Trace Metal Ion Retention Properties of Crosslinked Poly(4-Vinylpyridine) and Poly(Acrylic Acid)

Bernabé L. Rivas,[1] Benita Quilodrán,[2] Eduardo Quiroz[3]

[1]*Polymer Department, Faculty of Chemistry, University of Concepción, Casilla 160-C, Concepción, Chile*
[2]*Nature Resources and Environment Department, University of Lake, Casilla 557, Puerto Montt, Chile*
[3]*Chemistry Institute, Faculty of Sciences, Universidad Austral de Chile, Casilla 567, Valdivia, Chile*

ABSTRACT: The crosslinked resins poly(4-vinylpiridine) (PVPy) and poly(acrylic acid) (PAA) were obtained by radical polymerization. PVPy shows monodentate ligands and PAA at basic pH is basically as acrylate anion, which can contain end-carboxylates groups or form a bridge acting as mono- or bidentate ligands. The retention properties for trace metal ions from saline aqueous solutions and natural seawaters of these two resins were investigated by Batch equilibrium procedure. The metal ions studied were Cu(II), Pb(II), Cd(II), and Ni(II). The following effects were studied: pH, contact time, amount of the adsorbent, temperature, and salinity. The resin PVPy showed a high affinity for Cd(II) and PAA for Cu(II) and Cd(II). The metal ions were determined in the filtrate by atomic absorption spectrometry. By the treatment of the loaded resin with $4M$ HNO$_3$, it was possible to remove completely the Cu(II) ions. The retention properties of the resins were studied for trace metal ions present in the natural seawaters. Both resins showed a high affinity for Cd(II) when the natural seawater contained Cu(II) and Cd(II). © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 2908–2916, 2004

Key words: adsorbent; resin; metal ion; trace metal; resins; ion exchangers; polymer-metal complexes
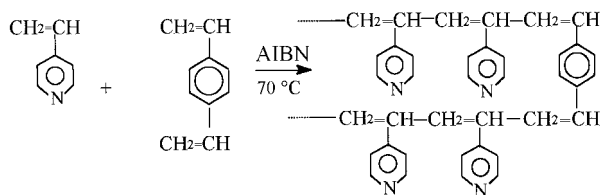
INTRODUCTION

Industrial plants are likely to discharge a lot of pollutants in the soil, rivers, and ground waters because of their wastewaters. Among these pollutants, heavy metals are very toxic, even at low concentrations, because of their possible storage in the food chain.[1–13] Metal ions are nonbiodegradable in nature, and their intake at a certain level is toxic.[14] Environmental contamination with heavy metal ions is of growing public concern because of health risks posed by human and animal exposure. Primary treatment by precipitation in a basic medium allows the elimination of a major part of the aqueous metal load. Methods to reach low levels involve ion exchange, adsorption onto activated carbon, membrane filtration, and reverse osmosis, which are efficient but expensive. The separation of metal ions, present as contaminant in water, is complicated because of the number of variables that must be considered, including the solution composition, salinity, pH, temperature, and the presence of organic substances. It is well known, for example, that heavy metal ions such as Pb(II) and Hg(II), which are toxic to most organisms, have found their way into the water system from different processes.[15] Therefore, there is a great interest in recovering metal ions because of both environmental and economic reasons.[16–17] A serious problem encountered in the removal of the metal ions is that the target species are usually in low concentration and in complex mixtures. The innocuous ions such as sodium and potassium can saturate the extractants before they can effectively remove the toxic metal ions. Attempts to solve problems of heavy metal ions removal have led to the development and application of several techniques such as precipitation, adsorption, extraction, and sorption or ion exchange.[18–20] 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.[21] This makes the use of exchangers for selective separation of heavy metal ions very attractive. The ion-exchange resins contain functional groups capable of complexing or ion exchanging with metal ions. Because the interacting functional group with the metal ions is covalently bound to an insoluble polymer, there is no loss of extractant into the aqueous phase. The chelating resins are ion-exchange-containing groups which are also able to complex metal ions. Their sorption mechanism would be through chelation instead of simple ion exchange, and as a consequence, they should be much more selective than ion-exchange resins. It has been

Scheme 1 Synthesis of the resin PVPy.

