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Heavy metal ions removal through poly(acrylamide-*co*-methacrylic acid) resin

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Abstract The resin poly(acrylamide-*co*-methacrylic acid) P(AAm-*co*-MA) by radical polymerization was synthesized and its metal ion binding was studied using the batch and column equilibrium procedures for: Cd(II), Zn(II), Pb(II), Hg(II), Al(III), and Cr(III). Experiments were carried out at different pH, metal ion concentration, temperature, and contact time. The resin's retention behavior was influenced by the pH. The highest retention 91% (0.248 mmol/g, 6.7 mg/g) was achieved at pH 5 for Al(III), and 87% (0.265 mmol/g, 54.9 mg/g) for Pb(II). For Hg(II), the yield was 85% (0.318 mmol/g, 63.7 mg/g) at pH 2. The metal-ion retention properties were dependent on the polymer/metal ion ratio. Under competitive conditions of Pb(II), Hg(II), and Al(III), the resin showed a higher retention of Hg(II), allowing the selective separation of this metal.

Keywords Resin · Pollutant metal ions · Removal

Introduction

The distribution of metals in the environment is a result of both natural processes (volcanoes, erosion, spring water, bacterial activity) and human activities (fossil fuel combustion, industrial and agricultural processes). Indeed, activities such as mining, smelting and agriculture have locally increased the levels of heavy metals such as cadmium, copper, chromium, lead, mercury, and aluminum in soils, air and water up to dangerous levels for plants, animals and humans beings [1]. Heavy metals produce serious human health problems once they enter the food chain. Heavy metal poisoning principally results in neurological and renal disturbances,

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and can also cause mental retardation and semi-permanent brain damage. Heavy metals are classified as persistent environmental toxic substances because they cannot be rendered harmless by chemical or biological remediation processes [2]. Reduction of their content in the environment may be achieved in two possible ways: by decreasing their influx into the environment or by removing them from contaminated media [3].

An ever increasing amount of wastewater needs to be purified within a reasonable time [4]. The separation of metal ions, present as contaminants in water, is complicated due to the numbers of variables that must be considered, including the solution composition, salinity, pH, temperature, and the presence of organic substances. A serious problem encountered in metal ion removal is that the target species are usually present in low concentration and in complex mixtures [5].

Metal ion adsorption through precipitation and ion exchanger/chelation is a commonly used to reduce metal toxicity in the environment. One way to remove metals from wastewater is polymeric adsorbent, which consists in a synthetic polymer and ligand, wherein the metal ions are bound to the polymer ligand by a coordinate bond. A ligand contains anchoring sites (such as nitrogen, oxygen or sulfur) obtained either by polymerization of monomer possessing the coordinating site or by a chemical reaction between a polymer and a low molecular weight compound with coordinating ability [6–8].

Much attention has been drawn to the synthesis of chelating resins and to the study of their adsorption behavior for metal ions owing to their triple function of ion exchange, chelate formation, and physical adsorption.

Several methods to remove heavy metals from aqueous solutions have been reported in the literature, including adsorption, precipitation, neutralization, ion-exchange, and complexing reagent modified polymers that are both water-soluble and water-insoluble [9–23].

Among these techniques, adsorption using functional polymers is generally preferred for heavy metal ion removal due to the availability of different adsorbents, its high efficiency, easy handling and low cost. A large number of polymers incorporating a variety of functional groups, including carboxylic acid, sulfonic acid, amine, amide, amidoxime, phosphoric acid, dithiocarbamate, have been prepared and their adsorption and analytical properties investigated [24].

In a polymeric ligand or polychelates, the function of a ligand is often only a small portion of three-dimensional polymer supports. Thus, it is subject to a larger number of structural variables in comparison with a low molecular weight ligand. This difference indicates the definite dependence on the complexing abilities of the insoluble polymeric ligands and physicochemical properties of the derivate polychelates [25]. Reactions between the functional group and the metal ion as well as the diffusion of metal ions into the resin's interior indicate that chelating resins play a key role in adsorbing metal ions. [25].

