Removal of Environmentally Impacting Metal Ions Using Functional Resin Poly(4-Styrene Sulfonate-*co*-4-Vinylpyridine): Synthesis and Metal Ion Retention Properties

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ABSTRACT: A water-insoluble polymer, poly(sodium 4-styrene sulfonate-*co*-4-vinylpyridine), was synthesized by radical polymerization at different amounts (2, 4, 6, and 8 mol %) of crosslinking reagent (CR). The polymerization yield ranged from 83.5% to 100.0%. The resin is characterized by FT IR spectroscopy, thermal analysis, and scanning electron microscopy. The water absorption capacity, WAC (110 g/g dry resin), was obtained for the resin with a 2 mol % of CR. The metal ion affinity is studied by *Batch* equilibrium procedure under different experimental condi-tions for the cations: Hg(II), Cd(II), Zn(II), Pb(II), Cr(III), and Al(III). The metal ion affinity increased as the pH increased. At pH 5, the resin presented an affinity above 90% for all metal ions. Hg(II) presented the highest reten-tion value at pH 2. The maximum metal ion retention capacity is determined at optimum pH for Hg(II), Cd(II), Pb(II), and Zn(II). © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 1769–1774, 2007

Key words: resin; radical polymerization; metal ions

INTRODUCTION

With increasing industrial development, environmental contamination has become one of the most important problems our world is facing. Toxic metal ions can be found in many natural places, including river and lake water, as well as in biological and inorganic-organic samples. Because of their toxicity and tendency to bioaccumulate, metal ion concentration in wastewaters needs to be reduced to acceptable levels. In response, there is increased interest in developing new technologies for more highly specific metal ion-recovery processes. The ability of several methods, such as ion exchange, adsorption, reverse osmosis, and precipitation, to remove metal ions from polluted liquids has been studied.[1–2] Although many of these methods have been developed and successfully used, their application can still cause problems, some of which are connected with heterogeneous reaction and interphase transfer. As a result, precipitation methods have been widely applied with hydroxides or sulfides. However, metal ions cannot be perfectly removed with these methods, and there are additional costs for the subsequent treatment of the resulting precipitation.

A polymeric ligand is usually used to selectively bind a specific metal ion in a mixture to isolate important metal ions from wastewater and aqueous media. A polymeric ligand is generally used in an insoluble resin form to separate a specific metal ion from a liquid containing a mixture of metal ions. One type that has been extensively used in the separation and preconcentration of metal ions is chelating ion-exchange resin with specific chelating groups attached to polymers.[3–19]

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 frequently coexist with metal ions, exhibiting little or no tendency to be transferred to a chelating polymer (ion-exchange resins). Metal ions are not only valuable intermediates in metal extraction, but are also important raw materials for technical applications. Accordingly, the metal ion complexation is an important technique for recovering metals from various sources (hydrometallurgy) and for their removal from public streams and industrial waters.

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

The aim of this paper is to report the metal ion removal properties using the *Batch* equilibrium proce-

dure of the resin poly(sodium-4 styrene sulfonate-*co*-4-vinylpyridine), which contains in its structure a pyridine group with a well-known capacity to coordinate with metal ions and sulfonate groups that present a different metal-ion interaction mechanism as well as a second functional group would increase the swelling capacity.

EXPERIMENTAL

Reagents

4-vinyl pyridine (Aldrich, VPy) was purified by distillation. *N,N′*-methylene-bisacrylamide (MBA 99%, Aldrich), 4-sodium styrene sulfonate 96% (Aldrich, StyS), ammonium persulphate (AP, Aldrich), are used without further purification.

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

Resin synthesis

The synthesis of the resin poly(4-sodium styrene sulfonate-*co*-4-vinyl pyridine) P(StyS-*co*-VPy) is carried out in a polymerization flask as follows: 0.014563 mol (3 g) of StyS, 0.014563 mol of VPy (1.5312 g), 5.8 $\times 10^{-4}$ mol (132.8 mg) of AP (2 mol %), and the equivalent amount to 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: 83.5–100.0%. Subsequently, the resin is screened, and the particle size fraction in the range of 250–180 μm is chosen for the analytical runs.

