

# Metal Ion Retention Properties of Water-Insoluble Polymers Containing Carboxylic Acid Groups

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**ABSTRACT:** Crosslinked poly(acrylic acid), PAA, and poly(2-acrylamidoglycolic acid), PAAG, were synthesized by radical polymerization. Both resins contain carboxylic acid groups. PAA at basic pH exists basically as an acrylate anion and PAAG shows three atoms or groups, carboxylic acid, hydroxyl, and amide groups, that can act as ion exchanger or chelating groups. Both resins are studied as adsorbents to trace metal ions from saline aqueous solutions and natural sea water and their properties by Batch equilibrium procedure are compared. The metal ions studied under competitive and noncompetitive conditions were Cu(II), Pb(II), Cd(II), and Ni(II). The effects of pH, time of contact, amount of resin, temperature, and salinity were

studied. Resin PAA shows a high affinity (>80%) for Cu(II) and Cd(II) and resin PAAG shows also a high affinity for Ni(II), Pb(II), and Cd(II). By treatment of the metal ion-loaded resin with 4M HNO<sub>3</sub> it is possible to recover completely the Cu(II) ions from resin PAA and Ni(II) and Pb(II) from resin PAAG. The metal ion retention properties were studied with natural sea water. For those natural sea waters containing Cu(II) and Cd(II), the resins showed a high affinity for Cd(II) ions. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 697–705, 2006

**Key words:** resin; radical polymerization; metal-polymer complex

## INTRODUCTION

The presence of heavy metal ions in the environment is one of the major concerns due to their toxicity to many life forms. Numerous research efforts are being performed to develop methods to remove metal ions, particularly in waste streams of hydrometallurgy and related industries, and to subsequently reuse them. Heavy metals are toxic to aquatic systems even in relatively low concentrations. The development of an effective treatment process for wastewater has been considered one of the most important requirements in recent wastewater treatment because numerous numbers of components are contained in wastewaters from various factories, and appropriate methods should be applied for treatment according to the components therein. Most treatment methods to remove metal ions from wastewater include extraction, chemical precipitation, simple and chelating ion exchange, sorption, membrane systems, etc.<sup>1–24</sup> Among these, selective adsorptions using biological materials, carbons, or polymer resins have generated great interest in the environmental and science fields. Ion exchange and chelating resins are very important to metal-ion bind-

ing reactions because of their hydrophylicity, accessibility, and high capacity, but the synthesis of a polymer with a greater degree of selectivity could be important to different applications. However, because there are a wide range of materials and methods of synthesis, it is not surprising that a chelating exchanger's physical form may vary from a rock-hard material to a soft gel. The desirable properties of chelating exchangers are fourfold: (1) a high capacity for the metal(s) of interest, (2) high selectivity, (3) fast kinetics and rapid equilibration with metal-containing solutions, and (4) high mechanical strength and toughness of the exchanger/chelating particles. Unfortunately the last two are competitive.

With respect to the low concentrations and handling of large volumes of aqueous solution, extraction procedures are uneconomic, and precipitation procedures require the addition of relatively large amounts of chemicals, whereas applications of sorption or exchange on solids are preferable. This makes the use of exchangers for selective separation of heavy metal ions very attractive.

Because of the chelating nature of the metal ions, chelating resins are widely used in the preconcentration, separation, recovery, and hydrometallurgy of metal ions, in which various chelating groups have been incorporated and are attached to the polymer matrix. Synthesis of such functionalized polymers has

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been accomplished using either polymerization or simple functionalization principles.

The aim of this paper is to describe the metal ion adsorption behavior for Cu(II), Ni(II), Pb(II), and Cd(II) of the crosslinked poly(acrylic acid), PAA, and poly(2-acrylamidoglycolic acid), PAAG, at different pH, time of contact, concentration, temperature, and salinity. This is because some of these trace metal ions such as Cu(II) and Ni(II) occur naturally in the sea and they are essential for marine organisms, but they are potentially toxic depending on the bioavailability.

## EXPERIMENTAL

### Reagents

Acrylic acid, (Merck, Stuttgart, Germany), was purified by distillation. Ammonium persulfate (PSA, Merck), *N,N'*-methylene-bisacrylamide, (MBA, 99% Aldrich, Milwaukee, WI, USA), were used as initiator and crosslinking reagents and used as received. Also used were diammonium citrate hydrogen (Merck), ammonium pyrrolidin dithiocarbamate (Aldrich), *N,N'*-diethyl diethylammonium dithiocarbamate, (Merck), nitric acid suprapur (Merck), sodium chloride (Merck), standard solutions of 1000 ppm (Merck) of each metal ion, and twice-distilled water (Millipore). All reagents were analytical grade.