For all these reasons, our study synthesized the resin P(AAm-*co*-MA), which contains two potential groups capable to produce an interaction between the resin and the metal ions.

Experimental part

Materials

Acrylamide (AAm, 99%, Aldrich) and methacrylic acid (MA, 99%, Aldrich) was utilized 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 nitrate metal salts used were $Cd(NO_3)_2$, $Cr(NO_3)_3$, $Hg(NO_3)_2$, $Pb(NO_3)_2$, $Al(NO_3)_3$, and $Zn(NO_3)_2$. Metal salts were purchased from Merck. The analytical grade HNO_3, $HClO_4$, and HCl were purchased from Fisher.

Synthesis of the resin

The synthesis of the resin P(AAm-*co*-MA) was performed in a polymerization flask with an equimol (0.0422) ratio of acrylamide (3.00 g) and methacrylic acid (3.63 g). AP, 2 mol-% (0.3852 g) was used as an initiator and MBA, 2 mol-% (1.688×10^{-3} moles) as a cross-linking reagent. The system was kept under N_2 at 70 °C for 4 h. Then, the resin was filtered and washed with distilled water and dried up to constant weight at 40 °C. The copolymerization yield for this resin was 90%.

The resin was screened, and a particle size fraction in the range of 180–250 μm was chosen for all experiments.

Metal ion adsorption

To determine the metal ion binding ability, a batch equilibrium procedure was applied to 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, and temperature. First, 0.05 g of dried resin and 5 mL of metal ion solution were shaken for 1 h at 20 °C. Then, the resin samples were filtered and washed with water at the same pH. The metal ions concentrations in the filtrate were determined by atomic absorption spectroscopy.

Accordingly, the metal ion 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. Batch metal uptake experiments under competitive conditions were performed with the following metal ion mixtures: Al(III)-Pb(II) at pH 5, and Hg(II)-Pb(II)-Al(III) at pH 2. For first test, 0.10 g of resin and 10 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 non-competitive experiments.

In the regeneration experiments, HNO_3, HCl, and $HClO_4$ at two concentrations were studied as potential stripping reagents using the batch method. A total of 0.05 g of resin loaded with Hg(II), Al(III), and Pb(II) ions were 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 passed through the column. The fractions were collected and analyzed for the metal ion concentration.

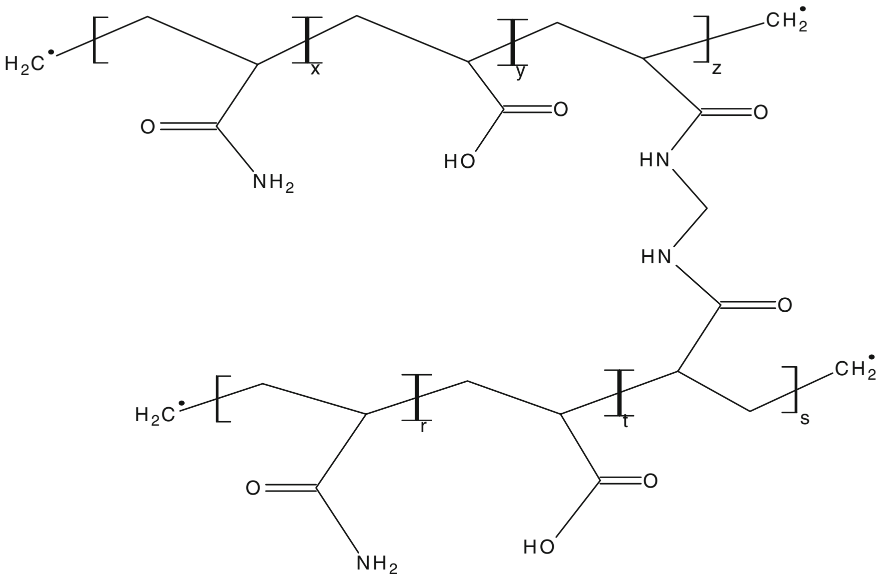
Measurements

A Julabo air-batch shaker was used for shaking the solution at a desired temperature. The pH was measured with a digital pH meter (H. Jürgens and Co). An atomic absorption spectrometer, Unicam Solar 5 M series was used for metal ion determination. 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 a 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

Synthesis of the resin

The resin P(AAm-*co*-MA) (see Scheme 1) shows high thermal stability up to 200 °C with a weight loss lower than 11%; after that point, the weight loss increased until reaching 87% at 500 °C, which was attributed to CO_2 evolution.