Figure 1 Effect of the pH on the metal ion retention (17°C, salinity: 28‰, 10 mg of PVPy, metal ion concentration: 4.0 μM).
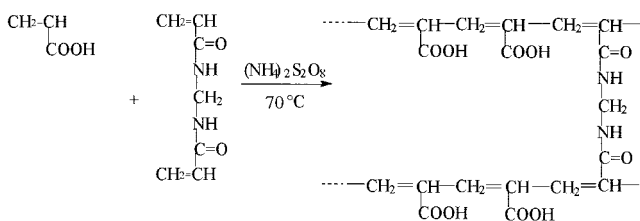
also claimed that their selectivity is at least qualitatively in agreement with the complexation constants of similar chelating monomers with metal ions in aqueous solution. This is true only very roughly. Such adsorbents have a larger specific surface and very small diameter, assuring high kinetic parameters. As a result, adsorption and concentration procedures become more convenient and easier.[14]

The aim of this article is to describe the metal ion-adsorption behavior for Cu(II), Ni(II), Pb(II), and Cd(II) of crosslinked poly(4-vinyl pyridine) (PVPy) and poly(acrylic acid) (PAA) at different pHs, concentrations, temperatures, and salinities. This is due to the finding that some of these trace metals such as Cu(II) and Ni(II) are naturally in the sea and are essential for the marine organisms, but are potentially toxic depending on the bioavailability. The concentration changes depending on the metal, species, and physicochemical characteristics of the aqueous medium. Some of them, such as Cu(II), may be toxic; nevertheless, it is an essential metal ion.

EXPERIMENTAL

Materials

4-Vinylpyridine (4-VPy, 95% Aldrich, Milwaukee, WI) and acrylic acid (AA, Merck, Stuttgart, Germany) were purified by distillation. 2,2′-Azoisobutyronitrile (AIBN) was recrystallized from methanol, and ammonium persulfate (PSA; 95% Aldrich) was used for 4-VPy and AA, respectively. N,N′-Methylene-bisacrylamide (MBA, 99% Aldrich) and divinylbenzene (DVB, Fluka, Saint Galen, Switzerland) were employed as crosslinking reagents for AA and 4-Vpy, respectively. Diammonium citrate hydrogen (Merck), ammonium ditiocarbamate pyrrolidin (APDC, Aldrich), N,N′-di-

ethyl diethylammonium dithiocarbamate (DDDC, Merck), nitric acid suprapur (Merck), sodium chlorate (Merck), standard solutions of 1000 ppm (Merck) of each metal ion, and deionized water (Millipore) were acquired. All reagents were of analytical grade.

Synthesis of the resins PVPy and PAA

The resin PVPy was synthesized by radical polymerization with 0.066 mol (7.37 g, 7.6 mL) 4-VPy, 0.333 mmol AIBN, and 4 mmol (0.52 g, 1.13 mL) DVB. The polymerization mixture was kept at 70°C for 1 h.

The resin PAA was obtained by radical polymerization by adding the following to a polymerization flask: 0.066 mol (4.8 g) of distilled acrylic acid dissolved in 5 mL water, 0.2 mmol (6 mol %) PSA, 4 mmol MBA. The polymerization mixture was kept at 70°C for 5 min. The resins are repeatedly washed with deionized water and dried under vacuum until constant weight.

Study of the metal ion retention properties by Batch equilibrium procedure

The effect of the pH on the metal ion retention properties was studied by Batch equilibrium procedure. For that, 10 mg of dry resin (180–250 μm) were placed in a quartz flask with 10 mL of $4.0 \times 10^{-6}M$ of each
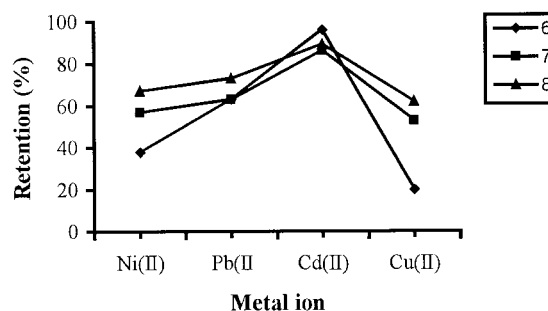