### Synthesis of resins PAA and PAAG

Resins PAA and PAAG were obtained by radical polymerization. To synthesize PAAG, 0.066 mol (11.6 g) of 2-acrylamidoglycolic acid was dissolved in twice-distilled water and added to a polymerization flask. A total of 4 mmol (0.61 g) of MBA as crosslinking and 0.2 mmol (6 mol %) of PSA as initiator reagents, respectively, were added. The polymerization mixture was kept for 1 h at 70°C.

To synthesize resin PAA, 0.066 mol (4.8 g) of acrylic acid, 4 mmol of MBA, and 0.2 mmol (6 mol %) of PSA were added to the polymerization flask. It was kept for 5 min at 70°C.

The resins were washed with abundant water and dried under vacuum until constant weight. The yields were 98% for PAAG and 93% for PAA.

### Study of the metal ion retention properties by Batch equilibrium procedure

The effect of pH on metal ion retention was studied for each resin. A total of 10 mg of dry resin (particle size: 180–250  $\mu\text{m}$ ) was placed in a quartz tube and contacted at 17°C for 1 h under constant stirring with 10 mL of the aqueous solution containing  $4.0 \times 10^{-6}$  M of each metal ion Ni(II), Pb(II), Cd(II), and Cu(II). The pH varied between 6.0 and 8.0. 0.1M NaOH and 0.1M

HNO<sub>3</sub> was used to adjust the pH. The solution was separated by decantation and centrifugation. The 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 was added to 10 mL of the quaternary aqueous metal ion solution containing  $1.0 \times 10^{-6}$  M (1.0  $\mu\text{M}$ ) of each metal ion. After 1 h under stirring, the sample was treated as described before for the noncompetitive run.

The effect of time on metal ion retention was studied by placing 10 mg of dry resin and 10 mL of aqueous solution of each metal ion (salinity 28‰, concentration of metal ion: 4  $\mu\text{M}$ , 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 salinity, temperature, and elution in acid medium was studied. Similar studies were conducted with natural sea water. For all runs the metal ion concentration was determined in the filtrate with adequate dilution. The retention capacity of each resin was obtained from the difference of the initial and final concentrations of metal ion.

### Buffer solution of complexing citrate

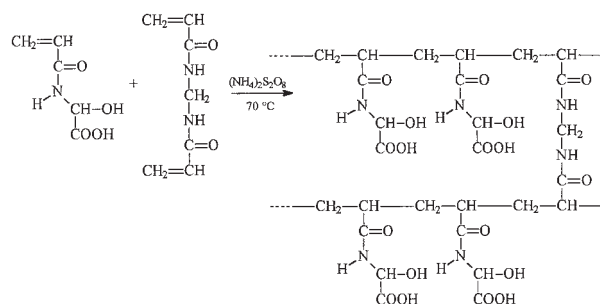
The complexant citrate buffer solution was prepared by dissolving 62.5 g of diammonium hydrogen citrate (Merck) in 125 mL of deionized water (Barnsted, Nanopure) and adding 55 mL of ammonia solution (25% Merck). It was carried out in a 250-mL volumetric flask made of quartz, which was finally filled up to a volume of 250 mL with deionized water.

### Complexation and extraction

To a flask containing a subsample of 50 mL, 2 mL of complexant citrate buffer solution and 2 mL of *n*-heptane were added. The mixture was vigorously shaken and stored for 15 min until both were separated and then the re-extraction was performed. The role of the complexant citrate buffer solution is to obtain the complete extraction of the metal ions and less interference determination.

### Collection of seawater samples

The sea water samples were collected in the regions of Chiquihue, Pargua, Huito, and Huelmo, places close to Puerto Montt. This city is located 1025 km south of the capital of Chile, Santiago. The samples corresponding to the surface waters were placed in glass bottles and immediately filtered with a sterilized membrane of 0.45  $\mu\text{m}$  and stored at  $-5^\circ\text{C}$ .



