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Metal ion sorption properties of water-insoluble resins based on sodium styrene sulfonate and different comonomers

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Abstract A set of water-insoluble resins based on sodium styrene sulfonate and different comonomers were synthesized. The resins poly(mono-2-(methacryloyloxy)ethyl succinate-*co*-sodium 4-styrene sulfonate) P(MOES-*co*-SSNa), poly(2-acrylamido glycolic acid-*co*-sodium 4-styrene sulfonate) P(AGA-*co*-SSNa), poly(acrylamide-*co*-sodium 4-styrene sulfonate) P(AAm-*co*-SSNa), and poly(2-(dimethylamine)ethyl acrylate-*co*-sodium 4-styrene sulfonate) P(DMAEA-*co*-SSNa) were synthesized by solution radical polymerization. The metal ion retention properties were studied by batch procedure for Cd(II), Zn(II), Pb(II), and Hg(II). Resins performance was compared with a poly(sodium 4-styrene sulfonate) (PSSNa) resin in order to evaluate the effect of comonomer on sorption properties. The effect of pH, time, temperature, and maximum retention capacity were studied. In addition, sorption experiments were carried out under competitive ion conditions to study the selectivity of resins. The resins P(AAm-*co*-SSNa) and P(AGA-*co*-SSNa), showed the most important differences compared with PSSNa resin, the former present higher sorption and the latter presented selectivity for Hg(II) at pH 2.

Keywords Adsorption · Metal–polymer complexes · Ion-exchange

Introduction

In recent years, the industrial and economic development has produced an important impact on environment. One of these impacts is the pollution by heavy metals ions in water, like lakes, sea, groundwater, etc., resulting in many serious environmental problems, because of their toxicity and tendency to bio-accumulation. A wide range

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of metal ions are present naturally in water, but the human activities have increased the concentration of toxic metal ions, such as lead, cadmium, chromium, mercury, etc., until toxic levels to animals and humans, being necessary to reduce the concentration to acceptable levels [1, 2].

As consequence, diverse technologies have been created to remove the metal ions from water sources, for example, ion exchange [3], reverse osmosis [4], adsorption [5, 6], etc., however, ion exchange is the most widely used method to remove metal ions from aqueous solution [7, 8].

Water-insoluble polymers with ligand groups of diverse functionalities able to interact with metal ions are an attractive research area. The functional groups can interact with metal ions by simple ion exchange (ion exchange resins) or chelation process (chelating resins). Chelating resins are widely used in the preconcentration, separation, recovery, and hydrometallurgy of metals [9, 10]. These resins possess donor atoms like nitrogen, oxygen, sulfur or phosphorous which can form a complex with metal ions, giving the possibility to retain ions selectively. For a potential application, it is necessary that resins have a strong and selective binding with the target metal ion, rapid interaction between the active site and the metal ion, and recovery of the resin, among others. Moreover, minimal loss of the metal ion retention capability after many cycles of applications is needed

In order to enhance the performance of ion exchange/chelating resins a wide variety of modifications have carried out in polymeric supports. An interesting example is the bifunctional resin, which consists in a polymeric matrix with phosphonic and sulfonic acid functional groups. The phosphonic group is responsible of recognition mechanism, while the sulfonic group is responsible of accessibility of metal ions into resin [11, 12]. Several enhancements have been carried out, incorporating new functionalities by modification of resins beads, synthesizing new monomer, or combination of monomers [13–18].

In the case of poly(sodium 4-styrene sulfonate) (PSSNa or as sulfonic acid) is used as model of polyelectrolyte and its versatility has been used to synthesized materials such as crosslinked nanoparticles [19], copolymerized with styrene [20], or even grafted onto membranes by radiation [21].

The resins with sulfonic acid groups are widely used as ion exchange resins in processes for water treatment. The interaction between the metal ion and the functional group is mainly electrostatic. Therefore, is interesting to study the combination of sulfonic acid groups with other compounds bearing functional groups of different nature. Our group has reported the synthesis of water-insoluble resins of sodium 4-styrene sulfonate by copolymerization with vinyl pyridine [17], acrylic acid [22], 4-acryloylmorpholine [23], etc.

