

Metal Ion Retention Properties of Poly(acrylic acid) and Poly[N-3-(dimethylamino)propyl acrylamide-co-acrylic acid]

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ABSTRACT: The crosslinked resins poly(acrylic acid) (PAA) and poly[N-3-(dimethylamino)propyl acrylamide-co-acrylic acid] [P(NDAPA-co-AA)] are obtained by radical polymerization and characterized by FTIR spectroscopy. PAA at basic pH exists basically as an acrylate anion that may contain end carboxylate groups or form bridges acting as mono- or bidentate ligands. P(NDAPA-co-AA) presents three potential ligand groups in its structure: carboxylic acid, amide, and amine. The trace metal ion retention properties of these two resins is compared by using the batch equilibrium procedure. The metal ions are contained in saline aqueous solutions and are found in natural seawater. The retention of Cu(II), Pb(II), Cd(II), and Ni(II) metal ions is studied under competitive and noncompetitive conditions.

The effects on the pH, contact time, amount of adsorbent, temperature, and salinity are investigated. The PAA resin presents a high affinity (>80%) for Cu(II) and Cd(II) ions. The P(NDAPA-co-AA) resin shows a high affinity for Pb(II) and Cd(II) ions. With 4M HNO₃ it is possible to completely recover the PAA resin charged with Cu(II) ions and the P(NDAPA-co-AA) resin charged with Pb(II) ions. The two resins show a high affinity for Cd(II) ions from the seawater containing Cu(II) and Cd(II) ions. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 1385–1394, 2005

Key words: resin; metal ion; polymer–metal ion complexes; trace; seawater

INTRODUCTION

Heavy metals are toxic to aquatic flora and fauna, even in relatively low concentrations. The development of an effective treatment process for wastewater has been considered as one of the most important requirements in recent wastewater treatment because numerous components are contained in wastewaters from various factories, and an appropriate method should be applied for the treatment according to the components therein. A number of approaches have been suggested for the removal of metal ions from aqueous solution.^{1–20} The techniques include precipitation, ion exchange, reverse osmosis, adsorption, and so forth. Among these, selective adsorption using biological materials, carbons, or polymer resins has generated much interest in the environmental and science fields.

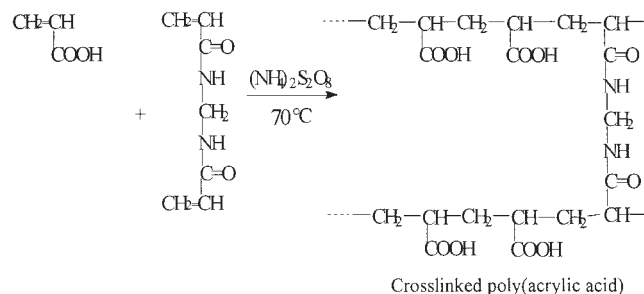
With respect to the low concentrations and handling of large volumes of aqueous solutions, extraction procedures are not economical and precipitation procedures require the addition of relatively large amounts

of chemicals. Thus, applications of sorption or exchange on solids are preferable. This makes the use of exchangers very attractive for selective separation of heavy metal ions.

Because of the chelating nature of metal ions, chelating resins are widely used in the preconcentration, separation, recovery, and hydrometallurgy of metals, in which various chelating groups have been incorporated and are attached to the polymer matrix. Synthesis of such functionalized polymers has been accomplished using either polymerization or simple functionalization principles. The former involves polymerization of the monomers containing the atom or ligand groups and the latter is achieved basically by a polymer-analogous reaction between the polymer and the compound containing the ligand group. The main advantages of these polymeric resins are high chemical and mechanical stabilities.

The aim of this article is to describe the metal ion adsorption behavior of crosslinked resins poly(acrylic acid) (PAA) and poly[N-3-(dimethylamino)propyl acrylamide-co-AA] [P(NDAPA-co-AA)] for Cu(II), Ni(II), Pb(II), and Cd(II) at different pHs, concentrations, temperatures, and salinities. This is undertaken because some of these trace metals such as Cu(II) and Ni(II) occur naturally in the sea and are essential for

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Scheme 1 The synthesis of crosslinked PAA.

marine organisms, but they are potentially toxic, depending on their bioavailability. The concentration changes depend on the metal, species, and physico-chemical characteristics of the aqueous medium. Some of them may be toxic, such as Cu(II); nevertheless, they are essential metal ions.

EXPERIMENTAL

Materials

AA (Merck, Stuttgart, Germany) was purified by distillation, and 2,2'-azoisobutyronitrile (AIBN) was recrystallized from methanol. Ammonium persulfate (PSA, 95%, Aldrich, Milwaukee, WI) was used as received. *N,N'*-Methylene-bis-acrylamide (MBA, 99%, Aldrich) and divinylbenzene (DVB, Fluka, Saint Gallen, Switzerland) were used as crosslinking reagents and used as received. *N*-3-(Dimethylamino)propylacrylamide (NDAPA, 97% Aldrich), diammonium citrate hydrogen (Merck), ammonium pyrrolidin dithiocarbamate (APDC, Aldrich), *N,N'*-diethylammonium

