DOI: 10.1002/masy.201150606

Metal Ion Removal Properties of Water-Insoluble Functional Polymers

Bernabé L. Rivas, Carla Muñoz*

Summary: Resins containing sulfonic acid groups by radical polymerization were synthesized. The metal ion retention properties were studied by batch and column methods for the polluting metal ions Cd(II), Pb(II), and Hg(II).

pH exercises an important effect on the retention: the metal ion sorption increases with increases in the pH. The maximum retention capacity was determined after three contacts at optimum pH. Resin R1 obtained the highest value 1.207 mmol/g resin for Cd(II). Different eluent reagents were used to recover the resin. Resin R1 loaded with Pb(II) was completely recovered using 4 M HCl as stripping reagent.

Keywords: environment; ion; metal; polluting ions; removal; resins

Introduction

In recent years, there has been a noticeable increase in the volume of heavy metal pollutants, resulting in many serious environmental problems. Heavy metals are metabolic poisons and enzyme inhibitors. These can cause mental retardation and semi-permanent brain damage. Since heavy metals cannot be rendered harmless by chemical or biological remediation processes, they are classified as environmental toxic substances. Since toxic metals are released into the environment in a number of different ways, removal of heavy metal ions from industrial effluents has received attention and the sophistication of separation methods has increased enormously.

Many metal ions, including Co(II), Cu(II), Fe(III), Ni(II), and Zn(II), are known to be biologically essential, especially in the action mechanism of specific enzymes. However, the adverse effect of metal ions is manifested when these levels exceed a certain threshold. Heavy metal toxicity may be caused by: (a) blocking the essential functional groups of biomolecules, (b) displacing essential metal ions from biomolecules, (c) modifying the active conformation of biomolecules, (d) disrupting the integrity of biomembranes; and (e) modifying some other biologically active agents.

Several methods, such as reduction and precipitation, ion exchange, electrolysis, electroplating and adsorption, liquid-phase polymer based retention, have been used to remove metal ions from water.

Nowadays, because of its high recovery, short extraction time, high enrichment factor, low cost, and low consumption of organic solvents over liquid–liquid extraction, solid-phase extraction (SPE) is the most common technique for environmental water sample pretreatment,[1,2] where, the choice of sorbent is key because it controls the analytical parameters such as selectivity, affinity and capacity.[3]

The use of chelating resins for the removal and separation of metal ions is of wide interest owing to its simplicity, elegance and range of variations. As solid sorbents, they should have selectivity, low consumption of organic solvents and can be repeatedly used.

These sorbents must exhibit certain essential properties, such as sufficient capacity, high distribution coefficients for analytes but not for matrix components, fast kinetics of sorption and elution processes, and tolerance against the flow rate.[4]

Polymer Department, Faculty of Chemistry, University of Concepción, Casilla 160-C, Concepción, Chile
E-mail: brivas@udec.cl

According to Pearson's hard and soft acid-base theory,[5] polymers containing functional groups with N or S donor atoms should be promising as sorbents of precious metal ions. Therefore, considerable effort has been made to prepare chelating resins containing these atoms for the preconcentration, separation and hydrometallurgy of precious metals and several studies have been published on this subject over the years.[6]

In addition to the existing commercial resins,[7–10] there is a special interest in the synthesis of new chelating sorbents bearing different coordinating groups with a view to enhancing selectivity and performance.

A large number of physically and chemically modified synthetic materials have been reported for the removal of heavy metals.[11–31]

The aim of the current manuscript is to study and compare the metal ion retention properties for Cd(II), Pb(II), and Hg(II) for different resins containing sulfonate groups.

Experimental Part

Materials

The following monomers were used in the synthesis of different resins studied: acrylic acid, (98% Merck), AA, 2-acrylamido glycolic acid (96%, Aldrich), AGA, 4-styrene sulfonate of sodium (100%, Aldrich), SS, 2-acrylamido-2-methyl-1-propansulfonic acid (99%, Merck), APSA, vinyl sulfonic acid, VSA, mono-2-(methacryloyloxy)ethyl succinate (98%, Aldrich), MOES, acrylamide (99%, Aldrich), AAm, N-3-dimethylaminopropyl methacrylamide (98%, Aldrich), NDAPA, N,N'-methylene bis acrylamide (MBA, 99%, Aldrich), and ammonium peroxide disulfate (AP, Fluka) as cross-linking and initiator reagents, respectively were used as received.

For adsorption studies, the metal salts used were $Cd(NO_3)_2 \cdot 4\,H_2O$, $Hg(NO_3)_2 \cdot H_2O$, and $Pb(NO_3)_2$. Metal salts were purchased from Merck. The analytical grade HNO_3, $HClO_4$, and HCl were purchased from Fisher.

