

Separation of Metal Ions by Water-Insoluble Polymers Containing Sulfonic/Sulfonate Groups

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ABSTRACT: A water-insoluble polymer, poly(sodium 4-styrene sulfonate), was synthesized by radical polymerization at different amounts (2, 4, 6, and 8 mol %) of crosslinking reagent (CR). At the lowest CR level (2 mol %), only a water-soluble polymer is obtained, and consequently it could not be studied as resin. The polymerization yield ranged from 82.6 to 91.6%. The resin is characterized by FTIR spectroscopy, thermal analysis, and scanning electron microscopy. The metal ion affinity is studied for the cations: Hg(II), Cd(II), Zn(II), Pb(II), Cr(III), and Al(III) with a batch

equilibrium procedure under different experimental conditions. The metal ion affinity increased as the pH increased. At pH 5, the resin showed an affinity greater than 97% for all metal ions. Hg(II) showed the highest retention value at pH 2. The maximum retention capacity is determined at optimum pH for Hg(II), Cd(II), Pb(II), and Zn(II). © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 4328–4333, 2006

Key words: radical polymerization; resins; adsorption

INTRODUCTION

The synthesis of polymers containing reactive functional groups has been an active field of research in polymer science because it provides an approach for a subsequent modification of the polymer for the required application.

Increased economic development has been accompanied by environmental contamination, becoming one of the most important problems worldwide. Toxic metal ions can now be found in many ecosystems, such as river or lake water, as well as biological and inorganic–organic samples. Because of the toxicity and tendency of metal ions to bioaccumulate, new technologies incorporating highly specific metal ion-recovery processes need to be developed to reduce metal ion concentration to acceptable levels in wastewaters. The capacity of several methods, such as ion exchange, adsorption, reverse osmosis, and precipitation, to remove metal ions from polluted liquids has been examined.^{1,2}

Although many of these methods have been developed and successfully used, their application can cause problems. Some problems can be connected with heterogeneous reaction and interphase transfer. Thus, precipitation methods have been widely applied with hydroxides or sulfides. However, metal ions cannot be perfectly removed by these methods, and there

are additional costs for the subsequent treatment of the resulting precipitation.

Chelating ion-exchange resins with specific chelating groups attached to polymers have found extensive use in the separation and preconcentration of metal ions.^{3–27}

The desirable properties of chelating exchangers are four-fold: (1) high capacity for the metal(s) of interest; (2) high selectivity; (3) fast kinetics-rapid equilibration with metal-containing solutions; and (4) high mechanical strength and toughness of the exchanger particles. Unfortunately, the last two properties are competitive.

Metal ions are present in water as hydrated ions or as complex species associated with various anions. In the electroplating industry, chelating agents in wastewater that frequently coexist with metal ions exhibit little or no tendency to be transferred to a chelating polymer (ion-exchange resins).

These resins are able to coordinate different metal ions through functional groups containing N, O, S, and P as donor atoms. As a result, several researchers have either incorporated low-molecular weight ligands into synthetic and natural polymeric materials or synthesized copolymers, basically by radical polymerization, containing these functional ligand groups.

The selective removal of metal ions from industrial wastewater streams and from contaminated water is a topic of great interest. Polymers 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 achieved by use of multidentate ligands, and the application of functional

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polymers offers the chance of immobilizing these ligands on a support.

The aim of this article is to report the synthesis, characterization, and metal ion affinity properties of poly(sodium-4 styrene sulfonate) by batch equilibrium procedure.

EXPERIMENTAL

Reagents

4-Sodium styrene sulfonate 96% (Aldrich, Milwaukee), *N,N'*-methylene-bisacrylamide (MBA) 99% (Aldrich), ammonium persulfate (AP) (Aldrich), are used without further purification.

The metal salts used were: cadmium(II) chloride dehydrated, chromium(III) nitrate nonhydrated (Merck, Stuttgart, Germany), mercury(II) nitrate monohydrated (Merck), lead(II) nitrate, aluminum (III) nitrate nonhydrated (Merck), and zinc(II) nitrate hexahydrated (Merck). The analytical grade, nitric acid, perchloric acid, and sodium hydroxide were purchased from Merck.