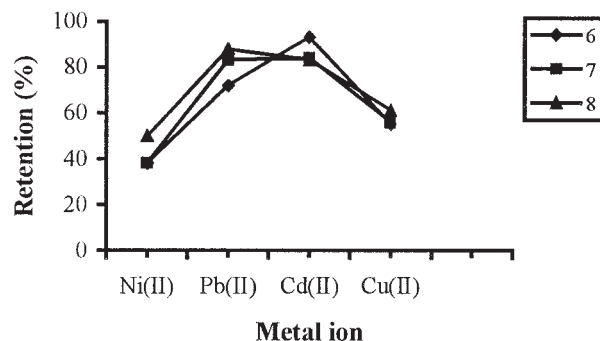


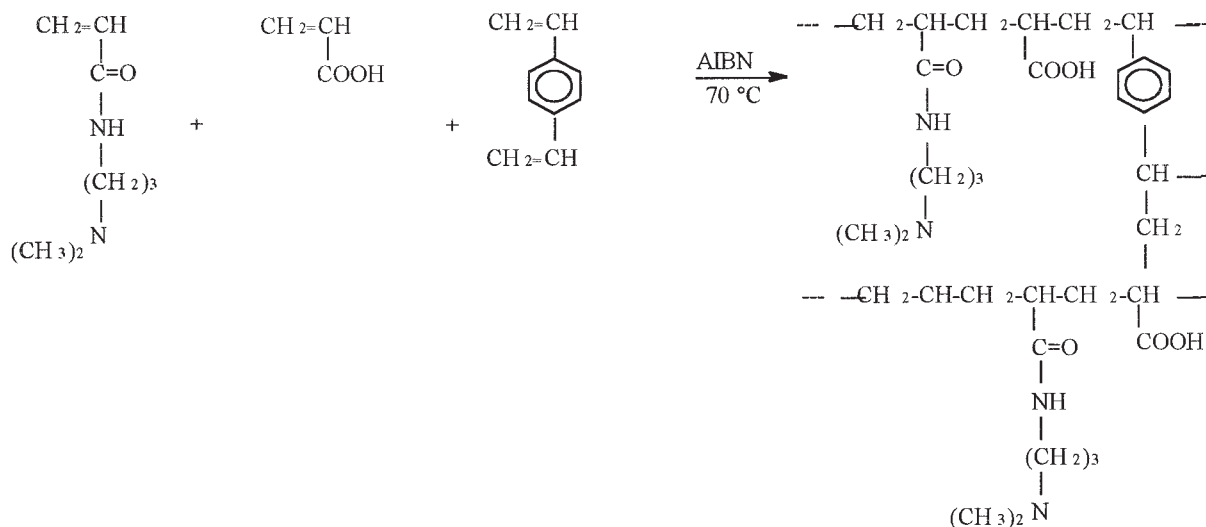
Figure 1 The effect of the pH on the metal ion retention at 17°C, 28‰ salinity, and 10 mg of P(NDAPA-co-AA) with 4.0 μ M metal ions.

diethyl dithiocarbamate (DDDC, Merck), nitric acid suprapure (HNO₃, Merck), sodium chloride (Merck), standard solutions of 1000 ppm (Merck) of each metal ion, and twice distilled water (Millipore) were utilized. All reagents were analytical grade.

Synthesis of PAA and P(NDAPA-co-AA) resins

PAA was synthesized by adding 0.066 mol (4.8 g) of AA dissolved in a small amount of twice distilled water, 4 mmol (0.616 g) of MBA as a crosslinking reagent, and 0.2 mmol (0.5 mol %) of PSA as an initiator at 70°C for 5 min.

P(NDAPA-co-AA) was synthesized by radical polymerization by mixing 0.10 mol (15.623 g, 17.0 mL) of P(NDAPA), 0.1 mol (6.9 mL) of AA, 0.012 mol (1.56 g, 3.4 mL, 6 mol %) of DVB, and 0.001 mol (0.5 mol %) of AIBN. The mixture was kept at 70°C for 1 h.



Scheme 2 The synthesis of P(NDAPA-co-AA).

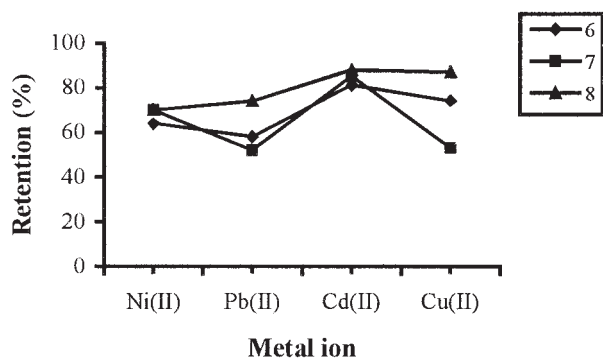


Figure 2 The effect of the pH on the metal ion retention at 17°C, 28‰ salinity, and 10 mg of PAA and 4.0 μM metal ions.

The resins were filtered, washed with abundant distilled water, and dried under a vacuum until constant weight.