Synthesis of the Resins

The resins were synthesized by free radical polymerization in a polymerization flask as follows: monomers, cross-linking and initiator reagents (in the quantity shown in the Table 1) were dissolved in 50 mL of bi-distilled water. The system was kept under N_2 at 70 °C for 4 hours. Then, the resin was filtered and washed with distilled water and dried up to constant weight at 40 °C. The resin was screened, and a particle size fraction in the range of 180-250 μm was chosen for all metal ion retention experiments.

Metal Ion Adsorption

A batch equilibrium procedure was applied to determine the synthesized adsorbent's metal ion binding ability. All experiments were performed in a flask mounted on shaker. A total of 0.05 g of dried resin in 5 mL of metal ion solution was shaken for 1 hour at 20 °C. After shaking, the resin samples were filtered and washed with water at the same pH. The concentrations

Table 1.
Acronyms and the names of the resins.

Acronym of the resin	Name of the resin: poly(monomer 1-*co*-monomer 2)
R 1	Poly(2-acrylamido glycolic acid-*co*-4-styrene sulfonate of sodium)
R 2	Poly(2-acrylamido glycolic acid-*co*-2-acrylamido-2-methyl-1-propanosulfonic acid)
R 3	Poly(vinyl sulfonic acid-*co*-acrylic acid)
R 4	Poly(vinyl sulfonic acid-*co*-2-acrylamido glycolic acid)
R 5	Poly(mono-2-(metacryloyloxy) ethyl succinate-*co*-2-acrylamido glycolic acid)
R 6	Poly(acrylamide-*co*-2-acrylamido-2-methyl-1-propanosulfonic acid)
R 7	Poly(2-acrylamido-2-methyl-1-propanosulfonic acid-*co*-N-3-dimethylaminopropyl methacrylamide)

of metal ions in the filtrate were determined by atomic absorption spectroscopy (AAS). To determine the maximum sorption capacity for Pb(II), Cd(II), and Hg(II), the following runs were carried out: 25 mL of an aqueous solution of each metal ion (1 g/L) was shaken with 0.500 g of dry resin for 1 hour at 20 °C. The process was repeated three times, and the metal ions in the supernatant were determined by atomic absorption spectrometry, AAS.

Measurements

A Julabo air-batch shaker was used for shaking the solution at a desired temperature. The pH was measured with a digital pH meter. An atomic absorption spectrometer (Unicam Solaar 5M series) was used for the determination of metal ions. The FTIR spectra of the polymer samples were recorded with a Magna Nicolet 550 spectrophotometer.

Results and Discussion

Water-insoluble resins were obtained by homo- and co-polymerization of different monomers. AP was used as an initiator and MBA as a cross-linking reagent (CR) respectively.

The following functional resins were synthesized and general characteristics are summarized in the Tables 1 and 2.

The resins were characterized by FTIR spectroscopy. Table 3 shows the most characteristic absorption bands.

Metal Ion Retention Properties

Effect of pH on the Uptake

Metal-ion sorption on chelating adsorbents is pH dependent. In the absence of metal-chelating groups, metal ion precipitation is affected by the concentration and form of soluble metal species. Solubility is governed by hydroxide or carbonate concentration. Metal ion precipitation becomes significant at approximately pH 7.0 for all metal ions and also depends on the concentration of metal ions in the medium. In order to avoid its precipitation, Hg(II) was studied only up to pH 2.

For all the studied metal ions Pb(II), Cd(II), and Hg(II), retention increases as the pH increased (see Figures 1–3). For these resins containing the sulfonic/sulfonate groups, this increase is due to the ionization of the sulfonic acid group, favoring electrostatic interaction with the positively charged metal ion.

Table 2.
Experimental synthesis conditions of the resins.

Resin	Monomer 1 (g)	Monomer 2 (g)	Crosslinker (mg)	Initiator (mg)
R 1	6.46	5.21	382	143
R 2	6.47	5.21	381	143
R 3	5.01	3.34	318	1319
R 4	5.20	4.07	357	1325
R 5	10.20	4.37	2086	72.6
R 6	3.04	8.85	263	399.3
R 7	5.15	6.43	173	412

Table 3.
Characteristic absorption FTIR bands of the resins.

Wavenumber (cm^{-1})	R 1	R 2	R 3	R 4	R 5	R 6	R 7
N–H	3435	3453	3436	3431	3436	3479	3435
O–H	1216	1327	–	–	–	–	–
COOH	1748	1757	1729	1745	–	–	–
C=O	1663	1653	1648	1664	1640	1667	1653
SO_3H	1036	1032	1202	1209	1210	1220	1217

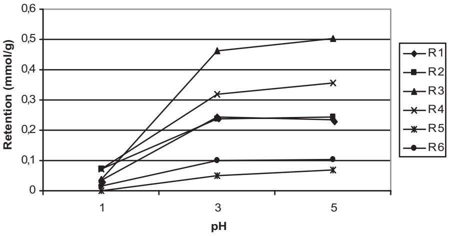

Figure 1.
Effect of the pH on the Cd(II) retention for the sulfonate‘s group resins.