Resin-metal ion uptake

The batch metal uptake experiments are performed using standard metal salts $CdCl_2$, $Hg(NO_3)_2$, $Zn(NO_3)_2$, $Pb(NO_3)_2$, $Al(NO_3)_3$, and $Cr(NO_3)_3$ in 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 di- and trivalent cations, Cd(II), Zn(II), Hg(II), Pb(II), Al(III), and Cr(III), under noncompetitive and competitive conditions is determined as a function of the 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 and washed with twice distilled water. Batch metal-uptake experiments

under competitive conditions are performed with the following divalent metal ion mixture: Cd-Hg-Pb-Zn at pH 2 and to Cd-Pb-Zn at pH 5. Batches of 0.15 g resin are used together with a mixture of 15 mL of metal ion 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(II), cadmium(II), zinc(II), and lead(II) ions. Three contacts are performed. Subsequently, the metal ion solution is filtered, the resin washed with twice-distilled water, and the solution transferred into a calibrated 50-mL flask and completed to the volume. The metal ion is determined by atomic absorption spectrometry.

In the regeneration experiments, (1*M*, 2*M*, and 4*M*) HNO_3, (1*M*, 2*M*, and 4*M*) HCl (1*M*, 2*M*, and 4*M*), $HClO_4$ and (1*M*, 2*M*, and 4*M*) H_2SO_4 were tested for their stripping potential using the *Batch* method. Batches of 0.05 g resin-loaded mercury, cadmium, zinc, and lead ions with 5 mL of eluent 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 for shaking the solution at a desired temperature. The pH was measured with a digital H. Jürgens & Co. pH meter. A Unicam Solaar 5*M* 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.

RESULTS AND DISCUSSION

Resin synthesis

A complete water-insoluble polymer is obtained by radical copolymerization of an equimol ratio of 4-sodium styrene sulfonate with 4-vinyl pyridine at different crosslinking mol % (2, 4, 6, and 8 mol %). The polymerization yields for these resins are:

TABLE I
Water Absorption Capacity, WAC, of the Resin P(StyS-*co*-VPy) with Different Amounts of Crosslinking Reagent at the Fee

Crosslinking (%)	WAC (g H_2O/g dry resin)
2	119.1
4	30.7
6	10.3
8	5.2

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TABLE II
Effect of the pH and Crosslinking Reagent Amount (MBA) on Metal Ion Retention Capacity of P(StyS-*co*-VPy)s

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Crosslinking		8% MBA		6% MBA		4% MBA		2% MBA	
Metal ion	pH	mmol metal ion/g resin	Retention (%)	mmol metal ion/g resin	Retention (%)	mmol metal ion/g resin	Retention (%)	mmol metal ion/g resin	Retention (%)
Cd(II)	1	0.0581	32.4	0.0038	23.7	0.0231	14.1	0.0672	46.8
Cd(II)	3	0.1588	88.6	0.1502	98.8	0.1450	97.2	0.1382	99.0
Cd(II)	5	0.1782	100	0.1489	100	0.1424	99.8	0.1384	99.9
Cr(III)	1	0.0288	17.4	0.0591	29.2	0.0470	23.8	0.0443	22.6
Cr(III)	3	0.1515	93.4	0.2007	100	0.1979	100	0.2018	100
Cr(III)	5	0.1613	100	0.2025	100	0.2011	95.0	0.1965	97.0
Zn(II)	1	0.0196	10.7	0.0172	10.2	0.0160	9.1	0.0691	31.5
Zn(II)	3	0.0172	95.2	0.1633	99.0	0.1660	98.3	0.1811	99.0
Zn(II)	5	0.1775	100	0.1592	100	0.1643	100	0.1841	99.8
Al(III)	1	0.0120	7.6	0.0155	10.5	0.0421	27.9	0.0119	7.9
Al(III)	3	0.1481	100	0.1509	100	0.1497	100	0.1515	100
Al(III)	5	0.1607	100	0.1474	100	0.1492	100	0.1489	100
Pb(II)	1	0.0167	10.0	0.0832	5.1	0.0143	18.7	0.0286	17.6
Pb(II)	3	0.1493	94.3	0.1581	98.7	0.1612	100	0.1524	98.2
Pb(II)	5	0.1532	100	0.1574	100	0.1548	100	0.1526	100
Hg(II)	1	0.1257	83.5	0.1089	75.8	0.1066	73.3	0.0928	62.8
Hg(II)	2	0.1473	100	0.1455	100	0.1515	100	0.1509	100

