Removal Properties of Crosslinked Poly(2-acrylamido glycolic acid) for Trace Heavy Metal Ions: Effect of pH, Temperature, Contact Time, and Salinity on the Adsorption Behavior

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ABSTRACT: Crosslinked poly(2-acrylamido glycolic acid) resin was synthesized by radical polymerization. This resin contains three potential ligand groups and was studied as an adsorbent of trace heavy metal ions from a saline aqueous solution and sea water by using the Batch equilibrium procedure. Adsorption characteristics of the resin toward Cu(II), Ni(II), Cd(II), and Pb(II) were studied spectrophotometrically, both in competitive and noncompetitive conditions. The effect of pH, contact time, amount of sorbent, temperature, and salinity were studied. The resin showed a

INTRODUCTION

Metal ions are nonbiodegradable in nature, and their intake at a certain level are toxic.¹ Environmental contamination with heavy metal ions is of growing public concern because of health risks posed by human and animal exposure. The separation of metal ions, present as contaminants 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.² Therefore, there is great interest in recovering metal ions for both environmental and economic reasons.^{3,4}

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 high affinity particularly for Ni(II). It was possible to remove completely Ni(II) and Pb(II) from the resin by 4M HNO₃. The retention properties of the resin were also investigated for Cu(II) contained in natural sea waters. The retention behavior was similar to that of the synthetic metal ion aqueous solution. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 2614–2621, 2003

Key words: heavy metal ions; resins; radical polymerization; adsorption

saturate the extractants before they can effectively remove the toxic metal ions. Attempts to solve problems of removal of heavy metal ions have led to the development and application of several techniques such as precipitation, adsorption, extraction, and sorption or ion exchange.5-7 With respect to the low concentrations and handling of large volumes of aqueous solution, extraction procedures are not economical, and precipitation procedures require the addition of relatively large amounts of chemicals, whereas applications of sorption or exchange on solids are preferable.⁸ 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 that are also able to complex metal ions. Their sorption mechanism is through chelation instead of simple ion exchange and, as a consequence, they should be much more selective than ion-exchange resins. It has been 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, although this is true only very roughly.9-12 Such adsorbents have a larger specific surface and very small diameter, thus ensuring

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Scheme 1

high kinetic parameters. As a result, adsorption and concentration procedures become more convenient and easier.^{2,13–23}

The aim of this investigation was to describe the metal ion–adsorption behavior for Cu(II), Ni(II), Pb(II), and Cd(II) of crosslinked poly(2-acrylamido glycolic acid) (PAGA) at different pH, concentration, temperature, and salinity. Although some of these trace metals such as Cu(II) and Ni(II) are naturally in the sea and are essential for marine organisms, they are potentially toxic depending on the bioavailability. The concentration changes depending on the metal, species, and physicochemical characteristics of the aqueous medium. Nevertheless, although some trace metals such as Cu(II) may be toxic, they remain essential metal ions.

EXPERIMENTAL

Materials

The 2-acrylamido glycolic acid (AGA; Aldrich, Milwaukee, WI) was used as received. Ammonium peroxy disulfate (APS; Merck, Darmstadt, Germany) and N,N'-methylene-bisacrylamide (MBA; Merck) were used as initiator and crosslinking reagents, respectively. Nitrate salts of copper, nickel, lead, and cadmium (Merck) were used as metal ion sources. Ultrapure H_2O from a Barnsted (Ames, IA) nanopure system and HNO_3 conc. (Merck suprapure) were analytical reagent grade and used as received.

Preparation of the resin PAGA

The resin was prepared by radical polymerization using a mixture of 0.066 mol (11.6 g) AGA, 0.2 mmol (6 mol %) APS, and 4 mmol (0.616 g) MBA at 70°C for 1 h.²⁴ Yield: 98%. The resin was washed repeatedly with deionized water and dried in vacuum to a constant weight. The dried resin was ground and the 180-to 250- μ m particle size fraction was used throughout the experiments.