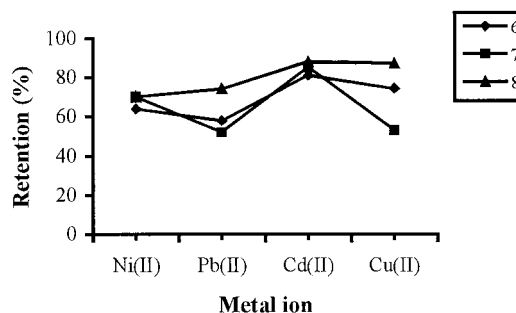**Scheme 2** Synthesis of the resin PAA.

Figure 2 Effect of the pH on the metal ion retention (17°C, salinity: 28‰, 10 mg of PAA, metal ion concentration: 4.0 μM).

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

Metal ion	Initial metal ion concentration		mmol of resin							
			0.0952		0.2381		0.4762		0.9542	
			Retention							
	(µg/L)	(µmol)	(µmol/mmol resin)	(%)	(µmol/mmol resin)	(%)	(µmol/mmol resin)	(%)	(µmol/mmol resin)	(%)
Ni(II)	234.77	0.04	0.282	67.0	0.101	60.0	0.052	62.0	0.026	63.0
Pb(II)	828.8	0.04	0.307	73.0	0.109	65.0	0.061	72.0	0.030	72.0
Cd(II)	449.64	0.04	0.374	89.0	0.144	86.0	0.072	86.0	0.038	90.0
Cu(II)	254.2	0.04	0.261	62.0	0.101	60.0	0.059	70.0	0.030	72.0

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

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

metal ion and kept for 1 h at 17°C. The pH ranged between 6 and 8. The solution was separated by decanting and centrifugation. The run under competitive conditions was performed with aqueous solution of metal ion mixture Ni(II)–Cu(II)–Pb(II)–Cd(II). To 10 mg of dry resin was added 10 mL of the metal ion mixture, which contains $1.0 \times 10^{-6} M$ (1.0 µM) of each metal ion. The solution was stirred for 1 h and then treated in the same way as the solution for noncompetitive conditions. The effect of the time 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 µM, temperature: 17°C). The solution was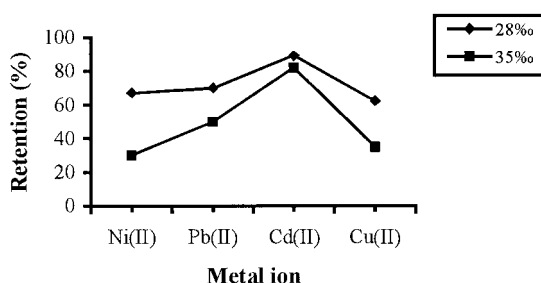 stirred for 1 h. An aliquot of 1 mL was taken at different times and the metal ion was analyzed in the filtrate. The time varied between 2 and 120 min. Moreover, the effect of the salinity and temperature was studied in a similar way. The metal ion retention capacity for natural seawater was also investigated.

Complexant citrate-buffer solution

The complexant citrate buffer solution was prepared by dissolution of 500 mg ammonium–pyrrolidine–dithiocarbamate (APDC, Aldrich) with 500 mg diethylammonium-*N,N*-diethyldithiocarbamate (DDDC, p.a. Merck)
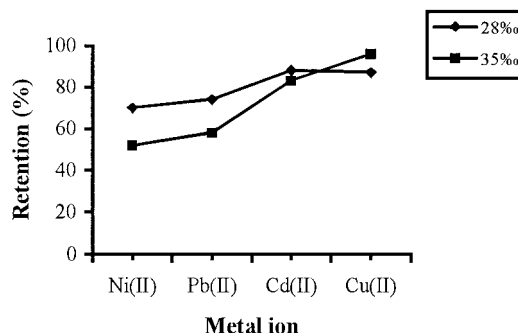
Figure 3 Effect of the salinity on the metal ion retention (17°C, pH 8.0, 10 mg of PVPy).