Scheme 1 Structure of the resin P(AAm-*co*-MA)

Among the most characteristic absorption bands shown in the FTIR spectrum of P(AAm-*co*-MA) are the following (in cm^{-1}): 3,453 (N–H), 2,926 (C–H), 1,665 (C=O) which corroborated the resin structure.

Metal ion retention properties

The resin P(AAM-*co*-MA) has an amide and carboxylic acid group as a potential ion exchange/complexing groups that are capable of interaction with the metal ion to produce retention. The affinity between the resin's active group and metal ions is studied by batch and column equilibrium procedures, using a resin particle size of 180–250 μm and the resin–metal ion relationship in mol between functional group on the resin and metal ion, 20:1. This ratio ensures the metal ion's access to ligand sites.

Effect of the pH

The pH was varied between 1 and 5 for: Cd(II), Zn(II), Pb(II), Al(III), and Cr(III); and between 1 and 2 for Hg(II). The pH studied depends on metal ion solubility.

Since the ligand groups' and the metal ions' forms change with the pH, the retention behavior is dependent of this parameter. The highest retention behavior was observed at pH 5 for Al(III) 91% (0.248 mmol/g), and Pb(II) 87% (0.265 mmol/g); and at pH 2 for Hg(II) 85% (0.318 mmol/g). Therefore, these pH values were chosen for the following runs. Table 1 summarizes the experimental results obtained at pH 1 and 5 by batch equilibrium procedure.

To explore the resin's applications, the maximum adsorption capacity (MAC) needs to be known. Based on the MAC, the maximum retention capacity (MRC) in batch and column equilibrium procedures was determined for Hg(II), Al(III), and Pb(II). These values are shown in Table 2.

The retention for Pb(II) and Al(III) is found to be lower for the column in comparison with the Batch method, the opposite is true for Hg(II). This difference could be attributed to the difference in contact time.

Effect of ion concentration

In order to investigate the effects of the initial metal concentration on metal uptake, the process was performed at the initial resin: metal ion ratio between 20:1 and 20:4 in mol. The adsorption study was performed for 1 h to ensure that equilibrium was attained. In all experiments, retention increased with the increment in the initial ion concentration, indicating that the resin could continue to retain metal ion (see Fig. 1).

Effect of contact time

To produce the interaction between the metal ion and the active site inside the resin, the contact time required varies for the different ions. For the resin P(AAm-*co*-MA), a longer contact time did not change the retention behavior in the case of Pb(II) and

Table 1 Effect of the pH on the metal ion retention behavior of the resin P(AAm-*co*-MA) at 20 °C, 0.5 g of resin

Metal ion	Initial metal ion concentration (ppm)	pH	Retention (mmol/g)	Retention (%)
Hg(II)	801	1	0.120	31
	756	2	0.317	85
Pb(II)	700	1	0.038	12
	730	3	0.167	48
	650	5	0.265	87
Zn(II)	230	1	0.046	13
	210	3	0.015	5
	200	5	0.121	40
Cd(II)	200	1	0.034	20
	200	3	0.034	20
	200	5	0.105	60
Cr(III)	160	1	0.052	18
	160	3	0.008	3
	150	5	0.189	67
Al(III)	77.2	1	0.008	3
	72.8	3	0.044	16
	76.4	5	0.247	91

Table 2 Maximum retention capacity for the resin P(AAm-*co*-MA) at the optimum pH, initial metal ion concentration 1 g/L