Batch binding capacity experiments

To analyze the influence of pH on the sorption, 10 mg of dry resin were transferred into 10 mL of an aqueous solution $(4 \times 10^{-6} M)$ of Cu(NO₃)₂, Cd(NO₃)₂, Pb(NO₃)₂, and Cd(NO₃)₂. These solutions were allowed to be in contact with the resin for 1 h at 17°C under constant stirring. The pH varied between 6 and 8. Then, the samples were filtered, washed with water, and dried under vacuum at 50°C. Batch metal uptake experiments under competitive conditions were per-

TABLE IEffect of pH on the Metal Ion Retention (17°C, 28‰, 10 mg of resin, metal ion concentration: 4.0 μM)

							Retention			
Metal	Initial metal ion concentration				pH 6		pH 7	pH 8		
ion	(µg/L)	(µmol)	(µmol/g resin)	(%)	(µmol/g resin)	(%)	(µmol/g resin)	(%)	(µmol/g resin)	
Ni(II) Ph(II)	234.77	0.04	4.0	60.0 45.0	2.4	50.0	2.0	94.0 81.0	3.8	
Cd(II) Cu(II)	449.64 254.2	0.04 0.04 0.04	4.0 4.0	35.0 75.0	1.4 3.0	41.0 48.0	1.6 1.9	85.0 70.0	3.4 2.8	

		Concent	ration of th	e metal io	n	Retention					
Binary mixture M ₁ (II)/M ₂ (II)	(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)/Pb(II)	2.0	117.39	0.02	117.39	2.0	87.5	1.75	53.7	1.0740	47.0	0.94
Pb(II)/Ni(II)	2.0	414.40	0.02	414.40	2.0	87.5	1.75	46.3	0.9260	40.5	0.81
Cd(II)/Ni(II)	2.0	224.80	0.02	224.80	2.0	91.5	1.83	46.5	0.9290	42.5	0.85
Ni(II)/Cd(II)	2.0	117.39	0.02	117.39	2.0	91.5	1.83	53.5	1.0710	49.0	0.98
Cd(II)/Pb(II)	2.0	224.80	0.02	224.80	2.0	60.0	1.20	58.3	1.1660	35.0	0.70
Pb(II)/Cd(II)	2.0	414.40	0.02	414.40	2.0	60.0	1.20	41.7	0.8334	25.0	0.50

 TABLE II

 Metal Ion Retention Under Competitive Conditions (17°C, pH 8.0, 28‰, 10 mg of resin)

^a Considering both metal ions in the mixture.

^b Considering the value in ^a as 100%

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

formed with the following metal ion mixtures: Ni(II)– Pb(II), Cd(II)–Pb(II), Ni(II)–Cd(II), and Ni(II)–Cu(II)– Pb(II)–Cd(II). Batches of 10 mg resin were added to a mixture of each metal ion solution ($2 \times 10^{-6} M$). After being shaken for 1 h, the samples were treated as described for the noncompetitive runs. The effect of time on metal ion retention was studied by placing 10 mg of the resin and 10 mL of a metal ion aqueous solution (salinity, 28%; metal ion concentration, 4 μM ; temperature, 17°C), from which a 1-mL aliquot was taken at different times, and the metal ions were analyzed in the filtrates. The contact time varied between 2 and 120 min. The effect of the salinity and the temperature were also investigated and the metal ions were determined as above.

Complexant-citrate buffer solution

The complexant–citrate buffer solution was prepared by dissolution of 500 mg ammonium–pyrrolidine–dithiocarbamate (APDC p.a., Aldrich) with 500 mg diethylammonium-*N*,*N*-diethyldithiocarbamate (DDDC p.a., Merck) in about 60 mL of citrate buffer solution (moderate heating); a quartz measurement flask was filled with the resulting solution to 100 mL with further buffer solution.