The aim of this research is to evaluate the sorption performance of water-insoluble resins, bearing sulfonate and a comonomer with weak acid–base functional groups, and compare with a control resin with only sulfonate group to study the comonomer effect on sorption properties. The sorption experiments were carried out under different experimental. The effect of pH, time, and competitive removal conditions, among others were evaluated.

Experimental

Materials

Monomer of sodium styrene sulfonate (SSNa, Merk), mono-2-(methacryloyloxy)ethyl succinate (MOES, 48% Aldrich), (2-dimethylamino)ethylacrylate (DMAEA, 98% Aldrich), 2-acrylamido glycolic acid (AGA, 98%, Aldrich) and acrylamide (AAm, 99%, Fluka) were used as received. The reagents *N*,*N*-methylene-bis-acrylamide (MBA, 99% Aldrich) and 1,4-divinylbenzene (DVB, Aldrich) were used as crosslinker reagents. The radical initiators used were ammonium peroxide disulfate (AP, Fluka) and 2,2′azoisobutyronitrile (AIBN), the last was previously crystallized.

The sorption experiments were carried out using metal nitrate salts, $Cd(NO_3)_2$, $Hg(NO_3)_2$, $Pb(NO_3)_2$, and $Zn(NO_3)_2$. The salts were purchased from Merck. In elution experiment analytical grade eluents, HNO_3, $HClO_4$, and HCl were used and purchased from Fisher.

Resins synthesis

The resins were synthesized in a polymerization flask as follows: monomer and comonomer were added in equimolar ratio; crosslinker reagent *N*,*N*-methylen-bis-acrylamide was added in a suitable nominal amount respect to the total amount of monomers and initiator (0.5–1.0 mol.%). The reagents were dissolved in 50 mL of bi-distilled water and the reactor was degassed and placed in a thermoregulated bath at 70 °C. The reactions were carried out for 4 h under nitrogen atmosphere. After gel point was reached, resins were extracted, filtered and washed with bi-distilled water and dried up to constant weight at 40 °C. The resins were screened, and the particle size fraction between 180 and 250 µm was chosen for all experiments. The resin P(MOES-*co*-SSNa) was polymerized using dimethylsulfoxide as solvent, DVB as a crosslinking reagent, and AIBN as an initiator because of MOES monomer is not water-soluble. Figure 1 shows the structure of the synthesized resins.

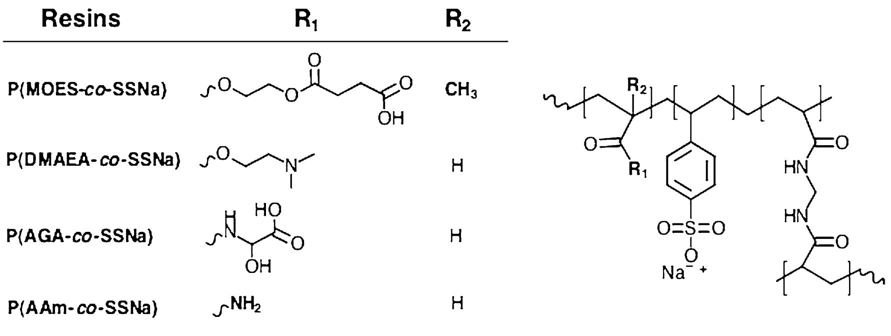

Fig. 1 Chemical structure of the synthesized resins

Metal ion sorption experiments

Sorption experiments were carried out by batch procedure to determine the metal ion binding ability of synthesized adsorbents. All experiments were performed in a test tube using a total of 0.05 g of dry resin and 5 mL of metal ion solution at determined pH. The tubes were placed in a shaker equipped with a thermoregulated bath, during 1 h at 20 °C and 140 rpm. The sorption experiments were performed and the effect of pH, contact time, maximum retention capacity, and temperature were evaluated. The resin/metal ion ratio used for all experiments was 20:1 (in mol). In addition, the retention ability for divalent cations was studied under competitive conditions using a quaternary mixture of Pb–Zn–Cd–Hg at pH 2 and at pH 5 for Pb–Zn–Cd to evaluate the selectivity properties of synthesized resins. Once contact experiments were accomplished, resins samples were filtered and washed with water at the same pH and concentrations of metal ions in the filtrate were determined by atomic absorption spectroscopy.