Study of metal ion retention properties by batch equilibrium procedure

The effect of the pH on the metal ion retention was studied for each resin. Ten milligrams of dry resin (particle size = 180–250 μm) were placed in a quartz tube and contacted at 17°C for 1 h under constant stirring with 10 mL of the aqueous solution containing 4.0×10^{-6} M of each metal ion [Ni(II), Pb(II), Cd(II), and Cu(II)]. The pH varied between 6.0 and 8.0. The solution was separated by decantation and centrifugation. A run under competitive conditions was carried out with a mixture containing Ni(II)–Cu(II)–Pb(II)–Cd(II) ions. Ten milligrams of dry resin were added to 10 mL of the quaternary aqueous metal ion solution containing 1.0×10^{-6} M (1.0 μM) of each metal ion. After 1 h under stirring, the sample was treated as described for the noncompetitive run.

The effect of time on the metal ion retention was studied by using 10 mg of dry resin and 10 mL of aqueous solution of each metal ion (salinity = 28‰,

concentration of metal ion = 4 μM , temperature = 17°C). An aliquot of 1 mL was obtained at different times and the metal ion was analyzed in the filtrate. The contact time ranged between 2 and 120 min. Moreover, the effect of the salinity, temperature, and elution in an acid medium was studied. Similar studies were conducted with natural seawater. For all runs, the metal ion concentration was determined in the filtrate with an adequate dilution. The retention capacity of each resin was obtained from the difference of the initial and final concentrations of the metal ion.

Buffer solution of complexing citrate

The complexant citrate buffer solution was prepared by dissolving 500 mg of APDC and 500 mg of DDDC in about 60 mL of the warm citrate buffer solution. The flask was filled to completion with 100 mL of the buffer solution.

Complexation and extraction

Two milliliters of complexant citrate buffer solution and 2 mL of *n*-heptane were added to a flask containing a 50-mL subsample. The mixture was vigorously shaken and stored for 15 min until both were separated. Then, reextraction was performed.

Collecting seawater samples

The seawater samples were collected in the Chilean regions of Chiquihue, Pargua, Huito, and Huelmo, which are close to Puerto Montt. This city is located 1025 km south of the capital, Santiago. These samples correspond to the surface waters. They were placed in glass bottles, immediately filtered with a 0.45- μm sterilized membrane, and stored at -5°C .

Measurements

The pH was measured with a pH meter (Hanna model HI 9023). Cu(II), Ni(II), Pb(II), and Cd(II) metal ions

TABLE I
Effect of Metal Ion/P(NDAPA-co-AA) Resin Ratio on Adsorption Behavior

Metal ion	Initial metal ion concn		Resin (mmol)							
			0.0439		0.1096		0.2193		0.4386	
			Retention		Retention		Retention		Retention	
$\mu\text{g/L}$	μmol	$\mu\text{mol}/\text{mmol}$ resin	%	$\mu\text{mol}/\text{mmol}$ resin	%	$\mu\text{mol}/\text{mmol}$ resin	%	$\mu\text{mol}/\text{mmol}$ resin	%	
Ni(II)	234.77	0.04	0.456	50.0	0.234	64.0	0.140	77.0	0.071	78.0
Pb(II)	828.80	0.04	0.802	88.0	0.343	94.0	0.179	98.0	0.089	98.0
Cd(II)	449.64	0.04	0.756	83.0	0.303	83.0	0.179	98.0	0.089	98.0
Cu(II)	254.20	0.04	0.556	61.0	0.226	62.0	0.126	69.0	0.062	68.0

The conditions were 17°C, pH 8.0, 28‰, and 4.0 μM .

TABLE II
Effect of Metal Ion/PAA Resin Ratio on Adsorption Behavior

Metal ion	Initial metal ion concn		Resin (mmol)							
			0.1389		0.3472		0.6944		1.3889	
	$\mu\text{g/L}$	μmol	$\mu\text{mol}/\text{mmol}$ resin		$\mu\text{mol}/\text{mmol}$ resin		$\mu\text{mol}/\text{mmol}$ resin		$\mu\text{mol}/\text{mmol}$ resin	
Ni(II)	234.77	0.04	0.202	70	0.083	72	0.043	75	0.021	73
Pb(II)	828.8	0.04	0.213	74	0.078	68	0.040	70	0.020	70
Cd(II)	449.64	0.04	0.245	85	0.090	78	0.044	77	0.022	75
Cu(II)	254.2	0.04	0.253	88	0.098	85	0.049	85	0.024	83

The conditions were 17°C, pH 8.0, 28‰, and 4.0 μM .

were determined by an atomic absorption spectrophotometer (UNICAM Solaar M-5) with a graphite furnace (GF-95) and an autosampler (FS-95, Analytical Automation Specialists, Inc.) and with an atomic absorption spectrophotometer with a graphite furnace (Perkin Elmer 3110 HGA-600, Wellesley, MA) and an autosampler (Perkin Elmer Cetus Instruments, Wellesley, MA).

RESULTS AND DISCUSSION

The PAA and P(NDAPA-co-AA) resins were synthesized by radical polymerization (see Schemes 1, 2). These resins are solids that are completely insoluble in water. The yields were 93 and 95%, respectively.

The copolymer composition of P(NDAPA-co-AA) is 1:2 according to elemental analysis data (N/C ratio = 0.1659).

The particle size immediately after the polymerization reaction is higher than 90%, corresponding to a fraction of $>1000 \mu\text{m}$. Therefore, the resins were crushed and fractionated. For all subsequent studies, a particle size fraction of 180–250 μm was selected.