Scheme 1

### Measurements

pH was measured with a pH meter Hanna Model HI 9023 (USA). Metal ions Cu(II), Ni(II), Pb(II), and Cd(II) were determined by an atomic absorption spectrophotometer UNICAM Solaar M-5 with graphite furnace GF-95 and "autosampler" FS-95 (AAS) (UK) and with an atomic absorption spectrophotometer GF-Perkin-Elmer, Model 3110 HGA-600 with "autosampler" (Perkin-Elmer Cetus Instruments, Norwalk, CT, USA).

The detection limits were as follows: Cd,  $0.1 \mu\text{g L}^{-1}$ ; Cu,  $0.4 \mu\text{g L}^{-1}$ ; Ni,  $1.0 \mu\text{g L}^{-1}$ ; and Pb,  $0.7 \mu\text{g L}^{-1}$ .

## RESULTS AND DISCUSSION

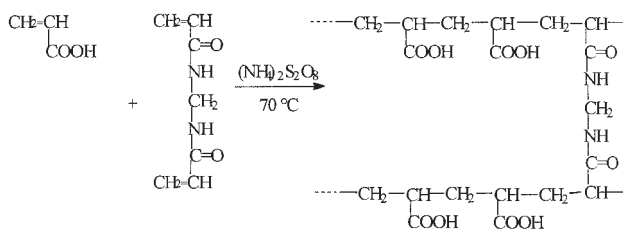
Resins PAAG and PAA, and were synthesized by radical polymerization (see Schemes 1 and 2). The resins are solids that are completely insoluble in water. The yields were 98 and 93%, respectively.

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

### Study of the metal ion retention properties of the resins by Batch equilibrium procedure

#### Effect of pH on metal ion retention

The effect of pH on metal ion retention is determined by modification of metal ion concentration and by



Scheme 2

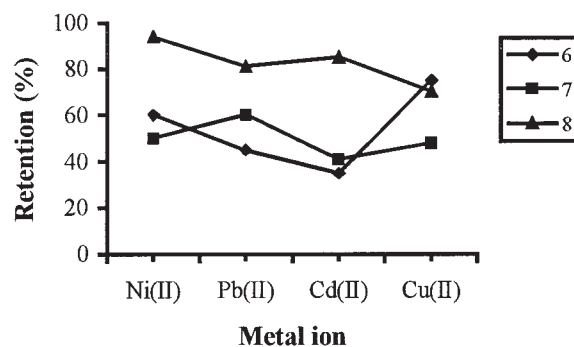


Figure 1 Effect of pH on metal ion retention (17°C, 28‰, 10 mg PAAG,  $4.0 \mu\text{M}$ ).

modification of the ratio between acid form (COOH) and basic form ( $-\text{COO}^-$ ) of the carboxylic groups.

Resin PAAG shows at pH 8.0 the highest retention values for Ni(II), Pb(II), Cd(II), and Cu(II). The increase of pH produces an important increase of the retention of Ni(II), Pb(II), and Cd(II) ions. The highest retention capacity for Ni(II), Pb(II), and Cd(II) at pH 8.0 is about 80%, but for Cu(II) it was observed at pH 6.0. Moreover, for the two resins, it is observed that at pH 7.0, the retention passes at the lowest value (see Figs. 1 and 2). This is observed for resin PAAG with Cu(II) and Ni(II) and for PAA with Pb(II) and Cu(II). This decrease is more pronounced for Cu(II) with resin PAA. This could be explained for the different types of interaction or binding between the ligand and the metal ion at different pH.

The high retention values at pH 8.0 for PAAG for Ni(II), Pb(II), and Cd(II) (see Fig. 1) could be explained by the predominant chemical species, for cadmium  $\text{Cd}(\text{OH})^+$  and  $\text{Cd}^{+2}$ , where the latter is favored by the low concentration in solution; nickel as soluble  $\text{Ni}^{+2}$ ; lead as soluble  $\text{Pb}(\text{OH})_2$ ; copper as  $\text{Cu}(\text{OH})_2$ , which could be soluble at this pH and low concentration.

For resin PAA (see Fig. 2) the highest retention affinity is observed at pH 8, Ni(II) (70%), Pb(II) (74%), Cd(II) (84%), and Cu(II) (88%). The change in retention

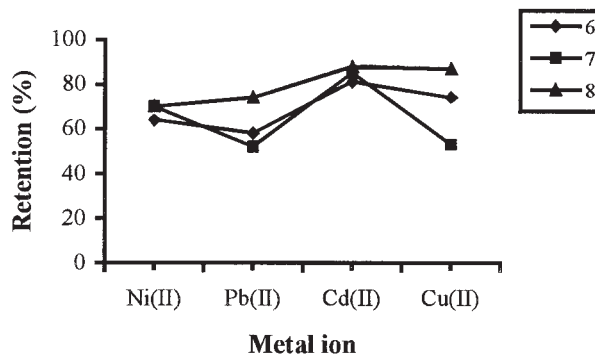


Figure 2 Effect of pH on metal ion retention (17°C, 28‰, 10 mg PAA,  $4.0 \mu\text{M}$ ).