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

TABLE III
Metal Ion Retention Behavior from Quaternary Metal Ion Mixture (10°C, pH 8.0, Salinity: 28‰, 10 mg of PVPy)

Metal ion mixture	Initial metal ion concentration					Retention					
	(μM)	(μg/L)	(μmol)	(μg/g resin)	(μmol/g resin)	(%)[a]	(μmol/g resin)[a]	(%)[b]	(μmol/g resin)[b]	(%)[c]	(μmol/g resin)[c]
Ni(II)	1.0	58.69	0.01	58.70	1.0	62.0	0.62	28.2	0.28	17.5	0.175
Pb(II)	1.0	207.2	0.01	207.20	1.0	62.0	0.62	24.2	0.24	15.0	0.150
Cd(II)	1.0	112.4	0.01	112.40	1.0	62.0	0.62	22.6	0.23	13.8	0.140
Cu(II)	1.0	63.55	0.01	63.55	1.0	62.0	0.62	25.0	0.25	15.5	0.155

[a] Considering all the metal ions in the mixture.
[b] Considering the value in [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 [a].

in about 60 mL citrate-buffer solution and by filling up in a quartz measurement flask the resulting solution to 100 mL with further buffer solution.

Buffering, complexation, and extraction

To the subsample of 50 mL, 2 mL of complexant–citrate buffer solution and 2 mL n-heptane were added by means of a micropipette. The mixture was vigorously shaken and stored for 15 min so that both layers could be separated from each other completely and then to perform a reextraction.

Collecting of the seawater samples

The seawater samples were collected from Chinquihue, Huito, Huelmo, and Pargua, which are near to Puerto Montt. This city is located 1025 km south of the capital of Santiago. These samples correspond to the surface waters. They were placed in flask bottles, immediately filtered with a sterilized membrane of 45 μm, and subsequently stored in polyethylene bottles. Two other samples were taken 30 and 200 m from the beach. The former was taken with low tide and the latter was taken with high tide, respectively. The samples of Pargua and Huito were collected from 30 m of the beach with low tide.

Measurements

The pH was measured with a pH meter Hanna model HI 2023. Cu(II), Ni(II), Cd(II), and Pb(II) were analyzed by a Unicam Solaar M5 series atomic absorption spectrophotometer (AAS) with graphite furnace GF-95 with autosampler FS-95 and by a GF Perkin–Elmer AAS model 3110 HGA-600 and autosampler. The complexant citrate buffer solution was prepared by dissolving 500 mg of APDC (Aldrich p.a.) plus 500 mg of DDDC (Merck p.a.) in approximately 60 mL of slightly hot buffer citrate solution. Then, the flask was completed to 100 mL with buffer solution.

RESULTS AND DISCUSSION

The resins PVPy and PAA were synthesized by radical polymerization (see Schemes 1 and 2). Both materials are completely insoluble in water. The polymerization yields were 91 and 93%, respectively. The particle size of the resins immediately after polymerization was 90% higher, 1000 μm. Subsequently, the resins were crushed and the particle size fraction between 180 and 250 μm was used to study the retention properties for Cu(II), Ni(II), Pb(II), and Cd(II).

TABLE IV
Metal Ion Retention Behavior from Quaternary Metal Ion Mixture (14°C, pH 8.0, Salinity: 28‰, 10 mg of PVPy)

Metal ion mixture	Initial metal ion concentration					Retention					
	(μM)	(μg/L)	(μmol)	(μg/g resin)	(μmol/g resin)	(%)[a]	(μmol/g resin)[a]	(%)[b]	(μmol/g resin)[b]	(%)[c]	(μmol/g resin)[c]
Ni(II)	1.0	58.69	0.01	58.70	1.0	66.8	0.67	26.6	0.27	17.8	0.178
Pb(II)	1.0	207.2	0.01	207.20	1.0	66.8	0.67	22.4	0.22	15.0	0.150
Cd(II)	1.0	112.4	0.01	112.50	1.0	66.8	0.67	25.1	0.25	16.8	0.168
Cu(II)	1.0	63.55	0.01	63.55	1.0	66.8	0.67	25.9	0.26	17.3	0.173

[a] Considering all the metal ions in the mixture.
[b] Considering the value in [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 [a].

