgens and Co). A Unicam Solar M series atomic absorption spectrometer was used to determine single and mixed metal ions. The sample's FTIR spectra are 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 heating rate of 20°C/min under a dynamic nitrogen atmosphere.

RESULTS AND DISCUSSION

Water-insoluble resins with sulfonate and morpholinic group were obtained by copolymerization of an equimol ratio of 4-sodium styrene sulfonate and 4-acryloylmorpholine, AP was used as an initiator and MBA as a cross-linking reagent at different mole percentages (2, 4, 6, and 8 mol%) (see Scheme 1). The yields for these resins were: 97%, 86%, 92%, and 96%, respectively. The resins show a high thermal stability up to 400°C with a weight loss lower than 17.6%; then, the weight loss increased until reaching 54.7% at 500°C. Among the most characteristic absorption bands shown in the FTIR spectrum of P(StyS-*co*-AM) are the following (in cm^{-1}): 1166.10(S = O), 626.01 (C-S), 1204.65 (C-N) (see Fig. 1).



Scheme 1. Synthesis of the resin poly(sodium 4-styrene sulfonate-*co*-4-acryloylmorpholine) P(StyS-*co*-AM).

Since metal ion retention is usually a controlled diffusion process, the resin's swelling capacity must be determined. For the resin studied, the water–adsorption capacity (WAC) was determined by gravimetry. The highest value, 46.9 g of water/g of resin, was obtained for the resin with a lower CR (2 mol%) (see Table 1).

Metal Ion Retention Properties

It is well known that hard acids, which are small and non-polarizable, have a higher affinity toward hard donor atoms (e.g. O or N); whereas soft acids, which are larger and more easily polarizable, have a greater affinity toward soft donor atoms (1). The affinity between the resin's active site and metal ions is studied by the batch and column equilibrium procedure, using a resin particle size of 180–250 μm and resin–metal ion relationship (in mol between repeat unit in the resin and metal ion) 20:1. This ratio ensures that the metal ion's access to ligand sites.

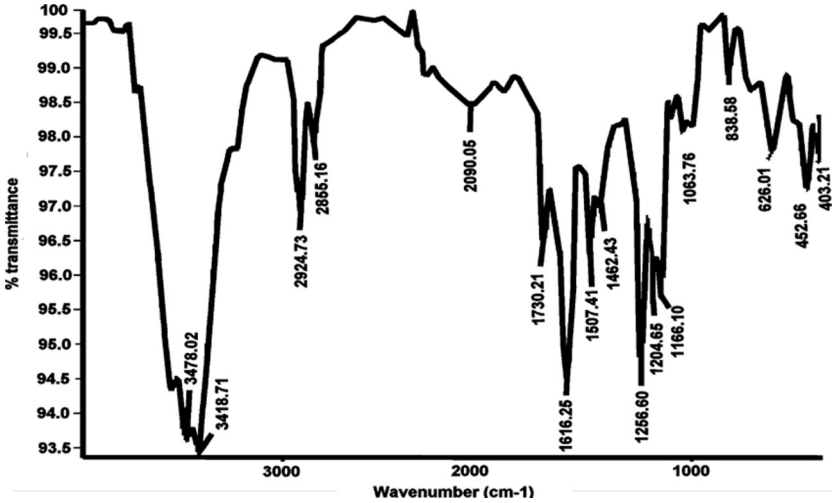


Figure 1. FTIR spectrum of the resin P(StyS-*co*-AM).

Effect of pH on the Metal Ion Removal

The uptake of Cd(II), Cr(III), Zn(II), Al(III), Pb(II), and Hg(II) ions as a function of pH by batch method was examined over pH range of 1–5. At this concentration was not observed precipitation of hydroxides, including aluminum. The pH range studied depends on metal ion solubility behavior. The resin showed a higher dependence on pH, since both metal ions and ligand groups change with the pH; the metal ion absorption is favored at higher pH because the ligand groups are deprotonated and the groups are free to exchange or complex the metal ion. In general, the cross-linking content does not affect the retention properties. The highest retention capacities were obtained a pH 5 for the resin with 8 mol% of MBA, for: Cd(II), 99.9%, (13 mg/g); Zn(II) 99.8%, (8.8 mg/g);

Table 1. Water absorption capacity, WAC of the resin P(StyS-*co*-AM) with different amounts of cross-linking reagent at the fee

Cross-linking reagent (mol%)	WAC (g H_2O/g dry resin)
2	46.9
4	13.1
6	17.6
8	5.35