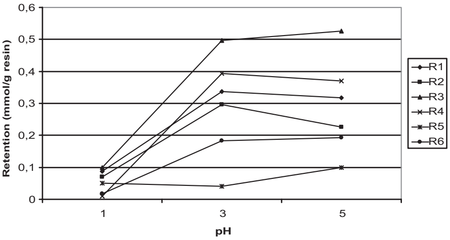

Figure 2.
Effect of the pH on the Pb(II) retention for the sulfonate‘s group resins.

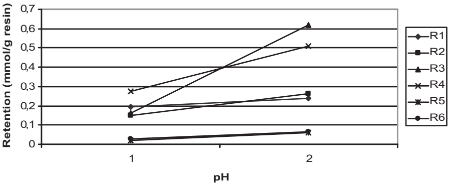

Figure 3.
Effect of the pH on the Hg(II) retention for the sulfonate’s group resins.

The highest retention of Cd(II) and Pb(II) were obtained for the resin R 3 (poly(vinyl sulfonic acid-*co*-acrylic acid): 0.50 mmol of Cd(II)/ g of dry resin and 0.52 mmol of Pb(II)/g of dry resin. This resin shows good metal ion retention because it has two groups that can be negatively charged at the optimum pH, and this charge is totally available for electrostatic attraction to the metal ion.

Resin R 5 shows the lowest retention, probably due to its large carbon chain and more hydrophobic properties, avoiding or complicating the access of the metal ions to the active sites.

Figure 4 shows the metal ion retention properties for each ion at optimum pH. The resin R3 at pH 5 achieved the highest values for the three metal ions

Maximum Retention Capacity(MRC)

According to the pH effect results, maximum retention capacity for the metal ions was determined. For this, batches of 500.0 mg adsorbent were used together with a mixture of 25.00 mL of 1.00 g/L metal ion solution. After a shaking time of 1 h at 20 °C, each sample was filtered. Then, the batches were reconstituted by adding 25.00 mL of fresh metal ion solution. The process was repeated three times. The last filtration step was followed by a washing step with water at the corresponding *p*H. Filtrate was collected into calibrated 100.0 mL volumetric flask and diluted to volume with water at the selected *p*H. The metal ions were determined by AAS. The results are summarized in Table 4. Resin R1 obtained both the highest value 1.207 mmol/g for Cd(II) and the lowest value for Pb(II). The MRC for the resins R 5 and R 7 were not determined.

Regeneration

In order to recover the resin, different eluents were tested for the metal ion loaded resin. The resin was loaded for the MRC assay.

Figure 5 shows that complete recovery of the resin is possible using 4 M HCl as eluent for the loaded resin with Pb(II). The elution behavior is about 85% for Cd(II).

For the resin R 2 loaded with Zn(II), its regeneration above 95% is possible with 1 M HNO_3.

Resins R 3 and R 4 show a lower elution (approx. 40%) behavior for the metal ions. This result suggests that the interactions are stronger and/or the access to the active sites is more difficult to achieve.

Resin R 6 loaded with Cd(II) can be recovered completely by acids at different concentrations, although the quantitative elution of Hg(II) was not possible.

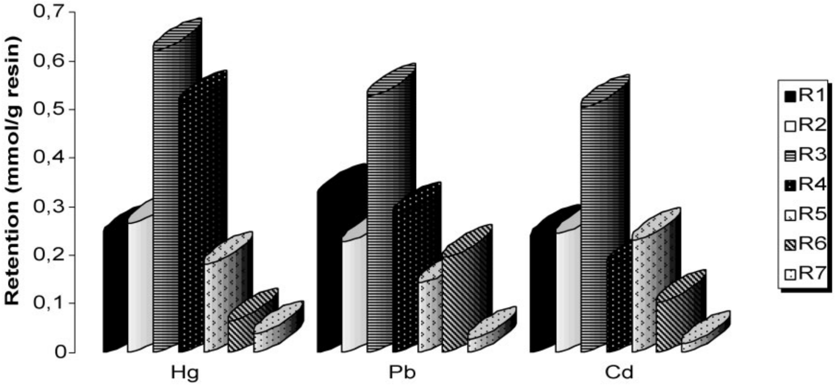

Figure 4.
Metal ion retention behaviour of the resins at optimum pH.

Table 4.
Maximum retention capacity of resins in mmol/g resin. Optimum pH, 20 °C, concentration of the solutions 1 g metal/L.