TABLE III
Metal Ion Retention Behavior Under Competitive Conditions (10°C, pH 8.0, 28‰, 10 mg of resin)

		Initial m	etal ion co	ncentratio	n		Retention					
Binary mixture M ₁ (II)/M ₂ (II)	(μ <i>M</i>)	(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)/Pb(II) Pb(II)/Ni(II) Cd(II)/Ni(II) Ni(II)/Cd(II) Cd(II)/Pb(II) Pb(II)/Cd(II)	2.0 2.0 2.0 2.0 2.0 2.0 2.0	117.39 414.40 224.80 117.39 224.80 414.40	0.02 0.02 0.02 0.02 0.02 0.02 0.02	117.39 414.40 224.80 117.39 224.80 414.40	2.0 2.0 2.0 2.0 2.0 2.0 2.0	100.0 100.0 87.5 87.5 78.0 78.0	2.00 2.00 1.75 1.75 1.56 1.56	50.0 50.0 44.6 55.4 50.6 49.4	117.40 414.40 175.50 113.87 177.60 319.09	50.0 50.0 39.0 48.5 39.5 38.5	1.00 1.00 0.78 0.97 0.79 0.77	

^a Considering both metal ions in the mixture.

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

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

TABLE IV										
Metal Ion Retention	Behavior from Qua	aternary Mixture	(17°C,]	pH 8.0,	28%‰, 3	10 mg c	of resin)			

Metal ion mixture		Initial con	ncentration	of metal ic	n	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	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

^a Considering all the metal ions in the mixture.

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

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

	wiet	al Ioli Kete	intion ben		Quaternary	wiixtui	e (10 C, pri	0.0, 20/00	, 10 mg 01 f	esiii)	
Metal		Initial n	netal ion co	ncentration	l	Retention					
ion mixture	(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	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

 TABLE V

 Metal Ion Retention Behavior from Quaternary Mixture (10°C, pH 8.0, 28‰, 10 mg of resin)

^a Considering all metal ions in the mixture.

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

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

Buffering, complexation, and extraction

In a quartz flask, to the 50 mL subsample of solution were added, by means of a micropipette, 2 mL of complexant–citrate buffer solution and 2 mL *n*-heptane. The mixture was vigorously shaken and stored 15 min for each component so that both layers could completely separate from each other, after which a reextraction could be performed.

Collecting the sea waters

Sea water samples were collected from Chinquihue, Huito, Huelmo, and Pargua, all of which are near Puerto Montt, a city located 1025 km south of the capital Santiago; these samples correspond to the surface waters. They were placed in flask bottles, immediately filtered with a sterilized 45- μ m membrane, and subsequently stored in polyethylene bottles. The other two samples were taken from 30 and 150 m from the beach, the former with low tide and the latter with high tide, respectively. The samples of Pargua and Huito were collected from 10 m of the beach with low tide.

Measurements

The pH was measured with a Hanna pH meter (model HI 2023) (USA). Cu(II), Ni(II), Cd(II), and Pb(II) were analyzed by a Unicam Solar M5 series atomic absorption

spectrophotometer (AAS) (UK) with graphite furnace GF-95 with autosampler FS-95 and by a GF/Perkin–Elmer AAS model 3110 HGA-600 and autosampler (Perkin Elmer Cetus Instruments, Norwalk, CT).

RESULTS AND DISCUSSION

The PAGA resin was synthesized by radical polymerization, yielding a solid completely insoluble in water (yield, 98%). The particle size of the resin after the polymerization ranged from 500 to 1000 μ m. Consequently, the resin was crushed to yield a material with a particle size of 180 to 250 μ m. This fraction was used to study the adsorption capacity for the metal ions Cu(II), Ni(II), Cd(II), and Pb(II). These metal ions were selected because of their possible impact on sea fish. The resin selected for this study contains three potential ligand groups, as shown in **Scheme 1**: carboxylic acid, amide, and hydroxyl groups.