To determine the maximum sorption capacity the experiments were carried out contacting 25 mL of an aqueous solution of each metal ion (1.0 g/L) with 0.50 g of dry resin at 20 °C and 140 rpm. The process was repeated thrice and samples were handled as mentioned above.

Elution experiments were carried out using three acids as potential stripping reagents; HNO_3, HCl, and $HClO_4$ at concentration 1 and 4 M. Experiments were carried out by batch procedure contacting 0.05 g of resin loaded with ions, and 5 mL of acid (eluent) for 1 h at 20 °C and 140 rpm. Resins were filtered and concentration of filtrated was determined by AAS.

Swelling capacity

The ability of resin to swell in aqueous solution was determined by the water absorption capacity (WAC). An amount of resins (0.05 g) was contacted with 80 mL of distilled water for a determined time. Once equilibrium sorption was reached, the mass of the swollen resins was determined. The WAC value was determined by difference mass of swollen hydrogel and dry hydrogel, and expressed as the mass of water per gram of dry resin.

Measurements

Resin-metal ion contact experiments were carried out in a shaker Julabo equipped with a thermoregulated system to control the temperature of bath. The pH was measured and controlled with a digital pH meter Jenway 3320 pH meter. Metal ion concentrations of stock and filtrated solutions were measured using an atomic absorption spectrometer model Unicam Solaar 5 M series. The FTIR spectrums of the samples were recorded with a Magna Nicolet 550 spectrophotometer.

Results and discussion

Infrared spectroscopy

Figures 2 and 3 present the infrared spectra of P(DMAEA-*co*-SSNa) and P(AAm-*co*-SSNa), respectively. Both spectra have the most characteristic bands associates to functional groups of resins. P(DMAEA-*co*-SSNa) spectrum shows the absorption bands at 1219 cm^{-1} st(S=O), 1004 cm^{-1} st(C–N), and at 1642 cm^{-1} appears an overlap band, possibly associated to vibration of aromatic ring (1,4 substituted) and ester stretching. P(AAm-*co*-SSNa) spectrum presents the following absorption bands: 2928 cm^{-1} st(C–C), 1121 cm^{-1} (C–H, 1,4 substitution), and 1225 cm^{-1} st(S=O), associated to 4-styrene sulfonate group, and absorption bands at 1548 cm^{-1} $\delta(\text{NH}_2)$, 1035 cm^{-1} st(C–N) related to acrylamide group and an overlapped band appear at 1666 cm^{-1} associated to 1,4 substitution of aromatic ring and carbonyl stretching of amide. Spectra of other synthesized resins (not shown) also present characteristic absorption bands, such is the case of P(AGA-*co*-SSNa) resins which presented the absorption bands at 2936 cm^{-1} st(C–C), 1663 cm^{-1} (C=C, aromatic), 1188 cm^{-1} (C–H, 1,4 substitution), and 1216 cm^{-1} st(S=O), 1748 cm^{-1} st(C=O), 1661 cm^{-1} st(C–N), 1537 cm^{-1} st(COO, as), 1036 cm^{-1} st(C–O, acid), and 1118 cm^{-1} st(C–O, alcohol). P(MOES-*co*-SSNa) spectrum showed absorption bands at 1690 cm^{-1} st(C=O), 1171 cm^{-1} (C–H, 1,4 substitution) and 1037 cm^{-1} st(C–O), among others. The observed vibration bands and information provided confirm the presence of functional groups in the synthesized resins.