Effect of pH on retention

The P(NDAPA-co-AA) resin shows three possible ligand sites in its structure, (carboxylic acid, amide, and

amine), which act as ion exchangers or chelating groups. PAA at basic pH basically exists in ionized form as an acrylate anion, which may contain end carboxylate groups or form bridges. In the first case it acts as a monodentate ligand and in the second case as a bidentate ligand. However, the interaction with the metal ion may be with one, two, three, or four carboxylate groups forming a polymer-metal ion complex, which may be an intra- or interpolymer chain.²¹

The speciation of the metal ion depends on the pH and on the solution concentration. At pH 8 and the employed concentration, the most probable dissolved species are the following: for CdCl^+ , it is CdOH^+ and Cd^{2+} ; for Pb(II), it is PbOH^+ , PbCl^+ , soluble species Pb(OH)_2 , and Pb^{+2} ; for Cu(II), it is the basic cation Cu(OH)^+ and Cu^{+2} ; and for Ni(II), it is Ni^{+2} .

Figure 1 shows the metal ion retention properties of the P(NDAPA-co-AA) resin. The highest retention at the three pH values is observed for Cd(II). For Pb(II) ions the highest retention values correspond to pH 8.0, and the retention of metal ions Ni(II) and Cu(II) is lower. The retention of Cu(II) and Ni(II) ions increases as the pH increases, achieving a maximum above 50%. Moreover, the variation with respect to the pH is close to linear behavior without a lower value at pH 7.0, as occurred for the PAA resin (see Fig. 2) for Pb(II) and Cu(II) ions. The decrease is too pronounced at pH 7.0

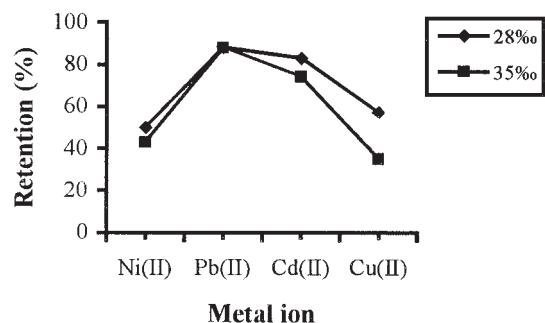


Figure 3 The effect of the salinity on the metal ion adsorption at 17°C, pH 8.0, 28 and 35‰ salinity, and 10 mg of P(NDAPA-co-AA).

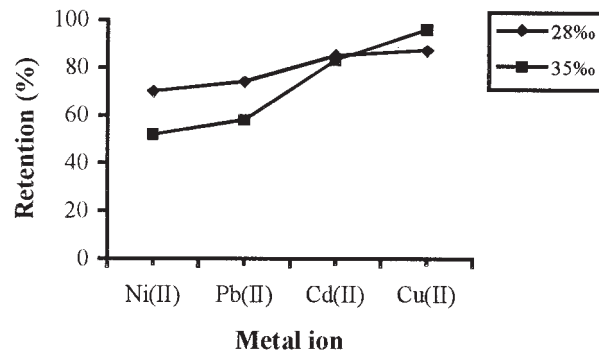


Figure 4 The effect of the salinity on the metal ion adsorption at 17°C, pH 8.0, 28 and 35‰ salinity, and 10 mg of PAA.

TABLE III
Metal Ion Retention Behavior from Quaternary Metal Ion Mixture

Metal ion mixture	Initial metal ion concn					Retention					
	μM	$\mu g/L$	μmol	$\mu g/g$ resin	$\mu mol/g$ resin	% ^a	$\mu mol/g$ resin ^a	% ^b	$\mu mol/g$ resin ^b	% ^c	$\mu mol/g$ resin ^c
Ni(II)	1.0	58.69	0.01	58.70	1.0	79.8	0.8	24.8	0.248	19.8	0.198
Pb(II)	1.0	207.20	0.01	207.20	1.0	79.8	0.8	30.1	0.301	24.0	0.240
Cd(II)	1.0	112.45	0.01	112.40	1.0	79.8	0.8	21.9	0.219	17.5	0.175
Cu(II)	1.0	63.55	0.01	63.55	1.0	79.8	0.8	23.2	0.232	18.5	0.185

The conditions were 10°C, pH 8.0, 28%, and 10 mg of P(NDAPA-co-AA resin)

^a Considering all the metal ions in the mixture.

^b Considering the value in footnote a as 100%.

^c Considering the retention of each metal ion in the mixture. The sum of the values gives the value determined in footnote a.

to increase again at pH 8.0. This could explain the different types of interactions or bindings between the ligand sites and metal ions at different pHs, as well as the fact that the autoprotolysis effect is not important for the P(NDAPA-co-AA) resin.

The highest retention values for PAA (see Fig. 2) are at pH 8.0: 70% for Ni(II), 74% for Pb(II), 88% for Cd(II), and 87% for Cu(II). It is different with respect to the P(NDAPA-co-AA) resin, which shows a higher retention of 80% for Pb(II) and Cd(II) ions, 50% for Ni(II), and 61% for Cu(II). The different retention capacities with respect to the pH (6.0–8.0) are significant for the two resins.