Resin synthesis

The synthesis of the resin poly(sodium 4-styrene sulfonate) P(StyS) is performed in a polymerization flask as follows: 0.0243 mol (5.0 g) of StyS, 4.86×10^{-4} mol (0.1108 g) of AP (2 mol %) and a equivalent amount of 2–8 mol % of MBA dissolved in 20 mL of twice-distilled water are placed in a polymerization flask. The reaction is kept under nitrogen at 70°C for 4 h. The resin was filtered and washed with abundant water, and dried up to constant weight. Yield: 82.6–91.6%. Afterwards, the resin is screened by molecular sieves and the particle size fraction in the range of 250–180 μm is chosen to study the metal ion retention properties.

Resin-metal ion uptake

The batch metal uptake experiments are performed using standard metal salt CdCl_2 , $\text{Hg}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$, $\text{Al}(\text{NO}_3)_3$, and $\text{Cr}(\text{NO}_3)_3$ at pH range 1–5, depending on the metal ion. All experiments are performed in flasks mounted on a shaker at 20°C. The retention ability for Cd(II), Zn(II), Hg(II), Pb(II), Al(III), and Cr(III) under noncompetitive and competitive conditions is determined as a function of pH. Batches of 0.05 g resin are used, together with a mixture of 5 mL of metal ion solution. After a shaking time of 1 h, the samples are filtered, washed with water, and dried under vacuum at 50°C. Batch metal-uptake experiments under competitive conditions are performed with the following metal ion mixture: Cd–Hg–Pb–Zn at pH 2. Batches of 0.2 g resin are used

together with a mixture of 20 mL of metal solution. The resin-metal ion ratio (in mol) is 20 : 1.0. After a shaking time of 1 h, the samples are further handled as described for the noncompetitive experiments.

The batch method is used to obtain the maximum adsorption capacity for mercury, cadmium, zinc, and lead ions, performing three contacts. Subsequently, the metal ion solution is filtered, the resin washed with water, and the solution transferred into a calibrated 50-mL flask, which is filled to the volume. The metal ion is determined by atomic absorption spectrometry.

In the regeneration experiments, the batch method was used to test (1M, 2M, and 4M) HNO_3 , (1M, 2M, and 4M) HCl and (1M, 2M, and 4M) HClO_4 for their stripping potential. Batches of 0.5 g resin-loaded mercury, cadmium, zinc, and lead ions with a metal ion solution (of Cd(II), Zn(II), and Pb(II)) at pH 5 and Hg(II) at pH 2 were stirred for a 1-h period. The loaded resin is washed with twice-distilled water and the filtrates collected.

Measurements

A Julabo air-batch shaker is used to shake the solution at a desired temperature. The pH was measured with a digital H. Jurgens and Co. pH meter. A Unicam Solaar 5M series atomic absorption spectrometer (UK) was used for the determination of single and mixed metal ions. The FTIR spectra of the sample are recorded with a Magna Nicolet 550 spectrophotometer. The thermograms of the loaded and unloaded resins are recorded on a STA-625 thermoanalyzer (Polymer Laboratories). Approximately 5 mg of the dry sample are heated at 20°C/min heating rate under dynamic nitrogen atmosphere.

RESULTS AND DISCUSSION

Resin synthesis

A complete water-insoluble polymer is obtained by radical polymerization of 4-sodium styrene sulfonate at different crosslinking mol % (2, 4, 6, and 8 mol %). The concentration of crosslinking agent is selected according to our studies and also by the literary sources. This range is the most used in this field. The polymerization reaction yields a soluble polymer with a 2 mol % of MBA. With the other three MBA levels, insoluble polymers are obtained. The yields for these three resins are: 82.6, 84.0, and 91.6%, respectively (see Table I). Yield is the ratio of the weight of the polymer obtained divided by the sum of the weights of the monomer and MBA. The yield according to the resin particle size distribution is summarized in Table II. The resin's general structure is shown Scheme 1.

TABLE I
Effect of the Crosslinking Reagent on the Polymerization Yield

	Resin\MBA (mol %)			
	2	4	6	8
P(StyS)	– ^a	82.6	84.0	91.6

^a The product is soluble in water.