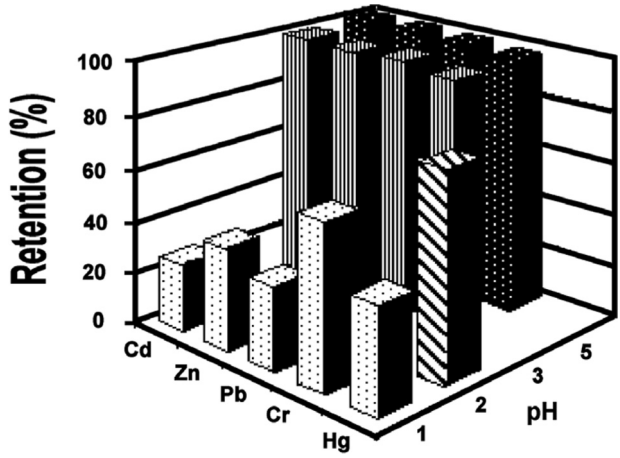


Figure 2. Effect of the pH on metal retention capacity of the resin P(StyS-*co*-AM). Particle size 180–250 μm, resin: metal ion ratio 20:1, contact time 1 hour, and cross-linking reagent amount 8 mol%.

; and Pb(II), 99.3%, (28.5 mg/g). The optimal retention value of pH 2 was for Hg(II) and for the other metal ions was pH 5. Therefore, these pH values were chosen for the following runs. Figure 2 shows experimental results obtained at pH 1 and 5 for the resins obtained with 8 mol% of MBA by batch equilibrium procedure.

To explore the applications of the resin, the maximum adsorption capacity (MAC) needs to be determined. Based on the MAC, the maximum retention capacity (MRC) was determined for Cd(II), Cr(III), Zn(II), and Pb(II). These values are shown in Table 2.

Table 2. The resin's Maximum Retention Capacity, MRC of the resin P(StyS-*co*-AM), 8 mol%

Metal ion	MRC[a]	MRC[b]
Cd(II)	199.8	1.77
Cr(III)	89.9	1.73
Zn(II)	215.2	3.29
Pb(II)	146.5	0.71

[a]mg of metal ion/g dry resin (5 for Cd(II), Cr(III), Zn(II), and Pb(II)).

[b]mmol of metal ion/g dry resin, at optimum pH (5 for Cd(II), Cr(III), Zn(II), and Pb(II)).

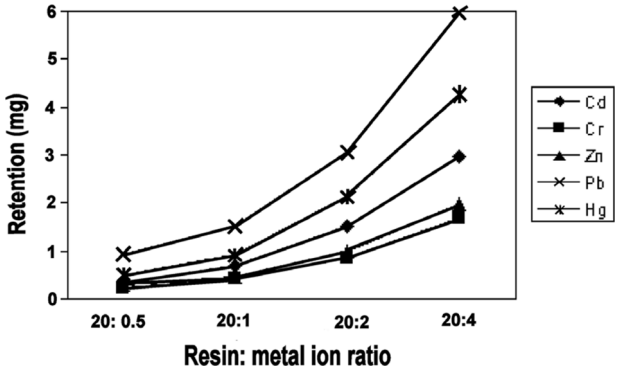


Figure 3. Effect of the initial metal ion concentration on metal ion retention capacity of P(StyS-*co*-AM), at optimum pH (5 for Cd(II), Cr(III), Zn(II), Pb(II), and 2 for Hg(II)), particle size 180–250 μm.

Effect of Ion Concentration

Maintaining the retention capacity, even when the concentration of the different species in the wastewater changes, it is essential for practical use. The effect on the metal uptake under metal ion concentration was studied for each metal ion. This concentration was varied between resins: metal ion ratio 20:0.5 and 20:4. For all resins, the metal ion retention increased with the increase in the ratio resin: metal ion. This result indicates that the resin still has active sites to retain the metal ions (see Fig. 3).

Selectivity Behavior

To determine metal ion retention under competitive conditions, several tests were performed. At first, 200 mg of dry resin were contacted at pH 5 during 1 hour with 20 mL of an aqueous solution containing the same amount of mole for each one, that of each metal ion Cd(II), Cr(III), Zn(II), and Pb(II). The resin showed almost the same retention (around the 20%) for Cd(II), Cr(III), Zn(II), and Pb(II). The resin did not show a selective retention behavior for any specific metal ion, which indicates that the retention does not depend on the size of the metal ions, because the metal ions have a different ionic radius (Zn(II) 0.074 nm, Cd(II) 0.097 nm, Cr(III) 0.063 nm, and Pb(II) 0.120 nm (20). According to the Pearson's concept, the group SO_3^{2-} is a borderline base; the metal cations are in different groups; Hg(II), and Cd(II), are soft acids; Zn(II), and Pb(II) are borderline acids; and Cr(III) is considered a hard

Table 3. Selectivity behavior of the resin P(StyS-*co*-AA), 8 mol% at pH 5 from the quaternary metal ion mixture Cd(II)-Cr(III)-Zn(II)-Pb(II)

Metal ion	Retention[a] (%)	Retention[b] (%)
Cd(II)	96.7	19.3
Pb(II)	98.6	26.6
Zn(II)	96.8	26.9
Cr(III)	99.1	27.1

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

acid (21). Thus, it can be concluded that the predominant interaction is an electrostatic interaction between the active group and the metal ions (see Table 3).