83.5%, 96.3%, 98.2%, and 100%, respectively. The yield according to the resin particle size distribution is over 98% for the fraction >1000 μm. General structure of the resin is shown below.

Characterization of the resins

The resins contain sulfonic acid, sulfonate/pyridine groups, and the presence of these groups is corroborated by FT-IR spectroscopy. The FT-IR spectra of the four resins are basically the same. Among the most characteristic absorption bands are those at 1637.7 cm^{-1} (C=C), 1185.96 cm^{-1} (C—H 1–4 substitution), and 1041.39 cm^{-1} (S=O).

Since metal ion retention is usually a controlled diffusion process, it is very important to determine the resin's swelling capacity. For the resin studied, the water-adsorption capacity (WAC) is determined

by gravimetry. The highest value, 119.0 g of water/g of resin, is obtained for the resin with a lower CR (2 mol %) (Table I).

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 resin-metal ion relationship (in mol) of 20:1.0. This ratio ensures an excess of ligand sites with respect to the metal ions.

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

In general, as the crosslinking content increases, the resin's affinity for the metal ions decreases, particularly at lower pH (Table II). Only Hg(II), was highly adsorbed at all crosslinking degrees investigated, and was adsorbed 100% at pH 2. This result means that the ligand-metal ion interaction occurs basically at the

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TABLE III
The Resin's Maximum Retention Capacity, MRC, of the Resin P(Sty-*co*-VPy), 8 mol % for Four Divalent Cations in (a) mg of metal ion/g dry resin and (b) meq of metal ion /g dry resin

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Metal ion	pH	MRC[a]	MRC[b]
Cd(II)	5	205	1.80
Hg(II)	2	114	0.57
Zn(II)	5	72	1.10
Pb(II)	5	147	0.71

[a] Corresponds to MRC in mg of metal ion/g dry resin after three contacts.
[b] Corresponds to MRC in mmol of metal ion/g dry resin after three contacts.

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TABLE IV
Effect of the Particle Size of the Resin P(Sty-*co*-VPy), 8 mol %, on Metal Ion Retention Ability at Optimun pH

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Metal ion	pH	Size (μm)				
		<180	180–250	250–500	500–1000	>1000
Cd(II)	5	99.8	99.8	99.8	99.8	99.8
Cr(III)	5	97.5	98.2	98.2	98.2	98.2
Zn(II)	5	99.8	99.8	99.8	99.8	99.7
Al(III)	5	85.1	85.1	85.1	85.1	85.1
Pb(II)	5	99.5	99.5	99.5	99.5	99.5
Hg(II)	2	87.8	87.8	87.8	87.8	87.8

TABLE V
Effect of Contact Time on Metal Ion Retention
Capability (%) at pH 5 for Cd(II), Zn(II), Pb(II), Cr(III),
and Al(III) at pH 5 and Hg(II) at pH 2

Metal ion	pH	Time (min)			
		15	30	60	120
Cd(II)	5	99.9	99.9	99.9	99.9
Cr(III)	5	98.2	98.2	98.2	98.2
Zn(II)	5	99.8	99.8	99.8	99.8
Al(III)	5	85.1	85.1	85.1	85.1
Pb(II)	5	99.5	99.5	99.5	99.5
Hg(II)	2	88.5	90.0	90.0	90.0

Resin P(Sty-*co*-VPy) 8 mol %.