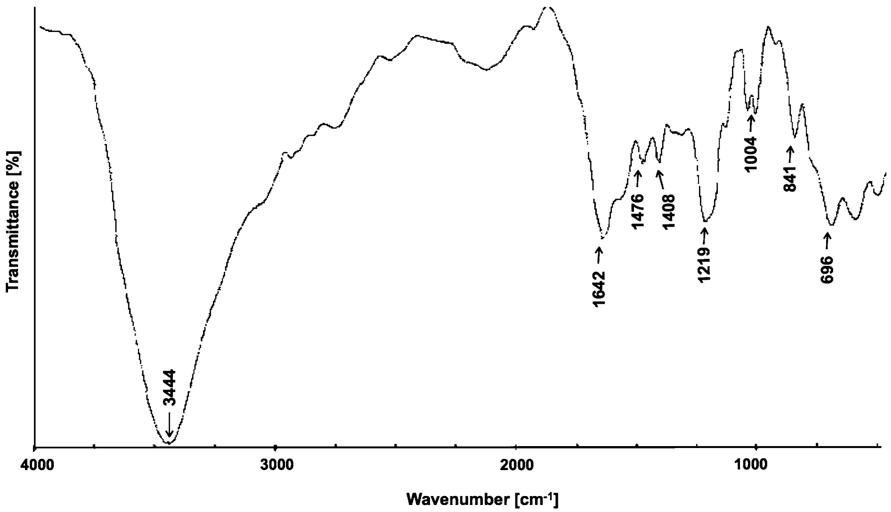

Fig. 2 FTIR spectrum resin P(DMAEA-*co*-SSNa)

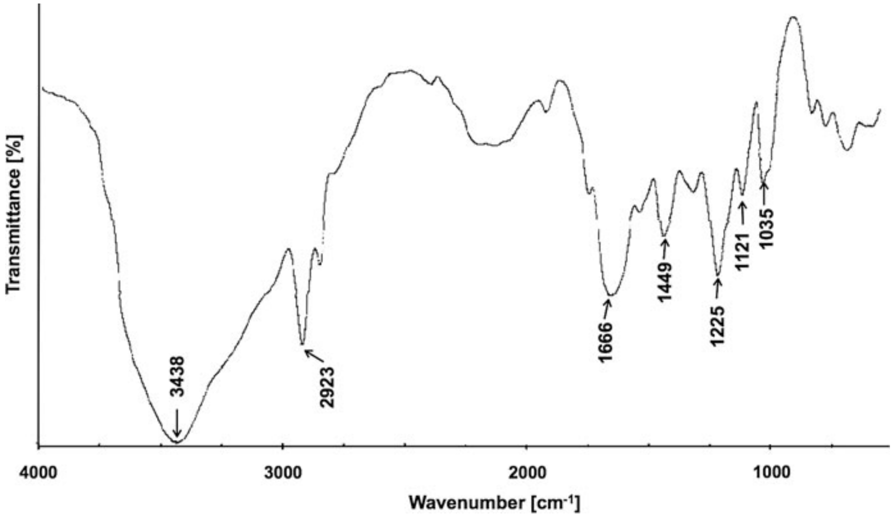

Fig. 3 FTIR spectrum of resin P(AAm-*co*-SSNa)

Effect of pH on the metal ion uptake

Metal–ion sorption on chelating adsorbents is a pH-dependent process. Hydronium concentration in water can change the structure properties of ligands and the speciation of metal ions in aqueous solution. Because of the low solubility of Hg(II), all experiments which contains mercury ions were carried out at pH 2. Table 1 shows the retention values obtained for PSSNa resin. These results can be used as control in order to evaluate the effect of comonomer on metal ion sorption. It is observed that as the pH increases the uptake is higher. However, it is important to consider that PSSNa resins bear sulfonate group derived from a strong acid, at high pH the ligand groups are totally ionized, the interaction is mainly electrostatic and the pH dependence is low, which explains the similar retention values observed at pH 3 and 5.