Characterization of the resin

Since metal ion retention is usually a controlled diffusion process, it is very important to determine the resin's swelling capacity. For this resin, the water-sorption capacity is determined by gravimetry. The value calculated for the resin with an 8 mol % of crosslinking reagent is 100.1 g of water per gram of resin.

The resin is characterized by FTIR spectroscopy. The spectrum shows the most characteristic absorption bands at 1637.7 cm^{-1} (C=C), 1185.96 cm^{-1} (C—H 1–4 substitution), 1041.39 cm^{-1} (S=O) (see Fig. 1). The thermal behavior shows that the resin loses 20% weight at 400°C and 40% at 550°C . This thermal stability behavior is attributed to the presence of the aromatic ring from styrene moiety (see Fig. 2).

Uptake metal ion properties

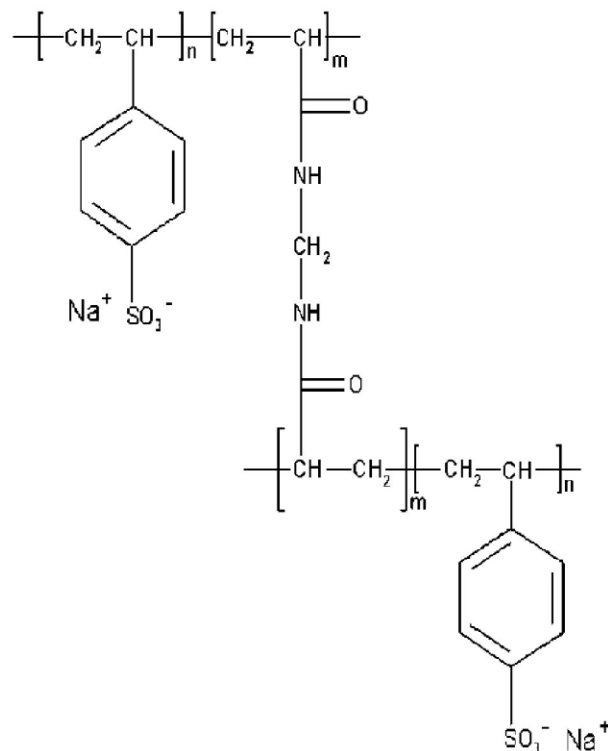
The resin's metal ion affinity is studied by batch equilibrium procedure using a resin particle size of 250–180 μm and a relationship (in mol) of resin:metal ion ratio of 20:1.0 to ensure an excess of the ligand sites with respect to metal ions.

To study the pH effect on retention, 0.05 g of dry resin are placed in contact with 5 mL of an aqueous solution of metal ion at the desired pH. The pH studied depends on the solubility of the metal ion.

By increasing the pH, the resin's metal ion affinity increases. At pH 1, only the trivalent cations, Al(III) and Cr(III), are significantly retained, 90.0 and 92.6%, respectively. The retention for all the other divalent cations is lower than 50%, except for Hg(II) (73.9%). The retention of all metal ions is above 89% at pH 3 and above 97% at pH 5. This result indicates that at low pH, where there is a low amount of sulfonate

TABLE II
Yield (%) for Different Particle Sizes

Resin	MBA (mol %)	Particle size (μm)				
		>1000	1000–500	500–250	250–180	<180
1	4	91.0	7.56	1.44	–	–
2	6	99.1	0.81	0.12	–	–
3	8	96.8	2.68	0.54	–	–



Scheme 1 General structure of the resin poly(sodium 4-styrene sulfonate).

groups, the most important ligand–metal ion interaction process is electrostatic; but at higher pH, where there is a higher content of sulfonate, the complex formation should be a more active process. Therefore, sulfonic acid/sulfonate are both important for metal ion removal, depending on the pH (see Fig. 3 and Table III).

In general, the crosslinking degree does not have an important effect on the resin's metal ion affinity, except for Pb(II) (see Fig. 3).

To increase the pH to 6, the Hg(II) concentration is decreased at 92 ppm, keeping the resin ratio (in mol) 20:1, by using 100 mg of resin and 0.46 mg of Hg(II), but the retention of resin 3 is only 32.9%.