Effect of pH on metal ion adsorption

Because of the protonation and deprotonation properties of the acidic and basic groups of the chelating resin, its sorption behavior for metal ions is influenced by the pH value, which in turn influences the surface structure of sorbents, the formation of metal ions, and the interaction between the sorbents and the metal

TABLE VI Effect of Metal Ion:Resin Ratio on Adsorption Behavior (17°C, pH 8.0, 28‰, concentration: 4.0 μM)

						Rete	ntion										
	Ini	tial			Am	ount of	resin (mmol)			0.68970 nol/mmol resin) (%)							
	concer of the n	itration netal ion	0.06896		0.17240		0.34480		0.68970								
Metal ion	(µg/L)	(µmol)	(µmol/mmol resin)	(%)	(µmol/mmol resin)	(%)	(µmol/mmol resin)	(%)	(µmol/mmol resin)	(%)							
Ni(II) Pb(II) Cd(II) Cu(II)	234.77 828.8 449.64 254.2	0.04 0.04 0.04 0.04	$\begin{array}{c} 0.54520 \\ 0.46404 \\ 0.49304 \\ 0.41760 \end{array}$	94.0 80.0 85.0 72.0	0.2204 0.1624 0.1995 0.1346	95.0 70.0 86.0 58.0	0.11140 0.18580 0.09861 0.07309	96.0 74.0 85.0 63.0	0.05394 0.04118 0.04814 0.03306	93.0 71.0 83.0 57.0							



Figure 1 Effect of the metal ion : resin ratio on the adsorption behavior.

ions.²⁵ Because of that, the pH dependency on the adsorption of Cu(II), Ni(II), Cd(II), and Pb(II) was examined under different experimental conditions.

234.77

828.8

449.64

4.0

4.0

4.0

Ni(II)

Pb(II)

Cd(II)

The metal-ion uptake behavior of PAGA resin was

tested under both competitive and noncompetitive conditions as a function of the pH.

The different ligand groups are predominantly as above, depending on the pH:

44.0

77.0

77.0

1.76

3.08

3.08

CH ₂ COO	CH ₂ COOH		ЮН	CH ₂ C	200-	CH ₂ CO	О С
		/		1		/	
$RCH_2NH^+NO_3^-$	$\rightarrow R$	CH ₂ NH ⁺	$\rightarrow RC$	CH_2NH^+	$\rightarrow RC$	CH ₂ N	
CH ₂ COO	Н	CH ₂ CC	00-	CH ₂ C	200-	CH ₂ CO	O-
pH 2.21	\rightarrow	3.99	\rightarrow	7.41	\rightarrow	12.30	

Effect of Salinity on Metal Ion Adsorption (17°C, pH 8.0, 10 mg of the resin)RetentionRetentionMetalInitial metal ion concentration28%(μM)($\mu g/L$)($\mu mol/g resin$)(%)($\mu mol/g resin$)(%)($\mu mol/g resin$)

4.0

4.0

4.0

94.0

80.0

85.0

3.76

3.20

3.40

 TABLE VII

 Effect of Salinity on Metal Ion Adsorption (17°C, pH 8.0, 10 mg of the resin)

TABLE VIII									
Effect of Temperature on Metal Ion Retention									

					Retention								
						Т	emperature						
Metal ion	Initial metal ion concentration				10°C		14°C	17°C					
	(µM)	(µg/L)	(µmol/g resin)	(%)	(µmol/g resin)	(%)	(µmol/g resin)	(%)	(µmol/g resin)				
Ni(II) Pb(II) Cd(II)	4.0 4.0 4.0	234.77 828.80 449.60	$4.0 \\ 4.0 \\ 4.0$	100.0 100.0 64.0	4.00 4.00 2.56	91.0 79.0 73.0	3.64 3.16 2.92	94.0 80.0 82.0	3.76 3.20 3.20				



Figure 2 Effect of time on the metal ion retention.

In Table I the uptake under noncompetitive conditions is given. Metal nitrate solutions were used. The highest retention values for the four metal ions were observed at pH 8 as follows: Cu(II), 70%; Ni(II), 94%; Cd(II), 85%; and Pb(II), 81%. Ni(II) formed the strongest complex with the ligand sites. During the course of adsorption of metal ions on chelating resin, changes in color were observed. The colors of metal-ion–containing resin are similar to those of the heavy metal ions. By evaluating the amount of the metals at pH 8, the selectivity order can be given as Ni(II) > Cd(II) \approx Pb(II) > Cu(II).