At neutral pH there is a decrease of the retention values of PAA for Pb(II) and Cu(II). This can be explained by the water autoprotolysis²² that occurs at this region, producing hydroxyl groups that can interfere with the adsorption of the trace metal ions.

At pH 8.0 PAA shows the highest retention values for Cd(II) and Cu(II).^{23–27} This occurs because of the similar acid properties of these metal ions, the stability of the complex, and the hard base characteristic of the polymer that is due to the presence of oxygen in the carboxylate groups, favoring polymer–metal ion complex formation.

The highest retention values of P(NDAPA-co-AA) at pH 8.0 correspond to Pb(II) and Cd(II). This can be attributed to the presence of two nitrogens at the ligand, giving a weak base character.

Effect of resin/metal ion ratio on retention of Ni(II), Pb(II), Cd(II), and Cu(II)

By keeping the concentration of the metal ion solution (4.0 μM) constant and changing the concentration of P(NDAPA-co-AA) (from 0.0439 to 0.4386 mmol), the metal ion retention capacity changed significantly for Ni(II). This indicates dependence on the number of ligand sites and probable steric hindrance on the retention capacity of the resin (see Table I).

For the PAA resin the concentration changed from 0.1389 to 1.3889 mmol. With a resin/metal ion ratio of 1:10, no important changes were observed on the retention, except for Cd(II), for which a decrease close to 10% was observed. This variation can be related to the study at low concentrations, which are close to the limit of detection. These results are important to determine the minimum amount and the optimum resin (see Table II).

TABLE IV
Metal Ion Retention Behavior from Quaternary Metal Ion Mixture

Metal ion mixture	Initial metal ion concn					Retention					
	μM	$\mu g/L$	μmol	$\mu g/g$ resin	$\mu mol/g$ resin	%	$\mu mol/g$ resin ^a	%	$\mu mol/g$ resin ^b	%	$\mu mol/g$ resin ^c
Ni(II)	1.0	58.69	0.01	58.70	1.0	76.0	0.76	25.3	0.253	19.25	0.193
Pb(II)	1.0	207.20	0.01	207.20	1.0	76.0	0.76	28.0	0.280	21.25	0.213
Cd(II)	1.0	112.45	0.01	112.50	1.0	76.0	0.76	22.7	0.227	17.25	0.173
Cu(II)	1.0	63.55	0.01	63.55	1.0	76.0	0.76	24.0	0.240	18.25	0.183

The conditions were 14°C, pH 8.0, 28%, and 10 mg of P(NDAPA-co-AA resin)

^a Considering all the metal ions in the mixture.

^b Considering the value in footnote a as 100%.

^c Considering the retention of each metal ion in the mixture. The sum of the values gives the value determined in footnote a.

TABLE V
Metal Ion Retention Behavior from Quaternary Metal Ion Mixture

Metal ion mixture	Initial metal ion concn					Retention					
	μM	$\mu\text{g/L}$	μmol	$\mu\text{g/g resin}$	$\mu\text{mol/g resin}$	% ^a	$\mu\text{mol/g resin}^a$	% ^b	$\mu\text{mol/g resin}^b$	% ^c	$\mu\text{mol/g resin}^c$
Ni(II)	1.0	58.69	0.01	58.70	1.0	77.0	0.77	25.7	0.257	19.8	0.198
Pb(II)	1.0	207.20	0.01	207.20	1.0	77.0	0.77	28.6	0.286	22.0	0.220
Cd(II)	1.0	112.45	0.01	112.50	1.0	77.0	0.77	21.0	0.210	16.2	0.162
Cu(II)	1.0	63.55	0.01	63.55	1.0	77.0	0.77	24.7	0.247	19.0	0.190

The conditions were 17°C, pH 8.0, 28‰, and 10 mg of P(NDAPA-co-AA resin).

^a Considering all the metal ions in the mixture.

^b Considering the value in footnote a as 100%.

^c Considering the retention of each metal ion in the mixture. The sum of the values gives the value determined in footnote a.

Effect of salinity on retention capacity of resins

For P(NDAPA-co-AA), as the concentration of the counterion increases from 0.48 to 0.60 mol/L, sodium chloride (see Fig. 3) increases the competition for polymer ligand sites and slightly decreases the retention of Ni(II) and Cd(II), but there is no effect on the adsorption of Pb(II). However, the retention of Cu(II) is strongly affected.

Figure 4 shows that an increase of the salinity from 28 to 35‰ sharply decreases the retention of Ni(II) and Pb(II) ions. This indicates that the equilibrium favors the proton exchange by sodium cations and only the trace metal ion transition, demonstrating that for Ni(II) and Pb(II) the retention with PAA is more important by ion exchange than by a complexing reaction.²⁸ The effect of the salinity on the retention is very complex because, on the one hand, they are acting as the link forces of the transition metal ion with the ligands and, on the other hand, competence exists between the cations of the binding sites. Moreover, the formation of chloride complexes in the solution is favored.

Effect of quaternary metal ion mixture on retention

In comparison, the retention behavior for the metal ion mixture for P(NDAPA-co-AA) at 17°C and pH 8.0 with

the noncompetitive run under the same experimental conditions shows the retention of Ni(II) and Pb(II) ions is not significantly affected, but for Cd(II) ions there is an important decrease and the retention of Cu(II) ions is also considerably increased. This demonstrates the competence of these ions for the same polymer ligand sites. However, the retention at different temperatures does not show an important effect for all metal ions (see Tables III–V).