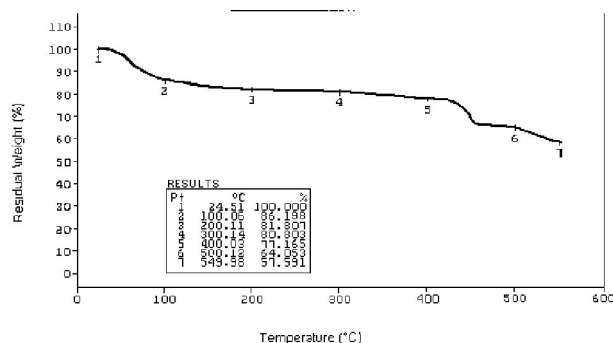


Figure 1 FTIR spectrum of the resin poly(sodium 4-styrene sulfonate).

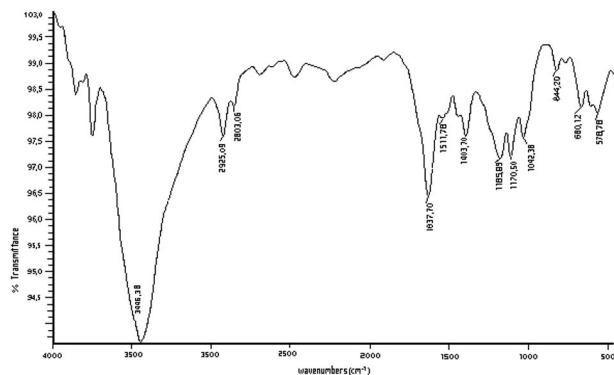


Figure 2 TGA of the resin poly(sodium 4-styrene sulfonate). Heating rate: 20°C/min, atmosphere: N₂, temperature range: 25–550°C.

TABLE III
Effect of pH on the Metal Ion Retention for P(StyS), 8% MBA

Metal ion	pH	mmol of metal ion/g dry resin	Retention (%)
Cd(II)	1	0.1229	45.7
Cd(II)	3	0.2647	98.7
Cd(II)	5	0.2720	99.3
Cr(III)	1	0.2259	92.6
Cr(III)	3	0.2287	98.7
Cr(III)	5	0.2251	98.3
Zn(II)	1	0.1256	47.2
Zn(II)	3	0.2601	98.5
Zn(II)	5	0.2605	99.2
Al(III)	1	0.2355	90.0
Al(III)	3	0.2203	89.6
Al(III)	5	0.2293	92.8
Pb(II)	1	0.1178	50.7
Pb(II)	3	0.2437	98.9
Pb(II)	5	0.2432	99.6
Hg(II)	1	0.1570	73.9
Hg(II)	2	0.2409	95.3