TABLE V
Metal Ion Retention Behavior from Quaternary Metal Ion Mixture (17°C, pH 8.0, Salinity: 28‰, 10 mg of PVPy)

Metal ion mixture	Initial metal ion concentration					Retention					
	(μM)	(μg/L)	(μmol)	(μg/g resin)	(μmol/g resin)	(%)[a]	(μmol/g resin)[a]	(%)[b]	(μmol/g resin)[b]	(%)[c]	(μmol/g resin)[c]
Ni(II)	1.0	58.69	0.01	58.70	1.0	71.0	0.71	25.4	0.254	18.0	0.180
Pb(II)	1.0	207.2	0.01	207.20	1.0	71.0	0.71	21.1	0.211	15.0	0.150
Cd(II)	1.0	112.4	0.01	112.50	1.0	71.0	0.71	27.5	0.275	19.5	0.195
Cu(II)	1.0	63.55	0.01	63.55	1.0	71.0	0.71	26.0	0.260	18.5	0.185

[a] Considering all the metal ions in the mixture.
[b] Considering the value in [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 [a].

Effect of the ph on the retention

PVPy shows a monodentate structure ligand with a high affinity for metal ions as Hg(I), Cd(II), Zn(II),[14] and other transition metal ions, depending on the pH of the solution. The 4-VPy could only form coordinating bonds as existing as one ligand with free electrons. On the other hand, the PAA at basic pH is basically in ionized form as acrylate anion, which can contain end-carboxylate groups or form bridges; in the former case, it acts as a bidentate ligand, but the interaction with the metal ion may be with one, two, three, or four carboxylate ligand groups forming a polymer–metal complex which can be an intra- or interpolymer–metal complex.

Figure 1 shows that for the resin 4-PVPy, the retention values for Cd(II) are higher for the three pH values, with a very low decrease when increasing the pH; for the other metal ions, the affinity is lower. For Cu(II) and Ni(II), the increase of pH increases the retention, achieving values close to 50% for Ni(II), Cu(II), and Pb(II). Moreover, the variation of the retention regarding the pH is linear without passing through a lower value at pH 7 as it occurs with the resin PAA for Pb(II) and Cu(II) being for the latter very pronounced, the decrease at pH 7 instead of at pH 8. This could explain the different types of interaction or bonding between the polymer ligand and the metal ion at different pHs.

PAA shows the highest retention values at pH 8 with 70% for Ni(II), 74% for Pb(II), 88% for Cd(II), and 87% for Cu(II) (see Fig. 2) and PVPy presents a high retention (>80%) only for one metal ion. The variation of the retention on the pH[6–8] is important for the metal ions Cu(II) and Pb(II) but the retention values for Cd(II) and Ni(II) did not show an important variation.

At neutral pH, there is a decrease of the retention value for Pb(II) and Cu(II). This could be attributed to self-protolysis[15] of water, which occurs in this region, producing hydroxyl groups that could disturb the adsorption of the metal ions at trace concentrations.

The high retention values of PAA for Cd(II) and Cu(II)[16–18] at pH 8 should be to similar to the acid properties of these metal ions, by the stability of the complex and the characteristics as a hard base of the polymer favoring the polymer–metal ion complex formation.

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

The concentration of metal ion was kept constant (4.0 μM) and put in contact with different concentrations of PVPy (0.0952–0.9542 mmol). The metal ion retention capacity of the resin was independent of the available ligand concentration (see Table I).

TABLE VI
Metal Ion Retention Behavior from Quaternary Metal Ion Mixture (10°C, pH 8.0, Salinity: 28‰, 10 mg of PAA)

Metal ion mixture	Initial metal ion concentration					Retention					
	(μM)	(μg/L)	(μmol)	(μg/g resin)	(μmol/g resin)	(%)[a]	(μmol/g resin)[a]	(%)[b]	(μmol/g resin)[b]	(%)[c]	(μmol/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

[a] Considering all the metal ions in the mixture.
[b] Considering the value in [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 [a].