**TABLE I**  
Effect of the Metal Ion : PAAG Resin Ratio on Adsorption Behavior (17°C, pH 8.0, 28‰, and 4.0 μM)

Metal ion	Initial metal ion concentration		mmol resin							
			0.06896		0.17240		0.34480		0.68970	
	(μg/L)	(μmol)	Retention		Retention		Retention		Retention	
		(μmol/mmol resin)	(%)	(μmol/mmol resin)	(%)	(μmol/mmol resin)	(%)	(μmol/mmol resin)	(%)	
Ni(II)	234.77	0.04	0.54520	94.0	0.2204	95.0	0.11140	96.0	0.05394	93.0
Pb(II)	828.8	0.04	0.46404	80.0	0.1624	70.0	0.18580	74.0	0.04118	71.0
Cd(II)	449.64	0.04	0.49304	85.0	0.1995	86.0	0.0986	85.0	0.04814	83.0
Cu(II)	254.2	0.04	0.41760	72.0	0.1346	60.0	0.07309	63.0	0.03306	60.0

by changing the pH from 6.0 to 8.0 is important only for Cu(II) and Pb(II) ions.

The retention capacity for Ni(II), Pb(II), and Cu(II) decreases at neutral pH for both resins, probably due to water autoprotolysis.<sup>25</sup>

The high retention values at pH 8.0 of resin PAA for Cd(II) and Cu(II)<sup>26–30</sup> could be explained by the similar acid properties of these two metal ions, the stability of the complex, and the hard base characteristics of the polymer, through the presence of the oxygen at the carboxylate groups, favor the polymer–metal ion complex formation.

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

The effect of resin/metal ion ratio on trace metal retention of Ni(II), Pb(II), Cd(II), and Cu(II) was studied by keeping constant the metal ion solution concentration (4.0 μM) and changing the amount of resin PAAG (0.06896 mmol to 0.6896 mmol) and PAA (0.1389 mmol to 1.3889 mmol). The retention capacity of the resins does not depend on the number of available ligands, as the amount of metal ion retained from the aqueous solution keeps almost constant the resin's capacity to retain the metallic ion (see Tables I and II). Upon increasing the resin metal ion ratio 10 times, no important changes were observed on retention behavior, except for Pb(II), Cu(II), and Cd(II) where a de-

crease close to 10% was observed, attributed probably to work at low concentrations, near the detection limit.

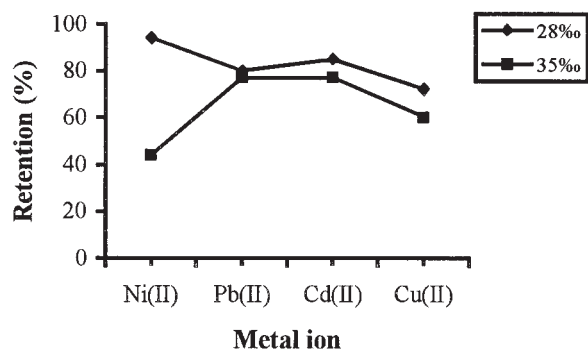
Effect of salinity on metal ion retention capacity

Sodium ion is a very common counterion in weakly acid chelating polymers, in sea waters, and in additives for different industrial processes. Therefore, it is possible to find concentrations of sodium of several higher magnitude orders with respect to the transition metal ions in different effluent systems, decreasing the polymer–metal ion complex.