Table 1 Metal ion uptake of poly(sodium 4-styrene sulfonate) (4 mol-% of MBA; resin/metal ion ratio of 20:1; 1 h contact)

Metal ion	pH	Retention (mmol/g resin)
Pb(II)	1	0.01
	3	0.24
	5	–
Cd(II)	1	0.02
	3	0.24
	5	0.26
Zn(II)	1	0.02
	3	0.21
	5	0.21
Hg(II)[a]	1	0.15
	2	0.24

[a] Obtained from Rivas and Muñoz [26]

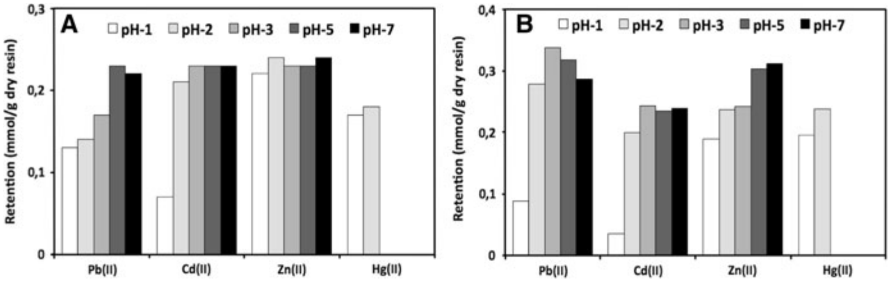

Fig. 4 pH effect on metal ion uptake for resins **a** P(MOES-*co*-SSNa) and **b** P(AGA-*co*-SSNa) (resin/metal ion ratio of 20:1; 1 h contact)

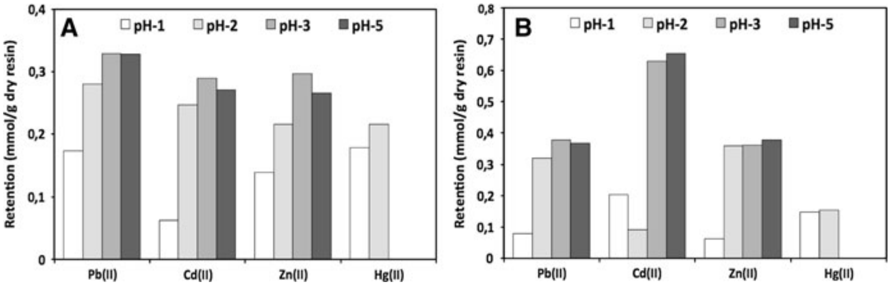

Fig. 5 pH effect on metal ion uptake for resins **a** P(DMAEA-*co*-SSNa) and **b** P(AAm-*co*-SSNa) (resin/metal ion ratio of 20:1; 1 h contact)

Figures 4 and 5 show the sorption values expressed in mmol/g resin for Pb(II), Cd(II), Zn(II), and Hg(II), depending of pH for synthesized resins. Results show the high dependence of sorption with pH, and it is observed that as pH increases the sorption also increase. All resins posses a sulfonate group in their structure (low pH dependence). Hence, results demonstrate the effect of comonomer on ion retention; acting as a cooperative process and the pH dependence is a consequence of the weak acid–base condition of functional groups of comonomers used. At high pH, amine and carboxylic group can be deprotonated and interact with metal ions by complexation or ion exchange.

It is important to note that for P(MOES-*co*-SSNa), Cd(II), and Zn(II) sorption show less dependence than other ions, observed in similar retention values at pH 2, 3, 5, and 7, indicating that comonomer presents less effect on retention. In addition, the retention values observed are similar to those observed for PSSNa resin ($\sim$0.23 mmol/g resin), indicating a low contribution of comonomer to sorption capacity. Similar behavior was observed for Cd(II) retention by P(AGA-*co*-SSNa) resin (see Fig. 4). On other hand, Pb(II) and Zn(II) reached retention of above 0.33 and 0.31 mmol/g resin, respectively, and by comparison with control resin, results suggested an effect of comonomer on metal ion sorption.