TABLE VII
Metal Ion Retention Behavior from Quaternary Metal Ion Mixture (14°C, pH 8.0, Salinity: 28‰, 10 mg of PAA)

Metal ion mixture	Initial metal ion concentration					Retention					
	(μM)	(μg/ L)	(μmol)	(μg/g resin)	(μmol/g resin)	(%)[a]	(μmol/g resin)[a]	(%)[b]	(μmol/g resin)[b]	(%)[c]	(μmol/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

[a] Considering all the metal ions in the mixture.
[b] Considering the value in [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 [a].

For the resin PAA, the concentration ranged from 0.1389 to 1.3889 mmol. For a relationship of 1 to 10 of resin and metal ion, an important variation was not observed, except for Cd(II), where a decrease of 10% was observed. This could be explained because of the use of low concentrations close to detection limits. These results are important to determine the minimum amount of the resin (see Table II).

Effect of the salinity on the metal ion retention capacity

Sodium is a counterion very common in the weakly acid chelating polymers in the seawater and in the additives of different industrial processes. Therefore, it is possible to find sodium concentrations at different magnitudes in different effluent systems. These concentrations could be higher than those of the transition metal ion, decreasing the polymer metal–ion interaction.

For PVPy resin, by increasing the counter ion concentration from 0.48 to 0.65 mol/L (see Fig. 3), the competitivity for the polymer ligand sites increases. This effect is important for Ni(II), Pb(II), and Cu(II), but does not affect the adsorption capacity Cd(II), which could be determined by the type of interaction between the polymer chain and the metal ion.

Figure 4 shows that at an increase of the salinity from 28 to 35‰, the retention values of Ni(II) and Pb(II) decrease strongly, which would indicate that the equilibrium would be favoring the proton exchange by sodium ions and it is only possible to exchange trace amounts of transition metal ions. It demonstrates that for Ni(II) and Pb(II) the ion exchange process with PAA is more important than that of the complexometric reaction. For Cd(II) and Cu(II), the K_d values did not vary significantly, indicating that there is not an important retention of sodium and that the retention mechanism should be by covalent coordinating bonds or physical adsorption in the polymer chain.

Effect of the quaternary metal ion mixture on the retention

It is possible to observe a difference between the retention of Cu(II) from an aqueous solution under non-competitive conditions with respect to those competitive conditions (17°C, pH 8.0). The total retention capacity depends on the temperature and it is more significant at 17°C (see Tables III–V).

Tables VI-VIII show the retention properties of PAA resin for metal ions from quaternary mixture ions at different temperatures. There is a small increase of the retention of Pb(II), Cd(II), and Cu(II) in mixtures by increasing from 10 to 14°C and then a slight decrease probably due to a synergic effect produced at higher temperature and lower salinity, giving faster adsorp-

TABLE VIII
Metal Ion Retention Behavior from Quaternary Metal Ion Mixture (17°C, pH 8.0, Salinity: 28‰, 10 mg of PAA)

Metal ion mixture	Initial metal ion concentration					Retention					
	(μM)	(μg/L)	(μmol)	(μg/g resin)	(μmol/g resin)	(%)[a]	(μmol/g resin)[a]	(%)[b]	(μmol/g resin)[b]	(%)[c]	(μmol/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

[a] Considering all the metal ions in the mixture.
[b] Considering the value in [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 [a].
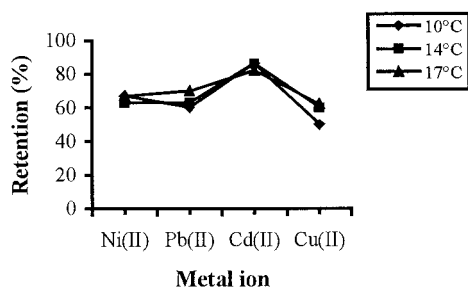
Figure 5 Effect of the temperature on the metal ion retention (pH 8.0, salinity: 28‰, 10 mg of PVPy).

Figure 7 Effect of time on the metal ion retention (17°C, pH 8.0, salinity: 28‰, 10 mg of PVPy).

tion rates. In general, the retention is similar in both conditions, except for Ni(II), which decreases about 20%, because of the retention mechanism and the affinity of the polymer ligand with respect to other ions. For both PVPy and PAA, the K_d values are high but with a low selectivity.