By increasing the concentration of the counterion from 0.48 to 0.65 mol/L (see Fig. 3), where the concentrations are 28‰ (0.48 mol/L) and 35‰ (0.65 mol/L), increases the competition for the ligand sites of resin PAAG, therefore decreasing the affinity for Ni(II) ions. For Ni(II) ions this would indicate that retention may be described through both cation exchange and chelation processes. For Cd(II), Pb(II), and Cu(II) the retention model would involve a complex formation, which is in agreement with the stability constant of the resin–metal ion complex. It would favor Cd(II) and Cu(II), which are weak acids, and they act more easily with a weak base as the nitrogen from the amide group. Moreover, for PAA (see Fig. 4) an increase of the salinity from 28 to 35‰ decreases significantly the retention of Ni(II) and Pb(II) ions, which would indi-

**TABLE II**  
Effect of the Metal Ion : PAA Resin Ratio on Adsorption Behavior (17°C, pH 8.0, 28‰, and 4.0 μM)

Metal ion	Initial metal ion concentration		mmol resin							
			0.1389		0.3472		0.6944		1.3889	
	(μg/L)	(μmol)	Retention		Retention		Retention		Retention	
		(μmol/mmol resin)	(%)	(μmol/mmol resin)	(%)	(μmol/mmol resin)	(%)	(μmol/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



**Figure 3** Effect of salinity on metal ion retention (17°C, pH 8.0, and 10 mg of PAAG).

cate that the equilibrium favors proton exchange by sodium ions and it could be possible to exchange trace amounts of the transition metal ion. This also would demonstrate that for Ni(II) and Pb(II) ions the exchange retention process of poly(acrylic acid) is more important than the complex formation. The  $K_d$  values for Cd(II) and Cu(II) ions do not vary significantly, which would indicate that there is an important increase of the retention of sodium and that the retention mechanism involves the coordinate covalent bonds or physically trapping at the polymer chain.<sup>30</sup>

#### Effect of metal ion quaternary mixture on retention

By comparison of the effect of the metal ion mixture at pH 8.0 and at 10 and 17°C on the retention properties of resin PAAG (see Tables III and IV) it is observed that the lower temperature favors the retention of Ni(II) and Pb(II) but there is not an important effect for Cd(II) and Cu(II) ions. The retention of copper depends strongly on whether it is present in a mixture or is alone (see Tables V and VI). The retention capacity of Ni(II), Pb(II), and Cd(II) ions decreases slightly by increasing the temperature, which is different for Cu(II). These differences would indicate that in the metal ion mixture there is a strong competition for the polymer ligand/exchanger sites, the weak acid characteristics of the cations, and the synergic effect at high temperatures and low salinities, yielding a faster rate of retention.

Either for PAAG and PAA, the  $K_d$  values are high but the selectivity is low.

#### Effect of temperature on metal ion retention capacity

Figure 5 shows that the retention of Cd(II) and Cu(II) ions on PAAG resin increases by increasing the temperature, which is different when the metal ion is found in a mixture.

Figure 6 demonstrates that there is no important effect of temperature on the retention of Pb(II), Cd(II), and Cu(II) on PAA resin, but the retention of Ni(II) shows a slight increase, which would indicate the presence of a different retention mechanism for this metal ion.

#### Effect of contact time on metal ion retention

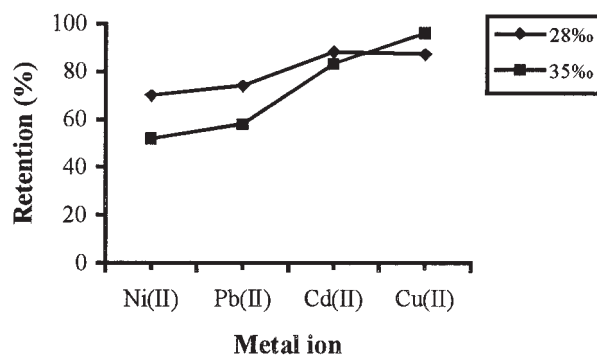
For the resin PAAG (see Fig. 7) it is observed that for Ni(II) and Cd(II) ions,  $t_{1/2}$  value is achieved within 1.0 min and for Pb(II) it is achieved before 5.0 min. Figure 7 shows the kinetics retention of the metal ions. Ni(II) presents the highest load rate. For resin PAA, only Cd(II) from the four metal ions studied achieves equilibrium within 10 min; Ni(II), Pb(II), and Cu(II) ions achieve equilibrium at 50 min approximately. The retention of Cu(II) is low during the first 30 min, increasing after 40 min (see Fig. 8). The  $t_{1/2}$  value for Ni(II) is achieved within 1.0 min and within 2.0 min for Pb(II) and Cd(II) and 40 min for Cu(II).