Tables VI, VII, and VIII show the results of the metal ion retention from the quaternary mixture for PAA. A slight increase was observed in the retention of Pb(II), Cd(II), and Cu(II) ions at three temperatures from 10 to 14°C, and then there was a slight decrease, which could be explained by the synergic effect produced at higher temperature and salinity, giving faster adsorption rates. The distribution constant (K_d) values are high for P(NDAPA-co-AA) and PAA with a lower selectivity for the metal ions. This is very important to applying the resin to purify water containing mixtures of trace metal ions.

Effect of temperature on retention capacity

Figure 5 shows that the retention of Ni(II), Pb(II), and Cd(II) ions does not depend on the temperature, but there is a tendency to decrease the retention of Cu(II),

TABLE VI
Metal Ion Retention Behavior from Quaternary Metal Ion Mixture

Metal ion mixture	Initial metal ion concn					Retention					
	μM	$\mu\text{g/L}$	μmol	$\mu\text{g/g resin}$	$\mu\text{mol/g resin}$	% ^a	$\mu\text{mol/g resin}^a$	% ^b	$\mu\text{mol/g resin}^b$	% ^c	$\mu\text{mol/g resin}^c$
Ni(II)	1.0	58.69	0.01	58.70	1.0	69.5	0.695	19.9	0.20	13.8	0.14
Pb(II)	1.0	207.20	0.01	207.20	1.0	69.5	0.695	23.7	0.24	16.5	0.17
Cd(II)	1.0	112.45	0.01	112.40	1.0	69.5	0.695	29.5	0.30	20.5	0.21
Cu(II)	1.0	63.55	0.01	63.55	1.0	69.5	0.965	27.0	0.27	18.8	0.19

The conditions were 10°C, pH 8.0, 28‰, and 10 mg of the DAPA resin).

^a Considering all the metal ions in the mixture.

^b Considering the value in footnote a as the 100%.

^c Considering the retention of each metal ion in the mixture. The sum of the values gives the value determined in footnote a.

TABLE VII
Metal Ion Retention Behavior from Quaternary Metal Ion Mixture

Metal ion mixture	Initial metal ion concn					Retention					
	μM	$\mu g/L$	μmol	$\mu g/g$ resin	$\mu mol/g$ resin	% ^a	$\mu mol/g$ resin ^a	% ^b	$\mu mol/g$ resin ^b	% ^c	$\mu mol/g$ resin ^c
Ni(II)	1.0	58.69	0.01	58.70	1.0	74.3	0.743	20.2	0.20	15.0	0.15
Pb(II)	1.0	207.20	0.01	207.20	1.0	74.3	0.743	21.3	0.21	15.8	0.16
Cd(II)	1.0	112.45	0.01	112.50	1.0	74.3	0.743	28.3	0.28	21.0	0.21
Cu(II)	1.0	63.55	0.01	63.55	1.0	74.3	0.743	30.3	0.30	22.5	0.23

The conditions were 14°C, pH 8.0, 28‰, and 10 mg of PAA resin.

which is different than the behavior shown by the mixture. Figure 6 shows that there is no affect on the retention of Pb(II), Cd(II), and Cu(II) ions at the studied temperatures, but the retention of Ni(II) shows a small increase that would imply a different retention mechanism.

Effect of time on retention

For P(NDAPA-co-AA) (see Fig. 7) the half-life ($t_{1/2}$) for Cd(II) is achieved before 2.0 min and for Ni(II), Pb(II), and Cu(II) before 5.0 min. Figure 7 shows the kinetics for the metal ion retention. The highest was obtained for Cd(II).

For PAA, Cd(II) achieves equilibrium at close to 10 min and Ni(II), Pb(II), and Cu(II) at about 50 min. The retention for Cu(II) is low during the first 30 min, increasing at 40 min (see Fig. 8). The $t_{1/2}$ value for Ni(II) is achieved at 1.0 min, for Pb(II) at 2.0 min, and Cd(II) and Cu(II) at 40 min.

Recovery of resin in acid medium

Four mole HNO₃ is a very good eluent to recover Pb(II) (100%) but only 53% Cd(II) was recovered from the loaded P(NDAPA-co-AA). For the other ions the elution was poor at Ni(II) and Cu(II) levels of 38 and 26%, respectively. It was necessary to carry out new

runs with other eluents and at other concentrations (see Table IX).

The desorption from loaded PAA with 4.0M HNO₃ was complete for Pb(II) and Cu(II) and 62 and 80% for Ni(II) and Cd(II), respectively (see Table X).

Retention from natural seawater

The physicochemical parameters of the coastal seawaters of Puerto Montt Bay vary among the normal range: 10–19°C, pH 7.5–8.4, and 23 and 33‰ salinity.^{29,30} Table XI summarizes the most important characteristics of the seawater. The values of the pH, salinity, and temperature variables are among the ranges employed in the different experimental essays to study the retention properties of the resins with artificial seawater.

Table XII shows the retention for both resins including a weak base commercial resin as a comparison.