Effect of the temperature on the retention capacity

Figure 5 shows that for the retention of Cu(II) ions there is an important effect of the temperature. This retention behavior is similar to that observed for Cu(II) from the metal ion mixture.

Figure 6 shows that there is not an important effect of the temperature on the retention Pb(II), Cd(II), and Cu(II), but the retention of Ni(II) increases slightly because of a different retention mechanism. This effect is contrary to that observed from the mixture of ions.

Time of retention

Figure 7 shows that for PVPy the $t_{1/2}$ values for Cu(II) and Cd(II) are achieved before 2.0 min, 20 min for Ni(II), and 30 min for Pb(II). Figure 7 also shows that Cd(II) has the highest charge rate. For the resin PAA, only Cd(II) achieves the equilibrium fast, before 10 min, but for Ni(II), Pb(II), and Cu(II), it was achieved close to 50 min. The retention for Cu(II) is low during
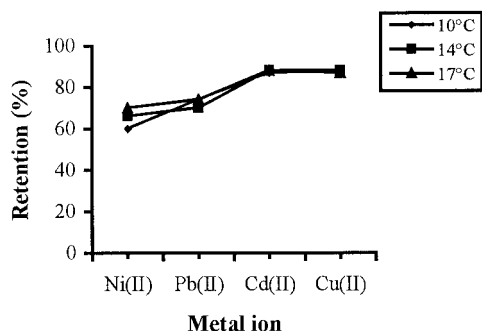
the first 30 min, increasing strongly after 45 min (see Fig. 8). $t_{1/2}$, for Ni(II), is achieved at 1.0 min, 2.0 min for Pb(II) and Cd(II), and 40 min for Cu(II).

Recovery of the resin by acid medium

HNO_3 (4.0M) shows to be a very good eluant to recover the loaded PVPy resin with Cu(II) and Cd(II). The elution was 100 and 91%, respectively. It was not possible to elute significantly Ni(II) and Pb(II) (see Table IX). Therefore, it was necessary to carry out new tests to elute these ions.

For the treatment of the loaded metal ion resin PAA with 4.0M HNO_3, it was possible to elute 100% of Pb(II) and Cu(II), 62.0 and 80% of Ni(II) and Cd(II), respectively (see Table X).

Retention from natural see waters

The physicochemical parameters of coast waters of Puerto Montt bay are in normal ranges: temperature ranging from 10 to 19°C, pH from 7.5 to 8.4, and salinity from 23 to 33‰,[9–10] depending on the month.

Figure 6 Effect of the temperature on the metal ion retention (pH 8.0, salinity: 28‰, 10 mg of PAA).
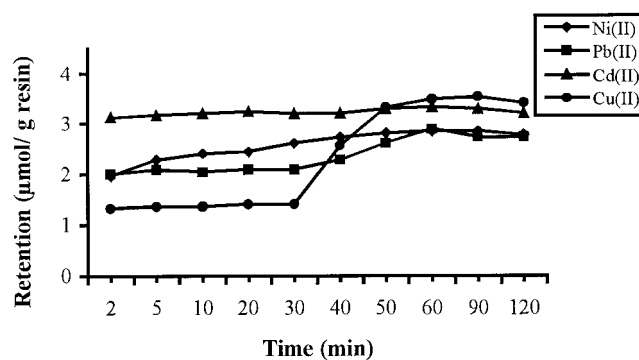

Figure 8 Effect of time on the metal ion retention (17°C, pH 8.0, salinity: 28‰, 10 mg of PAA).

Table XI summarizes the most important characteristics of the waters used.

Table XII shows the metal ion retention properties of both resins. To compare the values of one commercial weak base resin was included.

The samples were obtained during spring and summer, where only the presence of Cu(II) in high concentration was determined for the places of Chinquihue and Pargua. For Huito and Huelmo, the presence of Cd(II) and Cu(II) was determined. The point to take the sample was always the same depending on the tide type. The metal ion retention was studied by Batch equilibrium procedure without modifying the pH at 17°C.