Retention by Column Procedure

It is important that the resin maintains its retention behavior in a continuously operated process in comparison with a discontinuously operated process. A column (15 cm in length and 1 cm in diameter) was prepared. The resin was packed at the pH of the retention experiment. The retention behavior for different metal ions was maintained with respect to the batch equilibrium procedure. At the optimum pH, all the retentions in the column were over 96% (see Fig. 4), demonstrating that the equilibrium between the active sites and the metal ion was achieved in

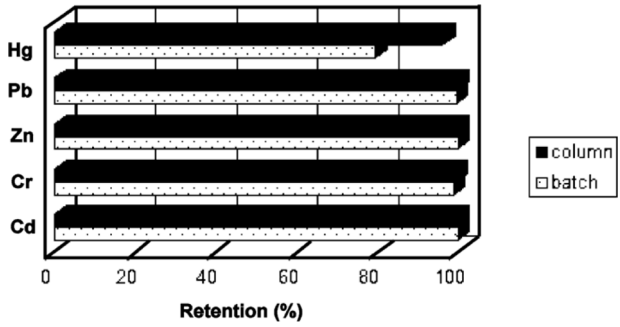


Figure 4. Metal ion retention in column and batch procedures to optimum pH (5 for Cd(II), Cr(III), Zn(II), Pb(II), and 2 for Hg(II)).

a short time period because there is less contact time in the column method in comparison with the batch method.

Resin Reusability

To use this resin in a continuously operated process, the resin's metal ion capacity should be maintained after the treatment with an eluent reagent and the metal ion adsorbent by the resin should be easily released under appropriate conditions. The batch desorption studies were carried out by first separately loading the resin samples. The four stripping reagents studied (HCl, $HClO_4$, HNO_3, and H_2SO_4), were selected because they should be able to displace the metal ions. Therefore, for resin reusability, the sorption-desorption cycle was repeated three times with the same sorbent in batch and column processes. The results presented in Fig. 5 correspond to loaded resin with Pb(II) and the desorption with 4 M $HClO_4$. The resin was able to maintain the retention capacity in the three cycles, and a high percentage of elution was produced in the three cycles in the column process. In the batch experiment, the resin gradually loses its retention capacity, and elution was produced in a lower percentage. The lower performance by the batch method respect to the column procedure can be attributed to the lower access of the eluent to disrupt the polymer-metal ion interaction. Considering this resin's behavior in a continuously operated process, it can be used to remove undesirable metal ions.

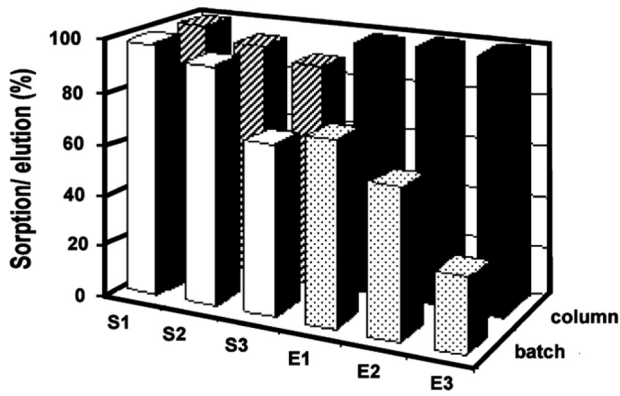


Figure 5. Reusability of the resin. Loaded resin with Pb(II), eluent 4 M $HClO_4$. Sorption (S)-Elution (E) cycles.

CONCLUSIONS

Using radical solution polymerization, the cross-linked P(StyS-*co*-AM) under different cross-linking degrees was synthesized. The resins showed a high retention for Cd(II), Cr(III), Zn(II), and Pb(II) at pH 5 and Hg(II) at pH 2. The most common equilibrium procedures, batch and column, were tested, finding no important differences in the results at the optimum pH. Consecutive sorption and elution showed the feasibility of using and reusing this resin to remove Cd(II).

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