The sampling was carried out during the spring and summer where only Cu(II) was detected at a high concentration at Chiquihue and Pargua. In Huito and Huelmo the presence of Cd(II) and Cu(II) was determined. The sampling point was always the same, depending on the type of tide. The retention was also studied by the batch equilibrium procedure without modifying the pH of the sample at 17°C.

TABLE VIII
Metal Ion Retention Behavior from Quaternary Metal Ion Mixture

Metal ion mixture	Initial metal ion concn					Retention					
	μM	$\mu g/L$	μmol	$\mu g/g$ resin	$\mu mol/g$ resin	% ^a	$\mu mol/g$ resin ^a	% ^b	$\mu mol/g$ resin ^b	% ^c	$\mu mol/g$ resin ^c
Ni(II)	1.0	58.69	0.01	58.70	1.0	72.5	0.725	17.2	0.17	12.5	0.13
Pb(II)	1.0	207.20	0.01	207.20	1.0	72.5	0.725	25.2	0.25	18.3	0.18
Cd(II)	1.0	112.45	0.01	112.50	1.0	72.5	0.725	27.6	0.28	20.0	0.20
Cu(II)	1.0	63.55	0.01	63.55	1.0	72.5	0.725	30.0	0.30	21.8	0.22

The conditions were 17°C, pH 8.0, 28‰, and 10 mg of PAA resin.

^a Considering all the metal ions in the mixture.

^b Considering the value in footnote a as 100%.

^c Considering the retention of each metal ion in the mixture. The sum of the values gives the value determined in footnote a.

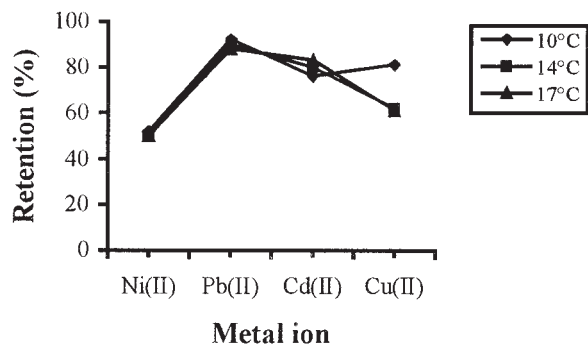


Figure 5 The effect of the temperature on the metal ion retention at pH 8.0, 28‰ salinity, and 10 mg of P(NDAPA-co-AA).

The metal ion retention capacity of both resins is similar with natural and artificial seawater and is also comparable with those values for the commercial resin (see Table XII).

For P(NDAPA-co-AA), the retention for the samples containing only Cu(II) is higher (83–86%) compared to that found for samples of artificial seawater (61%). This indicates that the effect of the other components of the natural seawater favors the ligand–Cu(II) interaction. For samples from Huito and Huelmo which

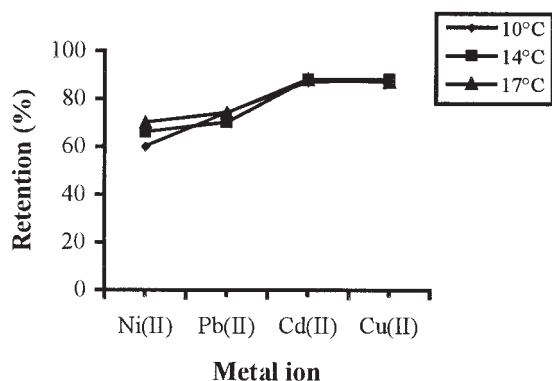


Figure 6 The effect of the temperature on the metal ion retention at pH 8.0, 28‰ salinity, and 10 mg of PAA.

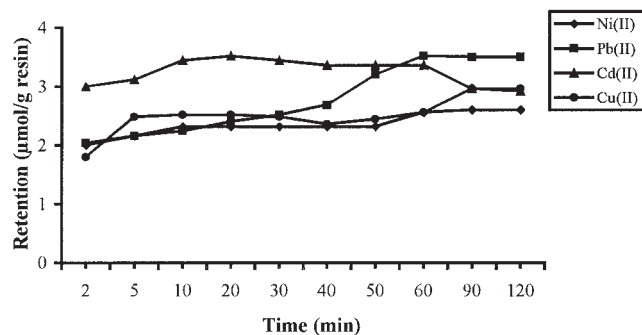


Figure 7 The effect of time on the metal ion retention at 17°C, pH 8.0, 28‰ salinity, and 10 mg of P(NDAPA-co-AA).

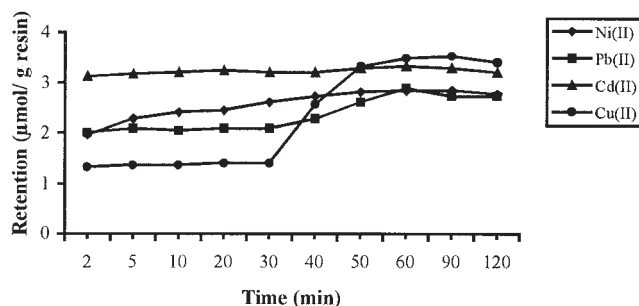


Figure 8 The effect of time on the metal ion retention at 17°C, pH 8.0, 28‰ salinity, and 10 mg of PAA.

contain Cd(II), the retention of Cu(II) decreases to close to the values obtained in experimental runs. Moreover, the retention values of Cd(II) are higher than those obtained with artificial seawater. For the sample from Huelmo, the retention of Cu(II) is lower than the value found for the sample from Huito. In this case it is an additional effect of the pH close to 7.0.