Metal ion	MRC (mmol/g) (by batch equilibrium procedure)	MRC (mmol/g) (by column equilibrium procedure)
Pb(II)	0.51	0.38
Hg(II)	0.54	0.79
Al(III)	2.36	0.61

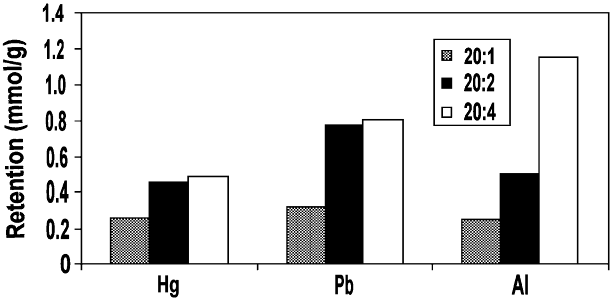


Fig. 1 Effect of the initial metal ion concentration on metal ion retention capacity at optimum pH

Al(III), although adsorption for Hg(II) did increase with longer contact times, indicating that more time is required to form the complexing species between Hg(II) and the active site in comparison with the other metal ions (see Table 3).

Table 3 Effect of the contact time on the retention behavior of the resin P(AAm-*co*-MA), initial resin :metal ion ratio in mole 20:1

Time (min)	Retention (%)		
	Pb(II)	Hg(II)	Al(III)
15	93	82	91
30	93	87	91
60	92	85	91
120	93	94	91

Table 4 Effect of the temperature on the retention behavior of the resin P(AAm-*co*-MA), initial resin :metal ion ratio in mole 20:1

Temperature (°C)	Retention (%)	
	Pb(II)	Al(III)
20	87	91
25	83	91
30	85	91
35	90	91

Effect of temperature

Temperature could affect metal ion retention in resins, depending on whether retention is chemical or physical. For this resin, changes in the temperature did not produce a significant effect on retention for Al(III), although retention for Pb(II) varied slightly for the different temperatures studied. The results are shown in Table 4.

Selectivity in the retention behavior

In general, metal ions are naturally found mixed with several metal ions. To determine the metal ion retention under competitive conditions, the following run was performed. First, 100 mg of dry resin was contacted at pH 5 during 1 h with 10 mL of an aqueous solution containing the same concentration (resin:metal ion ratio 20:1) of each metal ion Al(III), and Pb(II). The resin showed the highest retention for Al(III) 60% (0.237 mmol/g y/o 6.38 mg/g), while the retention for Pb(II) was 40% (0.166 mmol/g y/o 34.4 mg/g). Even though the difference in retention performance is 20%, which does not guarantee effective separation, the resin did demonstrate a slight preference because the charge of Al(III) is higher than that Pb(II). Thus, the interaction between the metal ion and the active group inside the resin would be through an electrostatic force as shown in Scheme 1a (see the Table 5).

Table 5 Selectivity retention behavior for the resin P(AAm-*co*-MA) in a binary metal ion mixture

Metal ion	Retention (%)[a]	Retention (%)[b]
Pb(II)	40	93
Al(III)	60	86

Resin–metal ion ratio in mole 20:1. This ratio is considering each metal ion

[a] Respect to the total of mole retained

[b] Respect to each metal ion

Table 6 Selectivity in the retention of the resin P(AAm-*co*-MA) in a quaternary metal ion mixture

Metal ion	Retention (%)[a]	Retention (%)[b]
Pb(II)	21	56
Hg(II)	66	94
Al(III)	13	23

Resin–metal ion ratio in mole 20:1. This ratio is considering each metal ion

[a] Respect to the total of mole retained

[b] Respect to each metal ion

Subsequently, 150 mg of dry resin was contacted at pH 2 during 1 h with 15 mL of an aqueous solution containing the same concentration of Al(III), Pb(II), and Hg(II). In this experiment, the difference between the metal ion retention was greater: retention for Hg(II) was 66% (0.32 mmol/g y/o 64.32 mg/g), for Pb(II) 21% (0.102 mmol/g y/o 21.0 mg/g), and for Al(III) 13% (0.062 mmol/g y/o 1.70 mg/g). These results indicate that the resin P(AAm-*co*-MA) would effectively separate Hg(II) in mixture with Al(III), and Pb(II) at pH 2. Thus, it can be concluded that the complex formed between Hg(II) and the active site inside the resin is more stable in comparison with the other metal ions tested as shown in Scheme 1 b (see Table 6).