For those resins with comonomers (2-dimethylamino)ethylacrylate and acrylamide, the pH dependence is more evident. Highest retention was found for Pb(II)

(0.37 mmol/g resin) and Cd(II) (0.65 mmol/g resin) for P(DMAEA-*co*-SSNa) and P(AAm-*co*-SSNa), respectively. Specially the resin P(AAm-*co*-SSNa) reached retentions above 0.30 mmol/g resin for Cd(II), Pb(II), and Zn(II), indicating the contribution of acrylamide to metal ion uptake. High retention values were observed at pH 3.0 and 5.0 where nitrogen atoms can be unprotonated and can interact better with metal ions. According to hard and soft acid–base theory [24], cadmium and lead are classified as soft acid and borderline, respectively. In case of ligands, both resins possess comonomers with nitrogen as interacting site, and nitrogen is less hard than oxygen atoms [25], favoring the interaction between ion and nitrogen.

Maximum retention capacity

According to the results of pH effect experiments, maximum retention capacity for the metal ions was determined at pH where the metal ion retention is favored. Synthesized resins (0.50 g) were contacted with 25 mL of 1.0 g/L metal ion solution. Then, the batches were reconstituted by adding 25.0 mL of fresh metal ion solution. Table 2 shows the maximum retention capacities of synthesized resins and is observed that resin P(DMAEA-*co*-SSNa) presents the highest retention values 1.682 and 1.084 mmol/g resin for Zn(II) and Pb(II), respectively. In case of Cd(II), it was obtained the highest retention for the resin P(AAm-*co*-SSNa)(1.168 mmol/g) and Hg(II), the highest retention (0.893 mmol/g) was reached using the resin P(AGA-*co*-SSNa). Besides, the table presents the maximum retention capacity for PSSNa resin, and the comparison with retention values of synthesized resins indicates that only P(DMAEA-*co*-SSNa) resin reaches a sorption higher than PSSNa resin (for Pb(II)). Other resins present similar or lower values than that PSSNa, suggesting low contribution of comonomer to maximum sorption capacity.

Table 2 Maximum retention capacity for all the resins (in mmol of metal ion/g resin)

Resin	Pb(II)	Cd(II)	Zn(II)	Hg(II)
PSSNa	0.646	1.150	1.860	0.703
P(AGA-*co*-SSNa)	0.543	1.207	1.051	0.893
P(AAm-*co*-SSNa)	0.434	1.168	1.254	0.621
P(MOES-*co*-SSNa)	0.770	0.790	0.630	0.740
P(DMAEA-*co*-SSNa)	1.084	1.157	1.682	–

Table 3 Water absorption capacity

Resin	g H_2O/g resin
P(AGA-*co*-SSNa)	13.4
P(AAm-co-SSNa)	12.2
P(DMAEA-*co*-SSNa)	18.2
P(MOES-*co*-SSNa)	20.3

Swelling capacity

The swelling capacity is an important property of ion exchange resins, because this process allows the diffusion of metal ions into the pores of resin particles, and then favors the interaction of ions with active sites. Table 3 shows the results of water absorption capacity of synthesized resins. The highest swelling capacity was founded for resin with 2-(methacryloyloxy)ethyl succinate comonomer (20.3 g H_2O/g resin) while the lowest value corresponds to resins with acrylamide (12.2 g H_2O/g resin). Functional groups with atoms like nitrogen or oxygen provides hydrophilicity to the carbon chain or polymeric matrix, thus a comparison of comonomers is possibly to observe that 2-(methacryloyloxy)ethyl succinate provides a higher hydrophilicity respect other comonomers due to major number of oxygen atoms, contributing to the osmotic pressure difference and increasing the swelling capacity. However, according to results provided above, the higher swelling of P(MOES-*co*-SSNa) was not reflected on sorption in metal ion uptake.

Selectivity of the resins

In consideration of resins possess active sites that can interact by electrostatic or chelation process, the sorption performance of resins was studied under competitive conditions to evaluate the selectivity of resins. Tables 4 and 5 summarized results of selectivity experiments, carried out using the resins P(AGA-*co*-SSNa) at pH 2 and 5. The results are expressed in percentages, and Retention 1 corresponds to the percentage of metal ion retained respect to initial amount of metal ion, while Retention 2 corresponds to percentage respect to total concentration of ions.