PAA presents a retention value for Cu(II) that is close to 90% for samples from Chinquihue and Pargua, which is similar to those found for the noncompetitive runs. However, this value ranges for Huito and Huelmo, where the effect of the pH and the mixture could be indicating the selectivity of the resin for one metal ion.

The commercial resin Dowex shows a similar retention capacity for the synthesized resins. However, P(NDAPA-co-AA) shows a higher retention capacity for Cd(II) in seawater samples.

TABLE IX
Regeneration of P(NDAPA-co-AA) resin by HNO₃ at 17°C

Metal ion	Initial metal ion concn			4.0M HNO ₃		
	μM	μg/L	μmol/g resin	%	μg/L	μmol/g resin
Ni(II)	3.10	181.77	3.10	38	69.0	1.18
Pb(II)	3.90	808.2	3.90	100	808.2	3.90
Cd(II)	3.32	373.2	3.32	53	197.8	1.76
Cu(II)	2.74	174.2	2.74	26	45.3	0.71

TABLE X
Regeneration of PAA resin by HNO₃ at 17°C

Metal ion	Initial metal ion concn			4.0M HNO ₃		
	μM	μg/L	μmol/g resin	%	μg/L	μmol/g resin
Ni(II)	2.58	164.34	2.58	62.0	101.9	1.74
Pb(II)	2.96	613.3	2.96	100.0	613.3	2.96
Cd(II)	2.88	323.7	2.88	80.0	259.0	2.30
Cu(II)	3.48	221.15	3.48	100.0	221.1	3.48

TABLE XI
Characteristics of Upper Part of Seawater Column

Sample	Acronym	Distance of beach (m)	pH	Salinity (%)	T (°C)	Observation
Chinquihue	Ch1	300	8.0	28	13	Low tide, cloudy
	Ch2	300	7.9	28	13	Low tide, cloudy
	Ch3	200	8.5	30	16	Low tide, sunny
Huito	H	30	8.4	30	17	Flood tide, sunny
Huelmo	Hu	50	7.2	29	17	Flood tide, sunny
Pargua	P1	30	7.8	28	14	Low tide, rain
	P2	30	8.0	29	13	Low tide, rain
	P3	20	8.1	33	16	Flood tide, sunny

TABLE XII
Retention Capacity of Resin on Seawater for PAA, P(NDAPA-co-AA), and Dowex (commercial resin)

Acronym	Metal ion	Initial concn mg/L	Retention					
			P(NDAPA-co-AA)		PAA		Dowex	
			%	µg/L	%	µg/L	%	µg/L
Ch1	Cu(II)	618.7	86.0	532.1	85.0	525.9	86.0	513.5
Ch2	Cu(II)	904.0	84.0	759.4	93.0	804.7	85.0	768.4
Ch3	Cu(II)	531.7	84.0	446.7	89.0	473.2	85.0	452.0
H	Cu(II)	222.8	67.0	149.3	67.0	149.3	63.0	140.3
	Cd(II)	13.10	100	13.1	86.0	11.30	81.0	10.60
Hu	Cu(II)	180.8	57.0	103.1	50.0	90.40	66.0	119.3
	Cd(II)	13.33	100	13.33	86.0	11.40	89.0	11.90
P1	Cu(II)	159.0	83.0	132.0	97.0	154.2	88.0	139.9
P2	Cu(II)	38.67	85.0	32.87	98.0	37.00	87.0	33.60
P3	Cu(II)	129.3	84.0	108.6	85.0	109.9	89.0	115.1

CONCLUSIONS

Two resins were synthesized by radical polymerization, P(NDAPA-co-AA) as a multidentate resin at pH 8.0 and PAA as a bidentate resin (2 atoms or possible groups to participate in the retention). P(NDAPA-co-AA) preferably retains >80% Pb(II) and Cd(II) ions and PAA retains >80% Cd(II) and Cu(II) ions. Steric hindrance plays an important role in the retention behavior of P(NDAPA-co-AA).

At pH 8.0, P(NDAPA-co-AA) showed the highest retention capacity for Pb(II) (88%) and Cd(II) (83%) and PAA showed the highest affinity for Cd(II) (88%) and Cu(II) (87%).

The K_d values are high for the metal ions and for both resins. This suggests that, nevertheless, the resins are not selective for interaction with metal ions from natural seawater. These resins behave as good adsorbents of metal ions from mixtures, which favor their use for the treatment of contaminated waters.

The differences in the metal ion retention capacity may be attributed to different sizes (hydrated ions) and to the type of binding with the ligand.

The effect of the salinity on the retention capacity showed that it decreases as the concentration of sodium chloride increases from 0.48 to 0.6M, except for Pb(II) for P(NDAPA-co-AA) and for Cd(II) for PAA.

The metal ion retention capacity results of the two resins for natural seawater are similar to those obtained for artificial seawater. Only Cu(II) showed erratic behavior.

According to these results, the variables that significantly affect the retention properties are the pH, salinity, composition of the sample, temperature, and presence of different metal ions.

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