Resin reusability

The metal ion needs to be adsorbed but then it must be desorbed in order to reuse the resin. Thus, the elution of several stripping reagents was studied. The resin's metal ion capacity should be maintained after the treatment with an eluent reagent and the metal ion adsorbed by the resin should be easily released under appropriate conditions. The batch desorption studies were carried out by first separately loading resin samples. The three stripping reagents were studied (HCl, $HClO_4$, and HNO_3) in two different concentrations because they should be able to displace the metal ions. A higher elution was obtained either HCl and HNO_3 (100%), and the lowest values were found for Pb(II), indicating that Pb(II) forms more stable complexes than Hg(II) and that these could not be disrupted under these conditions (see Table 7).

Table 7 Regeneration capacity of the resin P(AAm-*co*-MA), initial quantity of resin 0.05 g

Stripping reagent	Concentration (mol/L)	Elution (%)		
		Pb(II)	Hg(II)	Al(III)
HCl	1	26	100	57
	4	39	100	55
HNO_3	1	35	100	57
	4	29	100	71
$HClO_4$	1	32	97	67
	4	34	92	58

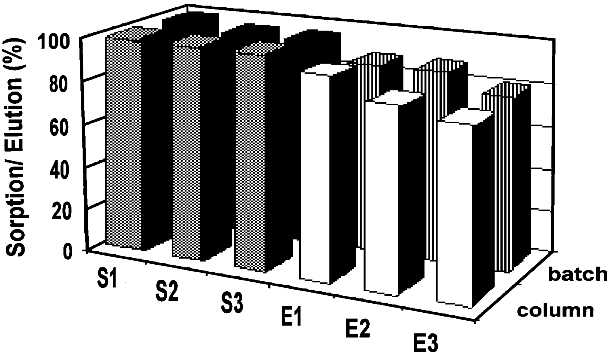


Fig. 2 Reusability of the resin loaded with Pb(II), eluent 4 M HCl. Sorption (S)–elution (E) cycles, initial quantity of resin 0.2 g

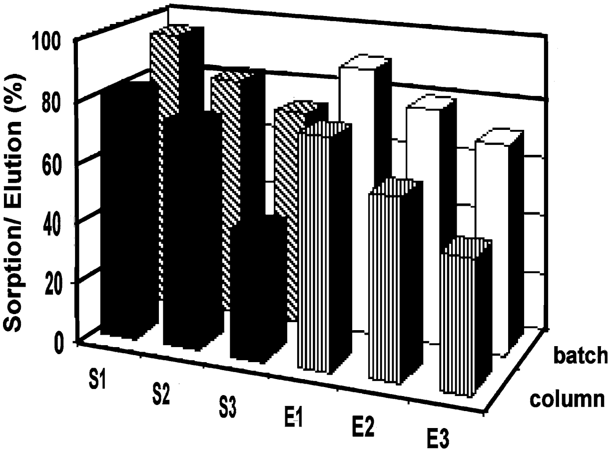


Fig. 3 Reusability of the resin loaded with Hg(II), eluent 1 M HCl. Sorption (S)–elution (E) cycles, initial quantity of resin 0.2 g

Therefore, for resin reusability, the sorption–desorption cycle was repeated three times with the same sorbent in batch and column processes. The results are presented in Fig. 2, 3, 4 and 5. Figure 2 shows where the resin was loaded with Pb(II) and desorption was performed with 4 M HCl. In this case, the resin was able to maintain its retention capacity after the three cycles, and a high percentage of elution was produced in three cycles in both the batch and column processes. Figure 3 shows the results of the resin loaded with Hg(II), and the desorption of the metal ion with 1 M HCl, where the resin loses its retention capacity in both the batch and column equilibrium procedures. The loss is higher in the column procedure due to the smaller contact time.