Results suggest that resin P(AGA-*co*-SSNa) could be considered as a selective resin, because its performance in presence of quaternary mixture of Cd(II), Pb(II), Zn(II), and Hg(II) at pH 2 show a retention above 50% of Hg(II) respect to other ions. Moreover, the individual retention percentages show that only Pb(II) and Hg(II) reached values over 90%. Previous study of our group [26] in an experiment using the same quaternary mixture at pH 2 and the resin PSSNa was found that the retention (%) respect to the total amount of ions were 23.0, 50.0, 19.2, and 7.8% for

Table 4 Selectivity of the resin P(AGA-*co*-SSNa) at pH 2 (resin/metal ion ratio 20:1)

Metal ion	Retention 1 (%)	Retention 2 (%)
Pb(II)	91.7	20.4
Cd(II)	66.7	17.1
Zn(II)	44.4	11.7
Hg(II)	91.4	50.8

Table 5 Selectivity of the resin P(AGA-*co*-SSNa) at pH 5 (resin/metal ion ratio 20:1)

Metal ion	Retention 1 (%)	Retention 2 (%)
Pb(II)	99.7	45.2
Cd(II)	98.6	17.0
Zn(II)	99.2	37.7

Cd(II), Pb(II), Zn(II), and Hg(II), respectively. These results indicate that a resin based only on sulfonate group does not show selectivity toward Hg(II), but selectivity toward Pb(II). These results confirm the effect on comonomer on selectivity, indicating that the addition of 2-acrylamido glycolic acid monomer switches the selectivity from Pb(II) to Hg(II). This change can be explained by the high affinity between mercury and nitrogen [27–29].

Table 5 presents the results of experiments carried out at pH 5, using the same resin but using a tertiary mixture of Pb(II)–Cd(II)–Zn(II) (see Table 5). It is observed all ion present high retention, and zinc and lead present the mayor retention respect to other ions with 37.7 and 45.2%, respectively.

Temperature and time effect

Figures 6 and 7 show the effect of temperature and time on the metal ion retention properties, respectively. It is expected that as the temperature rises, the increase of random motion of ions promotes diffusion of metal ions and probably also the interaction with active sites. However, it is observed that temperature does not affect significantly the ion retention, and all metal ions keep the same retention between 20 and 35 °C, similar tendencies have been observed in other similar polymeric matrix studied by our group [18]. In case of time effect, it is possible observe that retention does not change from 15 min of contact until 2 h, suggesting that interaction occurs in the early minutes of contact reaching the highest retention. These results are in agreement with a previous report of resins of poly(2-acrylamido glycolic acid) [30], where the *plateau* retention is reached at early period of time.

Elution experiments

The reusability of an ion exchange resins is a key factor for a potential application. Generally, in ion exchange processes, the resins are regenerated using a high concentrated solution of acid or base, depending of resins characteristics. Elution