#### Regeneration of the resin by treatment with acid medium

By treatment of the metal ion-loaded resin with 4M nitric acid it is possible to remove completely Ni(II) and Pb(II) ions from loaded PAAG (see Table VII) and Pb(II) from the loaded PAA resin (see Table VII). The elution of other ions is lower, 62% for Ni(II) and 80% for Cd(II) (see Table VIII).

#### Metal ion retention behavior from natural sea water

Table IX summarizes the most important characteristics of the sea water analyzed, the values of salinity, pH, and temperature, which are within the employed ranges in the different experimental assays for the artificial sea water.



**Figure 4** Effect of salinity on metal ion retention (17°C, pH 8.0, and 10 mg of PAA).

**TABLE III**  
**Metal Ion Retention Behavior from Quaternary Mixture (10°C, pH 8.0, 28%, and 10 mg of PAAG)**

Metal ion mixture	Initial concentration of metal ion					Retention					
	$\mu M$	$\mu g/L$	$\mu mol$	$\mu g/g$ resin	$\mu mol/g$ resin	% <sup>a</sup>	$\mu mol/g$ resin <sup>a</sup>	% <sup>b</sup>	$\mu mol/g$ resin <sup>b</sup>	% <sup>c</sup>	$\mu mol/g$ resin <sup>c</sup>
Ni(II)	1.0	58.69	0.01	58.70	1.0	85.8	0.858	29.0	0.29	25.00	0.250
Pb(II)	1.0	207.20	0.01	207.20	1.0	85.8	0.858	29.0	0.29	25.00	0.250
Cd(II)	1.0	112.45	0.01	112.50	1.0	85.8	0.858	26.0	0.26	22.3	0.223
Cu(II)	1.0	63.55	0.01	63.55	1.0	85.8	0.858	16.0	0.16	13.50	0.135

<sup>a</sup> Considering all metal ions in the mixture.

<sup>b</sup> Considering the value in footnote a as 100%.

<sup>c</sup> Considering the retention of each metal ion in the mixture. The sum of the values gives the value determined in footnote a.

**TABLE IV**  
**Metal Ion Retention Behavior from Quaternary Mixture (17°C, pH 8.0, 28%, and 10 mg of PAAG)**

Metal ion mixture	Initial metal ion concentration					Retention					
	$\mu M$	$\mu g/L$	$\mu mol$	$\mu g/g$ resin	$\mu mol/g$ resin	% <sup>a</sup>	$\mu mol/g$ resin <sup>a</sup>	% <sup>b</sup>	$\mu mol/g$ resin <sup>b</sup>	% <sup>c</sup>	$\mu mol/g$ resin <sup>c</sup>
Ni(II)	1.0	58.69	0.01	58.70	1.0	78.0	0.78	29.8	0.298	23.3	0.233
Pb(II)	1.0	207.20	0.01	207.20	1.0	78.0	0.78	26.0	0.260	20.3	0.203
Cd(II)	1.0	112.45	0.01	112.40	1.0	78.0	0.78	27.2	0.272	21.3	0.213
Cu(II)	1.0	63.55	0.01	63.55	1.0	78.0	0.78	17.0	0.170	13.3	0.133

<sup>a</sup> Considering all metal ions in the mixture.

<sup>b</sup> Considering the value in footnote a as 100%.

<sup>c</sup> 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 Mixture (10°C, pH 8.0, 28%, and 10 mg of PAA)**

Metal ion mixture	Initial metal ion concentration					Retention					
	$\mu M$	$\mu g/L$	$\mu mol$	$\mu g/g$ resin	$\mu mol/g$ resin	% <sup>a</sup>	$\mu mol/g$ resin <sup>a</sup>	% <sup>b</sup>	$\mu mol/g$ resin <sup>b</sup>	% <sup>c</sup>	$\mu mol/g$ resin <sup>c</sup>
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

<sup>a</sup> Considering all metal ions in the mixture.

<sup>b</sup> Considering the value in footnote a as 100%.

<sup>c</sup> Considering the retention of each metal ion in the mixture. The sum of the values gives the value determined in footnote a.