At lower pH values, the capture becomes lower, and this fact is very important in view of regeneration of the resin with acidic solution. As seen, Cu(II) showed the weakest binding characteristics among the metals studied. At pH 8 the predominant species are $Cu(OH)_2$, which should be soluble; Ni²⁺, soluble; Cd(OH)⁺, Cd²⁺ (which should be favored at this low concentration), and Pb(OH)₂, soluble.

Based on the sorption behavior of the resin at different pH values, the separation in both binary and quaternary mixtures was attempted. For that, several sets of experiments were carried out (see Tables II–V). The retention of Ni(II) decreased from 94% to 47 and 49% from those binary mixtures with Pb(II) and Cd(II), respectively.

The metal ion concentration was kept at 4.0 μ *M* and the amount of resin was varied from 0.06896 to 0.68970 mmol. No important effect was observed when increasing 10 times the relationship between the ligand sites and metal ion concentration (see Table VI). This demonstrates that Ni(II) ions form the strongest complexes. Cu(II) ions lose around 20% of the retention

	Regeneration of the Resin by HNO ₃ at 17°C											
Metal	Initi	al metal ion	concentration		1.0M I	HNO ₃	4.0M HNO ₃					
ion	(µM)	(µg/L)	(µmol/g resin)	(%)	(µg/L)	(µmol/g resin)	(%)	(µg/L)	(µmol/g resin)			
Ni(II)	3.96	232.42	3.96	38.0	88.3	1.50	100.0	3.96	232.42			
Pb(II)	3.36	696.19	3.36	44.2	307.7	1.49	100.0	3.36	696.19			
Cd(II)	3.28	368.71	3.28	44.8	165.2	1.47	55.0	1.80	202.79			

TABLE IXRegeneration of the Resin by HNO3 at 17°C

TABLE X Characteristics of Upper Part of the Sea Water Column

Sample	Acronym	Distance of the beach (m)	pН	Salinity (‰)	Т (°С)	Observation
Chinquihue	Ch	150	8.0	26	15	High tide, sunny
1	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	Н	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
0	P2	30	8.0	29	13	Low tide, rain
	P3	20	8.1	33	16	Flood tide, sunny

Metal Ion Retention from Chinquihue (Ch) Sea Waters							
	Initia conc	l metal ion centration	Retention				
Metal ion	(µg/L)	(µmol/L)	(%)	$(\mu g/L)$	(µmol/L)		
Ni(II)	23.87	0.41	89	21.24	0.365		
Pb(II)	0.02	$9.65 imes 10^{-5}$	100	0.02	$9.65 imes 10^{-5}$		
Cd(II) and							
Cu(II)	Not detected						

TABLE XI

TABLE XIII Metal Ion Retention from Huito (H) Sea Waters

	Initial metal ion concentration		Retention		
Metal ion	(µg/L)	(µmol/L)	(%)	(µg/L)	(µmol/L)
Cu(II) Cd(II) Ni(II) and Pb(II)	222.8 13.1	3.5 0.12	65 92	144.6 12.1	2.28 0.11

with the highest amount of resin with respect to the lower amount (see Fig. 1).

By increasing the salinity from 28 to 35%, the retention value of Ni(II) decreased strongly from 94 to 47%, which could be attributable to the adsorption of Ni(II) that would occur by both complexing and cation exchange, although there was no effect higher than 5 and 10% for Pb(II) and Cd(II), respectively. By increasing the salt concentration, Na⁺ ions would compete with Ni²⁺ by the active sites.²⁶ For Cd(II) and Pb(II), the retention should be preferable by complex formation (see Table VII).

The effect of temperature on metal ion retention is summarized in Table VIII. For Ni(II) and Pb(II) the retention decreases as the temperature increases from 10 to 17°C but Cd(II) increases from 2.56 to $3.2 \,\mu$ mol/g dry resin. This could be explained by the different retention mechanisms involved for these metal ions.