polymer surface because the interior ligand sites are less favorable for metal ion interaction. By increasing pH, the resin's affinity for metal ions increases. At lower pH, the sulfonic acid and pyridine groups are protonated and the metal cations must compete with the protons. At this pH, proton exchange is favored. At pH 1, the metal ion retention is lower than 40%, except for Hg(II) which ranged from 62.8% (0.0928 mmol Hg(II)/g resin) for the resin with a 2 mol % of CR up to 83.5% (0.12,576 mmol Hg(II)/g resin) for the resin with a 8 mol % of CR. The trivalent cations with higher charge density, Al(III) and Cr(III), are less retained: Al(III) 7.9% (0.0119 mmol Al(III)/g resin), and Cr(III) 22.6% (0.0443 mmol Cr(III)/g resin) for the resin with a 2 mol % of CR. At pH 3, retention increases significantly. Thus, the resin (with 8 mol % of CR) presented a retention of 100% for Al(III), and over 90% for Cr(III) (93.4%, 0.15,156 mmol Cr(III)/ g resin), Zn(II) (95.2%, 0.017241 mmol Zn(II)/g resin), and Pb(II) 94.3%, 014938 mmol Pb(II)/g resin). A similar result is observed for Hg(II) at pH 2 (100%, 014738 mmol (Hg(II)/g resin).

At pH 5, several metal ions (Cd(II), Cr(III), Al(III), and Pb(II)) are 100% retained. This result means that at low pH, where there is a low amount of sulfonate groups, the most important ligand-metal ion interac-
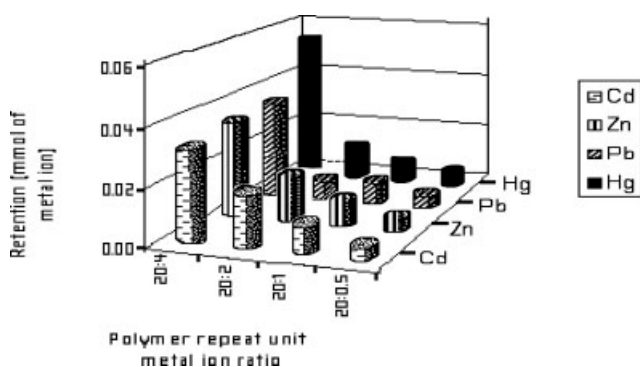
tion process is electrostatic; while at higher pH, where there is a higher content of sulfonate and pyridine groups, the complex formation should be a more active process. Therefore, the most important ligand group forms correspond to sulfonate and pyridine for metal ion removal (Table II).

The maximum retention capacity is carried out at the optimum pH (according to the results shown in Table II). The retention is determined after three contacts of the resin with each metal ion. A fresh metal ion solution was used each time. The amount of adsorbed metal ion corresponds to the amount after three contacts. The results are summarized in Table III. The highest value is obtained for Cd(II), 205 mg/g resin (1.8 mmol/g resin).

Based on these results, there was great interest for a deeper study of one resin (with 8 mol %) with respect to Cd(II), Cr(III), Zn(II), Al(III), Pb(II), and Hg(II). One of them, mercury, was chosen due to the high toxicity of all mercury compounds, which makes the extraction of mercuric ions from aqueous wastes and drinking water especially important.

The particle size of the resin is not very important in the resin's sorption properties for Cd(II), Cr(III), Zn(II), Al(III), Pb(II), and Hg(II). For Cd(II), Zn(II), Al(III), Pb(II), and Hg(II) the retention is the same
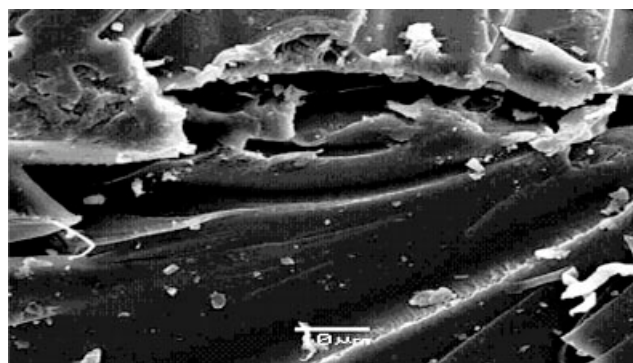
(a)
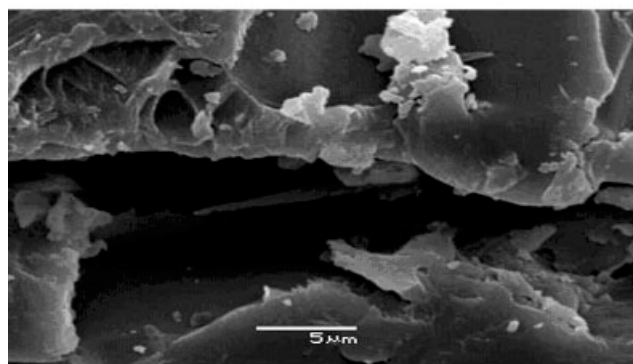
(b)