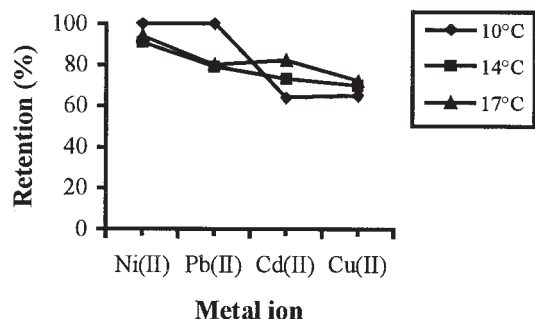
**TABLE VI**  
**Metal Ion Retention Behavior from Quaternary Mixture (17°C, pH 8.0, 28%, and 10 mg of PAA)**

Metal ion mixture	Initial metal ion concentration					Retention					
	$\mu M$	$\mu g/L$	$\mu mol$	$\mu g/g$ resin	$\mu mol/g$ resin	% <sup>a</sup>	$\mu mol/g$ resin <sup>a</sup>	% <sup>b</sup>	$\mu mol/g$ resin <sup>b</sup>	% <sup>c</sup>	$\mu mol/g$ resin <sup>c</sup>
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

<sup>a</sup> Considering all metal ions in the mixture.

<sup>b</sup> Considering the value in footnote a as 100%.

<sup>c</sup> Considering the retention of each metal ion in the mixture. The sum of the values gives the value determined in footnote a.



**Figure 5** Effect of temperature on metal ion retention (pH 8.0, 28%, and 10 mg of PAAG).

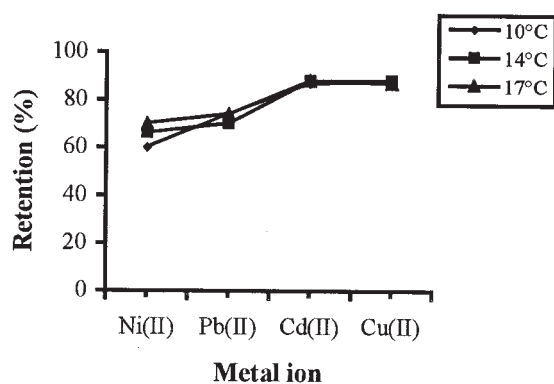
Table X shows the retention properties for the two synthesized resins and the weak acid commercial Dowex resin.

The sampling was carried out during Spring and Summer. Only the presence of Cu(II) was determined in high concentrations in Chinquihue and Pargua. For Huito and Huelmo the presence Cd(II) and Cu(II) ions was determined. The sampling point was always the same depending on the type of the tide; the retention studies were performed using the Batch equilibrium procedure at 17°C without modifying the pH.

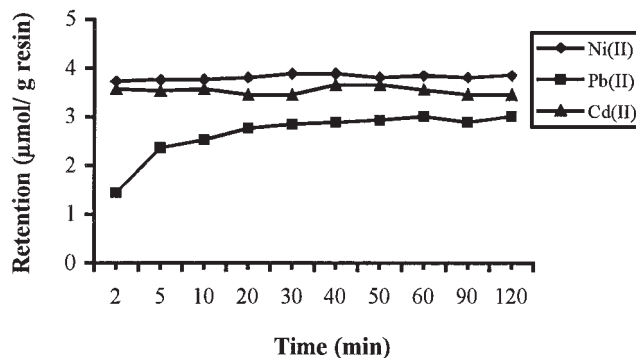
Resin PAAG shows a higher retention for copper(II) contained in an aqueous solution than that in artificial sea water (62%). This can be attributed to the presence of different alkaline and earth alkaline metals, which decrease the interaction of the ligand group with Cu(II) ions. For the samples from Huito and Huelmo, where Cd(II) ions are present, the retention capacity for Cu(II) ions decreased and the retention values of Cd(II) ions were close to those obtained with artificial sea water.

For the sample from Huelmo, the retention of Cu(II) was lower than that for Huito, which would indicate an additional effect by the effect near 7.0.

Resin PAA shows a Cu(II) retention capacity around 90% for samples from Chinquihue and Par-



**Figure 6** Effect of temperature on metal ion retention (pH 8.0, 28%, and 10 mg of PAA).



**Figure 7** Effect of time on metal ion retention (17°C, pH 8.0, 28%, and 10 mg of PAAG).

gua, which are similar to those determined from non-competitive conditions, but these values change for the samples from Huito and Huelmo, where the effect of pH and metal ion mixture could affect the metal ion retention capacity.