In general, the metal ion retention capacities of both resins are similar to those obtained with samples of

TABLE IX
Regeneration of the PVPy Resin by Treatment with 4M HNO$_3$ at 17°C

Metal ion	Initial metal ion concentration			4.0M HNO$_3$		
	(μM)	(μg/L)	(μmol/g resin)	(%)	(μg/L)	(μmol/g resin)
Ni(II)	2.48	145.6	2.48	0.0	145.6	2.48
Pb(II)	2.91	602.8	2.91	4.0	24.1	0.12
Cd(II)	3.44	386.7	3.44	91.0	351.9	3.13
Cu(II)	2.90	184.2	2.90	100.0	184.2	2.90

TABLE X
Regeneration of the PAA Resin by Treatment with 4M HNO$_3$ at 17°C

Metal ion	Initial metal ion concentration			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 the Seawater Column

Sample	Acronym	Distance of the 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
Study the Retention Capacity to the Resins on Seawater: PVPy, PAA, and Commercial Dowex

Acronym	Metal ion	Initial concentration (μg/L)	Retention					
			PAA		P4-VPy		Dowex	
			%	μg/L	%	μg/L	%	μg/L
Ch1	Cu(II)	618.7	85.0	525.9	83.0	513.5	86.0	513.5
Ch2	Cu(II)	904.0	93.0	804.7	83.0	750.3	85.0	768.4
Ch3	Cu(II)	531.7	89.0	473.2	84.0	446.7	85.0	452.0
H	Cu(II)	222.8	67.0	149.3	64.0	149.6	63.0	140.3
	Cd(II)	13.10	86.0	11.30	87.0	11.40	81.0	10.60
Hu	Cu(II)	180.8	50.0	90.40	54.0	97.60	66.0	119.3
	Cd(II)	13.33	86.0	11.40	90.0	12.00	89.0	11.90
P1	Cu(II)	159.0	97.0	154.2	81.0	128.8	88.0	139.9
P2	Cu(II)	38.67	98.0	37.00	82.0	31.70	87.0	33.60
P3	Cu(II)	129.3	85.0	109.9	83.0	107.3	89.0	115.1

artificial seawater and are also similar to those with the commercial resin (see Table XII).

For resin PVPy, the metal ion retention percentages for those samples where only Cu(II) is found are higher than those obtained in the tests with artificial seawater (62%). This could be explained by the presence of different alkaline and alkaline earth metal ions, which could be a positive effect on the polymer ligand–Cu(II) interaction. In the samples of Huito and Huelmo, where Cd(II) ions were found, the retention of Cu(II) decreases up to values very close to experimental results. The retention values for Cd(II) are close to those obtained with the artificial seawaters. For the sample of Huelmo, the retention of Cu(II) is lower than that determined for the sample of Huito. This could indicate an additional effect by the pH value close to 7.0.

The resin PAA retains 90% of Cu(II) for the samples from Chinquihue and Pargua, which is similar to that obtained for the run under noncompetitive conditions. This value varies for the places Huito and Huelmo, where the effect of the pH and the mixture of metal ions could be affecting the metal ion retention capacity of the resin.

The commercial resin Dowex shows a similar behavior to that of PVPy, indicating basically that the sample of seawater determines the metal ion retention capacity.

CONCLUSION

The resin PVPy showed the highest retention capacity for Cd(II) (89%) at pH 8.0 and the resin PAA for Cd(II) and Cu(II) with 88 and 87%, respectively.

The K_d values of both resins were high for all metal ions, demonstrating that these resins behave as good adsorbents of metal ions from mixtures that would favor its use in the treatment of waste waters.

The differences in the metal ion retention capacity may be attributed to the different sizes of the hydrated ion and the type of bonding between the ligand and metal ion.

At pH 8.0, both resins are as basic form, being a strong base, the carboxylate group, affecting the affinity for the metal ion.

The salinity, in general, increased the concentration of NaCl from 0.48 to 0.60M, and the metal ion retention capacity decreased, except for Cd(II). However, it

is necessary to consider that the matrix of seawater is complex, particularly by the presence of alkaline, alkaline earth ions, and organic substances in suspension.

Both resins achieved the $t_{1/2}$ approximately during the first 10 min, indicating an adequate accessibility of the ligand groups. The results of natural and artificial seawaters were very similar for both resins. Finally, the more important variables on the metal ion retention are pH, temperature, salinity, and the presence of different metal ions.

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