Figure 2 Scanning electron micrographs of (a) P(StyS-*co*-VPy) ×1300 and (b) P(StyS-*co*-VPy) loaded with Cd(II) ×4000.

Figure 1 Polymer ligand concentration effect on metal ion retention properties for Hg(II) at pH 2 and for Cd(II), Zn(II), and Pb(II) at pH 5.

for all sizes. For Hg(II) from > 1000 μm to <180 μm the retention is 87.8%. Retention for Cr(III) with <180 μm is 97.5%, while the retention is 98.2% for the larger particle (Table IV).

The metal ion-ligand site equilibrium is quickly achieved, within 15 min for all metal ions at the optimum pH for each metal ion. The lowest value (85.1%) corresponds to Al(III). The determination was not a continuous procedure, therefore it is not possible to determine what is occurring at the lowest time. This rapidity is very important considering that the process is occurring in heterogeneous medium (Table V).

The concentration in the metal ion solution was studied to determine its effect on retention. Increasing the concentration also increased the amount retained of Hg(II), Cd(II), Zn(II), and Pb(II) by the resin. This effect is more remarkable for Hg(II) (Fig. 1).

Figure 2 shows the scanning electron micrograph of a) P(StyS-*co*-VPy) 1300×. and b) P(StyS-*co*-VPy) loaded with Cd(II). There is not an important change on the morphology of the resin by the sorption of Cd(II).

Respect to the polymer-metal ion interaction mechanism, there are two different functional groups at the resin: pyridine which could form complexes and
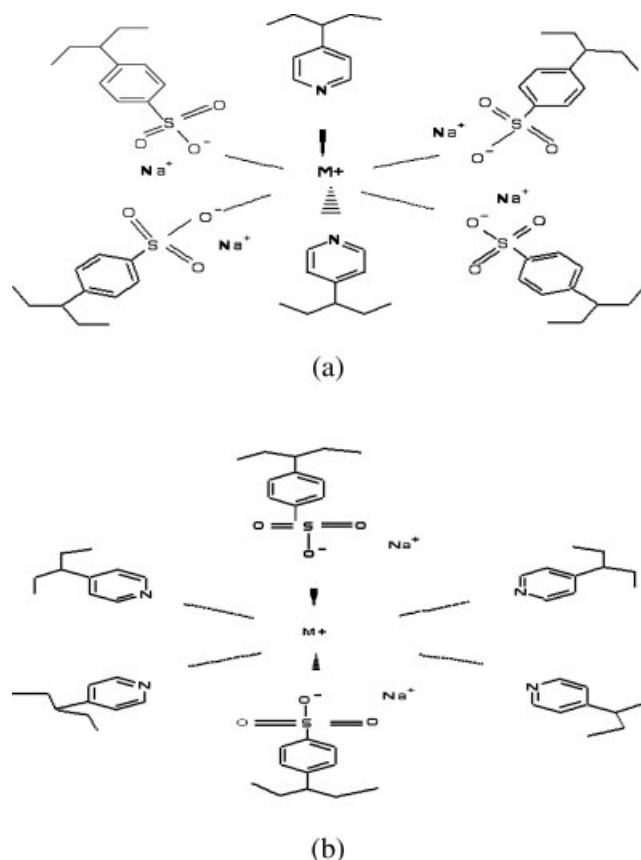
TABLE VI
Selectivity Behavior of the Resin P(StyS-*co*-VPy) 8 mol % at pH 2 from the Quaternary Metal-Ion Mixture Cd(II)-Pb(II)-Zn(II)-Hg(II)

Metal ion	Retention[a] (%)	Retention[b] (%)
Cd(II)	93.7	23.0
Pb(II)	95.2	50.0
Zn(II)	93.3	19.2
Hg(II)	17.8	7.8

Total amount of metal ion retained: 10.38 mg.
[a] Corresponds to metal ion retention considering each metal ion concentration.
[b] Corresponds to metal ion retention considering all metal ion concentrations.

the sulfonic acid which could interact with the metal ions through electrostatic interactions (Fig. 3).