The equilibrium time of adsorption for the respective metal ions was determined by adding 10 mg of the resin to 10 mL of metal ion solution (4.0 μ *M*, pH 8, salinity 28‰) at pH 8. A number of stoppered quartz flasks containing metal ion solution and resin were stirred continuously at 17°C. The flasks were removed after regular intervals, the contents filtered off, and the amount of the metal ion in the filtrate and the washings were determined. The equilibrium time was about 5 min for Ni(II) and Cd(II) and about 30 min for Pb(II) (see Fig. 2). The higher efficiency of the resin apparently results from the easy accessibility of its

TABLE XII Retention of Cu(II) from Chinquihue and Pargua Sea Waters

	Initial metal ion concentration		Retention		
Sample ^a	(µg/L)	(µmol/L)	(%)	$(\mu g/L)$	(µmol/L)
Ch1	618.66	9.74	75	461.6	7.3
Ch2	904.00	14.22	72	650.9	10.2
Ch3	531.73	8.37	66	352.13	5.5
P1	159.00	2.50	72	114.5	1.8
P2	38.67	0.61	73	28.23	0.45
P3	129.3	2.00	62	80.17	1.24

^a See TABLE X.

coordination sites to the metal ions, which is related to the extent of the crosslinking.

Desorption of metal ions Ni(II), Pb(II), and Cd(II) from the loaded resin was studied with 1 and 4M HNO₃ solutions at 25°C of shaking time. The final amount of metal ions was determined by AAS. The highest concentrated solution was very efficient at destroying the resin–metal ion complex; the three metal ions were completely eluted. At 1M HNO₃ the elution was lower than 45% (see Table IX).

To investigate the retention capacity of the PAGA resin in the upper part of the sea water column, nine samples from four places (Chinquihue, Huito, Huelmo, and Pargua) were taken and tested. Table X summarizes their characteristics.

Table XI shows the retention capacity of the PAGA resin for Ni(II) (89%) and Pb(II) (100%) in the sample taken in Chinquihue (Ch) at 15°C, with a salinity of 26%. Cd(II) and Cu(II) ions were not detected in this sample. Nevertheless, in the other samples taken at Chinquihue and Pargua only Cu(II) ions were found whose concentrations ranged between 129.30 and 904 μ g/L (see Table XII). These concentrations are considered high, considering the type of water.

The samples from Huito and Huelmo also contained Cd(II) (0.12 μ mol/L). The metal ion retention behavior was investigated by Batch equilibrium procedure in a similar way to that observed for synthetic saline aqueous solution. The results are summarized in Tables XI–XIV. Ni(II) and Pb(II) ions were not detected in all sea waters. In general, the metal ion retention is similar to that observed with a synthetic aqueous solution. Pb(II) was completely adsorbed from the Chinquihue sea water and Cd(II), 92% (0.12 μ mol/L) and 91% were retained from Huito and

TABLE XIV Metal Ion Retention from Huelmo (Hu) Sea Waters

	Metal ion concentration		Retention		
Metal ion	(µg/L)	(µmol/L)	(%)	(µg/L)	(µmol/L)
Cu(II)	180.8	2.85	43	72.3	1.14
Ni(II) and Pb(II)	13.5	0.12 No	91 t detec	ted	0.11

Huelmo sea waters, respectively. In comparison, Cu(II) ions were retained in a lower level (43–72%).

CONCLUSIONS

The poly(2-acrylamido glycolic acid) resin synthesized by radical polymerization showed a high affinity for trace heavy metal ions under different experimental conditions, particularly for Ni(II), which could be explained by a favored diffusion of the Ni(II) ions to the ligand sites as well as a higher affinity of the carboxylate groups for Ni(II) ions. It was possible to recover completely the loaded resin with Ni(II) and Pb(II) by elution with HNO₃. The natural sea waters showed a high content in Cu(II) ions, except for one sample taken in Chinquihue, where Ni(II) and Pb(II) were detected only in low concentrations. The samples from Huito and Huelmo contained a low level of Cd(II) ions. The resin also showed a high adsorption capability to Cu(II) ions from the sea waters and, according to that, it should be possible to use this resin to purify these waters.

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