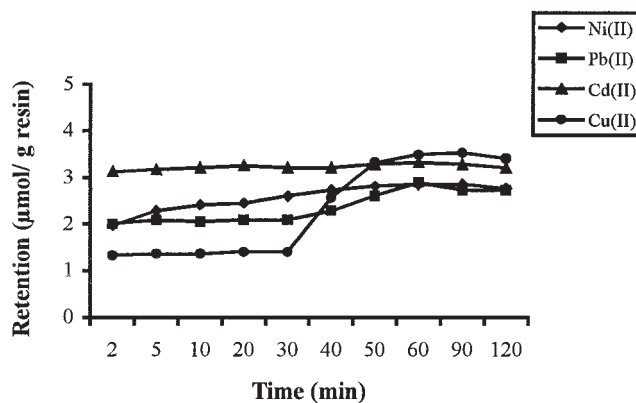
The commercial resin Dowex showed similar metal ion retention changes compared to those for the synthesized PAA and PAAG resins.

## CONCLUSIONS

PAAG showed the highest retention capacity (>80%) at pH 8.0 for Ni(II), Cd(II), and Pb(II) ions. PAA showed the highest affinity at pH 8 for Cd(II) (84%) and Cu(II) (88%).

The  $K_d$  values are high for all metal ions and for both synthesized resins, which would suggest that these resins behave as good resins; nevertheless, they did not show selectivity for natural sea water.

The different metal ion retention behavior may be attributed to the different size (hydrated ion) and the type of interaction between the ligand/exchange group and the metal ion.



**Figure 8** Effect of time on metal ion retention (17°C, pH 8.0, 28%, and 10 mg of PAA).

**TABLE VII**  
Regeneration of Resin PAAG by HNO<sub>3</sub> at 17°C

Metal ion	Initial metal ion concentration			%	4.0 M HNO <sub>3</sub>	
	$\mu\text{M}$	$\mu\text{g/L}$	$\mu\text{mol/g resin}$		$\mu\text{g/L}$	$\mu\text{mol/g resin}$
Ni(II)	3.96	232.42	3.96	100.0	3.96	232.42
Pb(II)	3.36	696.19	3.36	100.0	3.36	696.19
Cd(II)	3.28	368.71	3.28	55.0	1.80	202.79
Cu(II)	—	—	—	—	—	—

**TABLE VIII**  
Regeneration of Resin PAA by HNO<sub>3</sub> at 17°C

Metal ion	Initial metal ion concentration			%	4.0 M HNO <sub>3</sub>	
	$\mu\text{M}$	$\mu\text{g/L}$	$\mu\text{mol/g resin}$		$\mu\text{g/L}$	$\mu\text{mol/g resin}$
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 IX**  
Characteristics of the Upper Part of the Sea Water Column

Sample	Acronym	Distance of the beach (m)	pH	Salinity (‰)	T (°C)	Observation
Chiniquihue	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 X**  
Study of Metal Ion Retention Capacity from Sea Waters for the Resins: PAAG, PAA, and Dowex (Commercial Resin)

Acronym	Metal ion	Initial concentration ( $\mu\text{g/L}$ )	Retention					
			PAAG		PAA		Dowex	
			%	mg/L	%	$\mu\text{g/L}$	%	$\mu\text{g/L}$
Ch1	Cu(II)	618.7	75.0	461.6	85.0	525.9	86.0	513.5
Ch2	Cu(II)	904.0	72.0	650.9	93.0	804.7	85.0	768.4
Ch3	Cu(II)	531.7	66.0	352.1	89.0	473.2	85.0	452.0
H	Cu(II)	222.8	65.0	144.6	67.0	149.3	63.0	140.3
	Cd(II)	13.10	92.0	12.10	86.0	11.30	81.0	10.60
Hu	Cu(II)	180.8	40.0	72.30	50.0	90.40	66.0	119.3
	Cd(II)	13.33	91.0	12.10	86.0	11.40	89.0	11.90
P1	Cu(II)	159.0	72.0	114.5	97.0	154.2	88.0	139.9
P2	Cu(II)	38.67	73.0	28.23	98.0	37.00	87.0	33.60
P3	Cu(II)	129.3	62.0	80.17	85.0	109.9	89.0	115.1

At pH 8.0 both resins are as base form, where PAA behaves as a strong base, therefore affecting metal ion affinity.

The metal ion retention decreased as the concentration of NaCl increased from 0.48 to 0.6M, except Pb(II) for PAAG and Cd(II) and Cu(II) ions for resin PAA.

Both resins achieved  $t_{1/2}$  within the first 10 min, indicating a very good accessibility of the chelating/exchange sites.

The comparison of metal ion retention behavior of the resins with artificial and natural sea waters revealed that these results are very similar, except for Cu(II) ions.



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