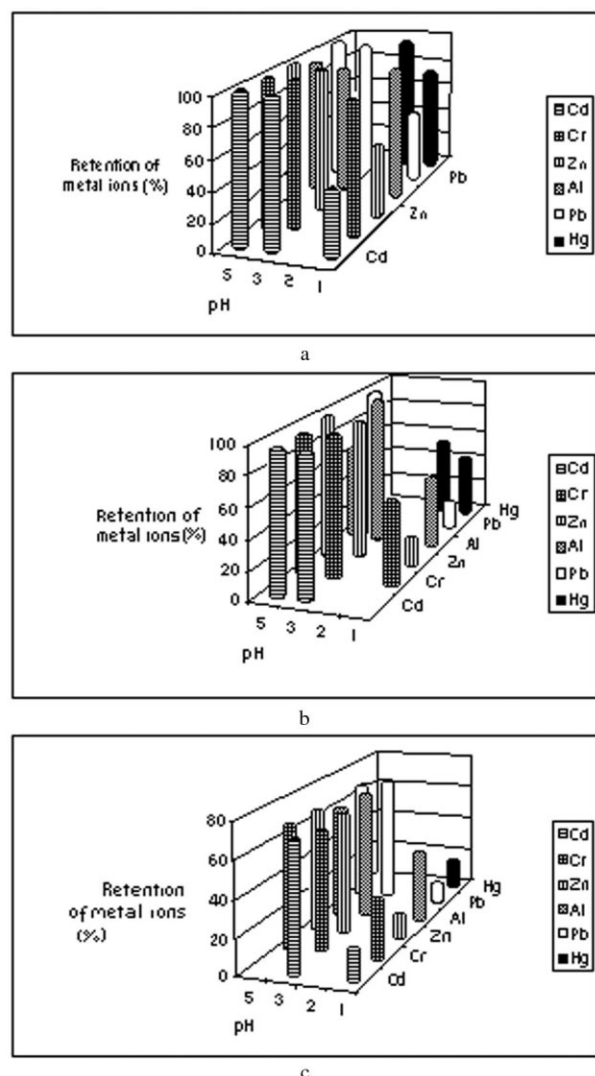


Figure 3 Effect of the crosslinking reagent amount on metal ion retention: (a) 8 mol % of MBA, (b) 6 mol % of MBA, and (c) 4 mol % of MBA.

Based on these results, all the following studies are done with resin 3 (with 8 mol % of MBA).

To determine the metal ion retention under competitive conditions, 200 mg of resin were placed in contact at pH 2 during 1 h with 20 mL of an aqueous solution containing the same concentration of each metal ion. The resin presents high retention (>90%) for a Pb(II), Cd(II), and Zn(II), but very low retention for Hg(II) and a high selectivity for Pb(II) (50%) in comparison with the other metal ions (Cd(II) 23.0%, Zn(II) 19.2%, and Hg(II) 7.8%) (see Table IV).

With these results, the maximum retention capacity (MRC) of the resin is determined at optimum pH for the cations Hg(II) at pH 2, and Cd(II), Zn(II), and Pb(II) at pH 5. Mercury ions are studied at this pH to avoid precipitation. The retention is determined after three contacts of the resin with each metal ion, using a fresh metal ion solution each time. The results are summarized in Table V.

To be useful in the ion-recycling process, the metal ion adsorbed by the resin should be easily released

TABLE IV
Selectivity Behavior for the Resin P(StyS) at pH 2 from the Metal Ion Mixture Cd(II)-Pb(II)-Zn(II)-Hg(II)^a

Metal ion	Retention ^b (%)	Retention ^c (%)
Cd	93.7	23.0
Pb	95.2	50.0
Zn	93.3	19.2
Hg	17.8	7.8

^a Total amount of metal ion is 5.222 mg.

^b Corresponds to metal ion retention from each metal ion concentration.

^c Corresponds to the retention of the metal ion from all metal ion concentrations.

TABLE V
Maximum Retention Capacity (MRC) of Resin

Metal ion	pH	MRC ^a	MRC ^b
Cd(II)	5	129.3	1.15
Hg(II)	2	141.2	0.70
Zn(II)	5	121.7	1.86
Pb(II)	5	134.0	0.65

^a mg of metal ion/g dry resin.

^b meq of metal ion/g dry resin.

under appropriate conditions. The batch desorption studies are carried out by separately loading resin samples with Hg(II), Cd(II), Pb(II), and Zn(II) followed by the treatment with an excess of the extracting reagent. Three extractives have been chosen: HCl, HClO₄, and HNO₃. They are able to displace anionic metal complexes being ionically sorbed onto cationic functional groups. The desorption results are summarized in Table VI. In the elution data, the reagents behave differently. The best eluents for Hg(II), Cd(II), and Pb(II) are 3M HClO₄ (28.1%), 1M HCl (79.8%), and 1M HClO₄ (78.2%) respectively. Based on these results, the adsorption-desorption cycles for Cd(II) ions at pH 5 are performed. After three cycles, the metal ion retention ability decreased 20% approximately. This decrease can be explained by the resin's loss of active sites due to eluent treatment (see Fig. 4).

The resin's surface is flat without holes, while the loaded resins present a morphology with some holes and folds, which means that the site of ligand-metal ion interaction is occurring basically at the surface (see Fig. 5).