To determine metal ion retention under competitive conditions, several tests were performed. First, 200 mg of the resin were contacted at pH 2 during 1 h with 20 mL of an aqueous solution containing the same concentration of each metal ion. The resin shows a high retention (>90%) for a Pb(II), Cd(II), and Zn(II), but it is very low (17.8%) for Hg(II) (Table VI). Secondly, 150 mg of the resin were contacted at pH 5 during 1 h with 15 mL of an aqueous solution containing the same concentration of each metal ion. The metal ions Pb(II), Cd(II), and Zn(II) were retained over the 99% (Table VII). However, the retention is below 40% when the total metal ion concentration is considered.

To be useful in the ion-recycling process, the metal ion adsorbed by the resin should be easily released under appropriate conditions. The batch desorption studies are carried out by first separately loading resin samples with Hg(II), Cd(II), Zn(II), and Pb(II), and then following with the excess treatment of the extracting reagent. Four stripping reagents should be HCl, HClO_4, HClO_4, and H_2SO_4 because they are able to displace the metal ions, although this displacement is small. The best eluent for Pb(II) is 4M HClO_4 (57.3%) and for Zn(II) is 1M HNO_3 (55.8%). The metal ion desorption results are summarized in Table VIII.

(a)

(b)

Figure 3 Suggested polymer-metal ion interaction mechanisms involving the two functional groups.

TABLE VII
Selectivity Behavior of the Resin P(StyS-co-VPy) at pH 5 from the Ternary Metal Ion Mixture Cd(II)-Pb(II)-Zn(II)

Metal ion	Retention[a] (%)	Retention[b] (%)
Cd(II)	99.9	25.5
Pb(II)	99.8	37.6
Zn(II)	99.9	36.9

Total amount of metal ion retained: 8.217 mg.
[a] Corresponds to metal ion retention considering each metal ion concentration.
[b] Corresponds to metal ion retention considering all metal ion concentrations.

TABLE VIII
Elution of the Metal Ion from the Loaded Resin
P(StyS-*co*-VPy) Using Different Eluent Media

Metal ion	Eluent	Eluent concentration		
		1*M*	2*M*	4*M*
Hg(II)	HCl	21.1	19.0	23.5
Hg(II)	HNO$_3$	37.3	39.2	30.0
Hg(II)	HClO$_4$	30.7	40.1	40.1
Cd(II)	HCl	45.2	40.2	41.3
Cd(II)	HNO$_3$	39.9	46.3	52.0
Cd(II)	HClO$_4$	46.7	42.0	–
Cd(II)	H$_2$SO$_4$	41.8	42.9	53.7
Pb(II)	HCl	20.2	27.1	30.3
Pb(II)	HNO$_3$	48.3	41.3	50.5
Pb(II)	HClO$_4$	–	47.4	57.3
Pb(II)	H$_2$SO$_4$	0.48	0.16	0.26
Zn(II)	HCl	48.8	45.2	45.9
Zn(II)	HNO$_3$	55.8	53.6	46.4
Zn(II)	H$_2$SO$_4$	42.9	50.7	52.7

CONCLUSIONS

The crosslinked P(StyS-*co*-4VPy) was synthesized under different crosslinking degrees by solution radical polymerization. The yield is above 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), Pb(II), Al(III), and Cr(III) at pH 5, and for Hg(II) at pH 2, An elution above 55% for Zn(II) was achieved by using 1*M* HNO$_3$, and above 57% for Pb(II) using 4*M* HClO$_4$.

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