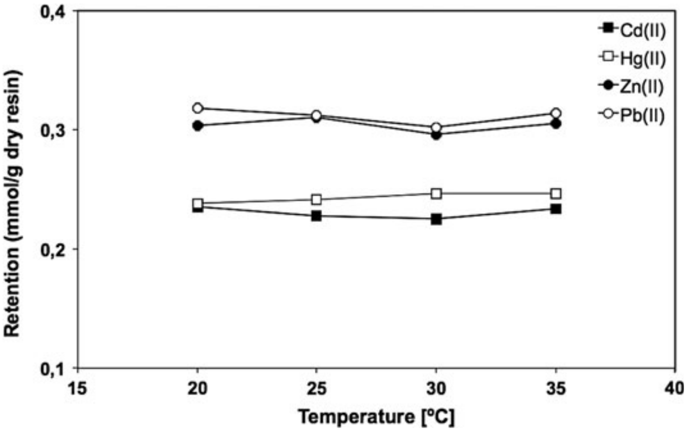

Fig. 6 Effect of temperature on ion retention for P(AGA-*co*-SSNa) resin

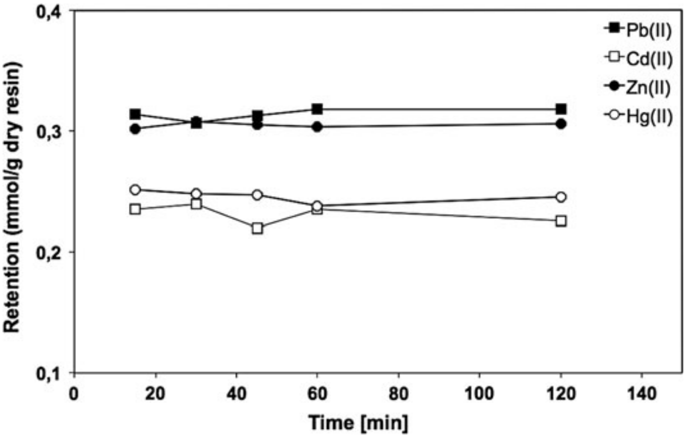

Fig. 7 Effect of time contact on retention of metal ion for P(AGA-*co*-SSNa) resin

Table 6 Metal ion elution of P(AAm-*co*-SSNa) resin

Eluent	Conc. (M)	Elution (%)			
		Pb(II)	Hg(II)	Zn(II)	Cd(II)
HNO_3	1	40.5	32.1	73.2	76.2
HCl	1	13.5	3.24	73.1	75.6
$HClO_4$	1	40.5	4.32	73.2	76.2
HNO_3	4	40.5	35.3	97.6	76.2
HCl	4	13.0	1.36	73.2	76.2
$HClO_4$	4	54.1	0.76	73.2	91.4

Table 7 Metal ion elution of P(AGA-*co*-SSNa) resin

Eluent	Conc. (M)	Elution (%)			
		Pb(II)	Hg(II)	Zn(II)	Cd(II)
HNO_3	1	70.9	29.0	87.5	74.5
HCl	1	36.4	13.5	92.3	86.2
$HClO_4$	1	87.1	51.2	84.7	75.3
HNO_3	4	71.7	61.4	97.8	75.3
HCl	4	100.0	14.4	94.8	87.3
$HClO_4$	4	86.9	54.1	93.7	72.6

performance depends of certain characteristics of adsorbent, like crosslinking degree and microstructure, however, an important factor is the binding strength. To study the elution performance of metal ions, loaded resins were contacted with the following acids: HCl, HNO_3, and $HClO_4$. Tables 6 and 7 show the elution experiments carried out for P(AAm-*co*-SSNa) and P(AGA-*co*-SSNa) resins. In case of resin with acrylamide as comonomer, the elution of Hg(II) and Pb(II) was low compared with Zn(II) and Cd(II) elution. Best eluents were nitric and perchloric acid, however, the maximum elution reached for Hg(II) and Pb(II) were ~54 and 35%, respectively. Same behavior was observed for P(AGA-*co*-SSNa), where Hg(II) presented low elution, however, the elution of Pb(II) was high compared with P(AAm-*co*-SSNa) resin, reaching retention higher than 80%. It is important to note that the Hg(II) elution performance for PSSNa resin showed similar behavior (28% elution using 3 M $HClO_4$). Hence, associate the low elution of Hg(II) to binding strength (N···Hg) is not appropriated. To that, further studies using more suitable eluent reagents are recommended.

Conclusions

Copolymer resins P(MOES-*co*-SSNa), P(AGA-*co*-SSNa), P(AAm-*co*-SSNa), and P(DMAEA-*co*-SSNa) were successfully synthesized by radical polymerization in solution. Sorption experiments as function of pH demonstrated the effect of comonomer on ion retention, specially those resins with comonomer bearing amide and amine functions. However, the best contribution of comonomers to metal ion uptake was evidenced only for P(AAm-*co*-SSNa), showing higher retention compared to a resins based only in sulfonate functional groups. Selectivity experiments showed that P(AGA-*co*-SSNa) resin present certain selectivity toward Hg(II) and Pb(II) at pH 2 and 5, respectively. Comparison of selectivity performance with PSSNa resins, showed that 2-acrylamido glycolic acid comonomer changed the selectivity of Pb(II) to Hg(II).

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