CONCLUSIONS

The crosslinked P(StyS) was synthesized at different crosslinking degrees by radical solution polymeriza-

TABLE VI
Recovery of the Resin P(StyS) by Different Eluent Media

Eluent	Loaded metal ion	Elution (%)
1M HClO ₄	Hg	17.8
2M HClO ₄	Hg	27.8
3M HClO ₄	Hg	28.1
1M HCl	Hg	17.7
2M HCl	Hg	22.0
4M HCl	Hg	26.1
1M HNO ₃	Hg	19.4
1M HClO ₄	Cd	62.9
1M HCl	Cd	79.8
2M HCl	Cd	73.3
1M HNO ₃	Cd	68.9
1M HClO ₄	Pb	78.2
1M HCl	Pb	54.8
1M HNO ₃	Pb	78.8
1M HCl	Zn	69.6
1M HClO ₄	Zn	70.0

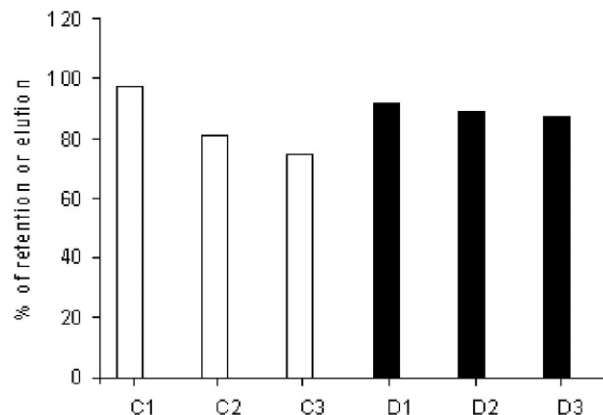


Figure 4 Charge (C) and discharge (D) cycles for Cd(II) at pH 5. Eluent 1M HClO₄.

tion. An insoluble polymer is only obtained from a 4 mol % of crosslinking reagent with a yield greater than 80%. No important effect of the crosslinking degree on the metal ion retention was observed. The resin showed a high retention for Cd(II), Zn(II), and Pb(II) as well as a selectivity for Pb(II) from a quaternary

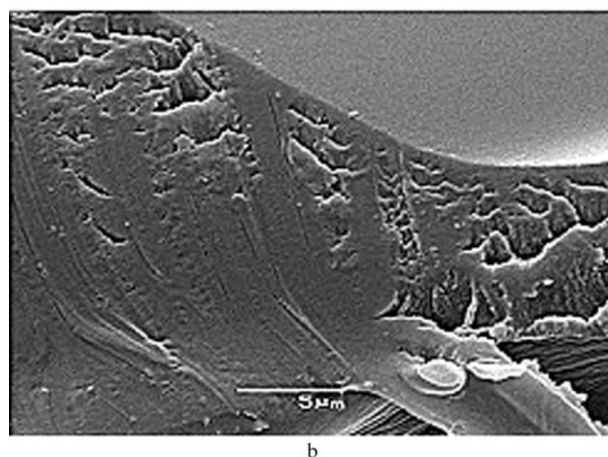
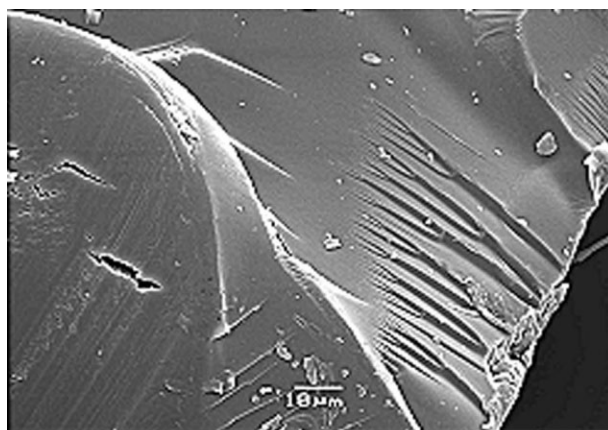


Figure 5 Scanning electron micrographs of (a) resin P(StyS) ($\times 1500$) and (b) Pb(II)-loaded P(StyS) ($\times 4500$).

metal ion mixture (Hg(II)–Cd(II)–Zn(II)–Pb(II)). An elution over 75% for Cd(II) and Pb(II) was obtained by using 1M HCl and 1M HClO₄, respectively. Consecutive adsorption and desorption indicated the feasibility of this resin for Cd(II) ion adsorption.

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