The resin lost its elution capacity, where the highest loss was in the column process. Figure 4 shows the results of the resin loaded with Hg(II), and the desorption performed with 1 M HNO_3. The resin in the batch and column

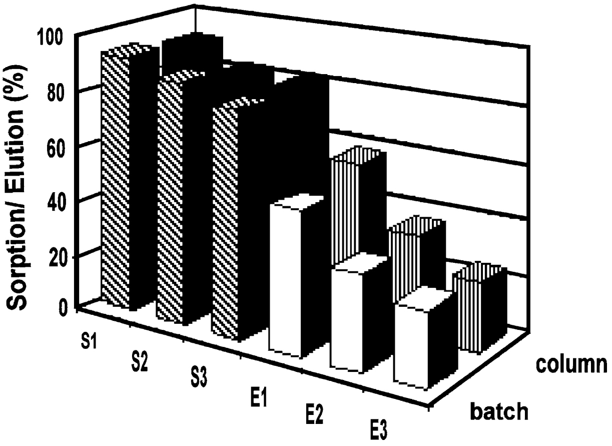


Fig. 4 Reusability of the resin loaded with Hg(II), eluent 1 M HNO_3. Sorption (S)–elution (E) cycles, initial quantity of resin 0.2 g

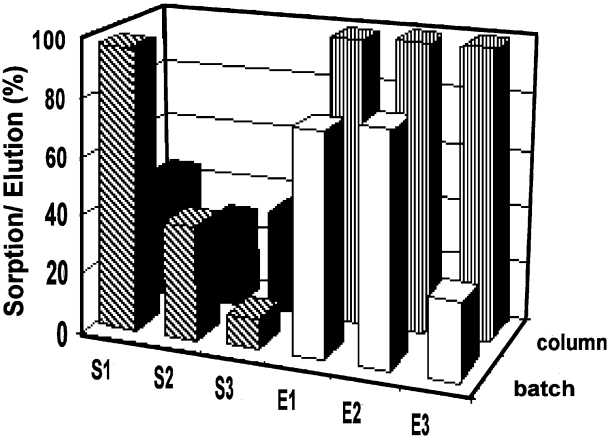


Fig. 5 Reusability of the resin loaded with Al(III), eluent 4 M HNO_3. Sorption (S)–elution (E) cycles, initial quantity of resin 0.2 g

procedures gradually loses its retention capacity until around 80% in both cases. It also loses its elution capacity in a high percentage: the resin is stripped of the metal ion between 59 and 25%. Figure 5 shows the results of the resin loaded with Al(III) and the desorption performed with 4 M HNO_3. In batch process, the resin totally loses its retention capacity falling to 11%; metal ion desorption in the first and second cycles was over 75%, but then falls to 27%. In the column procedure, metal ion retention was always lower than 45% because the formation of complexing species between the active site inside the resin and the metal ion is slower. Due to low retention, the stripping reagent can elute all metal ions. Considering this resin's behavior in a continuously operated process, it can be used to remove Pb(II) with the possibility of resin regeneration and reusability.

Conclusions

The resin P(AAm-*co*-MA) was obtained with a high yield percentage. The retention behavior for all metal ions depended on the pH. The maximum retention capacities were lower in column than batch technique because the contact time between the resin and the metal ions in the column is smaller than in the batch process, and thus the reaction was not produced. The resin showed a preferred retention behavior for Hg(II) in a mixture that also contained Al(III) and Pb(II).

The resin maintained its retention capacity for Pb(II) in three cycles.

In general, the results suggest that the carboxylic/carboxylate groups are interacting more strongly than the amide groups. Thus, it appears that a resin with a higher content of the methacrylic monomer unit would increase the affinity for metal ions. Still, it is important to consider that the acrylamide monomer unit would also increase the swelling degree, thus favoring the interaction between the active sites and the metal ions.

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