Resin	Hg(II)	Pb(II)	Cd(II)
R 1	0.893	0.543	1.207
R 2	0.864	0.557	1.136
R 3	0.647	0.833	0.897
R 4	0.772	0.825	1.025
R 6	0.714	–	0.691

Sorption-Elution Cycles

The resin that shows the best behavior corresponds to R6, which was loaded with Cd(II) and eluted by 1 M HNO_3. It kept retention above 0.2 mmol/g resin for both batch and column methods. According to these results, it should be possible to reuse this resin (see Figure 6).

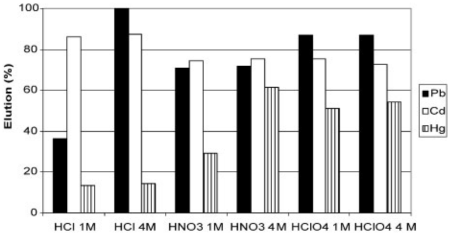

Figure 5.
Regeneration of the resin R 1 by different eluents.

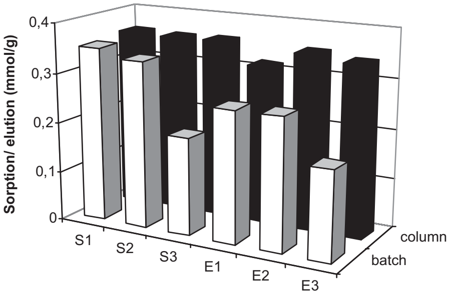

Figure 6.
Sorption-elution cycles by batch and column procedures for the resin R 6 charged with Cd(II) and 1 M HNO_3 as eluent. S= sorption, E= elution.

Conclusion

The resins containing sulfonic/sulfonate groups at the side chain showed high metal ion retention properties for Hg(II), Cd(II), and Pb(II). This interaction depended on the pH and it is considered to have occurred electrostatically.

The studied resins containing shorter spacer groups showed the higher retention behavior.An important effect of the carboxylic acid moiety on retention was not observed.

By changing the pH, the resin could be recovered with acid eluents and then reused three times without a significant loss of the retention properties.

Acknowledgements: The authors thank to FONDECYT Grant No 1070542, PIA (Anillo ACT 130), and CIPA for financial support.

[1] K. Pyrzynska, M. Trojanowicz, *Crit. Rev. Anal. Chem.* **1999**, *29*, 313.
[2] Y. Q. Cai, G. B. Jiang, J. F. Liu, Q. X. Zhou, *Anal. Chem.* **2003**, *75*, 2517.
[3] C. F. Poole, *Trends Anal. Chem.* **2003**, *22*, 362.
[4] V. Camel, *Spectrochim. Acta Part B* **2003**, *58*, 1177.
[5] R. G. Pearson, *J. Am. Chem. Soc.* **1963**, *85*, 3533.
[6] K. Pyrzynska, *Talanta* **1998**, *47*, 841.
[7] J. M. Sánchez, M. Hidalgo, V. Salvado, *Solv. Extr. Ion Exch.* **2004**, *22*, 285.
[8] M. Iglesias, E. Antico, V. Salvado, *Solv. Extr. Ion Exch.* **2000**, *18*, 965.
[9] Z. Hubicki, M. Leszczynska, B. Lodyga, A. Lodyga, *Min. Eng.* **2006**, *19*, 1341.
[10] K. A. Venkatesan, B. Robert Selvan, M. P. Antony, T. G. Srinivasan, P. R. Vasudeva Rao, *J. Radioanal. Nucl. Chem.* **2005**, *266*, 431.
[11] D. Perez-Quintanilla, I. Hierro, M. Fajardo, I. Sierra, *J. Mater Chem* **2006**, *16*, 1757.
[12] Z. H. Xie, F. Z. Xie, L. Q. Guo, X. C. Lin, G. N. Chen, *J. Sep. Sci.* **2005**, *470*, 462.
[13] G. Bortoleto, G. T. Macarovscha, S. Cadore, *J. Braz Chem Soc* **2004**, *15*, 313.
[14] M. A. A. Akl, I. M. M. Kenawy, R. R. Lasheen, *Microchem J* **2004**, *78*, 143.
[15] R. A. Beuvais, S. D. Alexandratos, *React. Funct. Polym.* **1998**, *36*, 113.
[16] A. Aklil, M. Mouflih, S. J. Sebti, *Hazard Mater A* **2004**, *112*, 183.
[17] M. E. Paez-Hernández, K. Aguilar-Arteaga, C. A. Galan-Vidal, M. Palomar Vardave, M. Romero-Romo, M. T. Ramirez-Silva, *Environ. Sci. Technol.* **2005**, *39*, 7667.
[18] R. Saliba, H. Gauthier, R. Gauthier, M. Petit-Ramel, *J. Appl. Polym. Sci.* **2000**, *75*, 1624.
[19] C. C. Wang, C. C. Chang, C. Y. Chen, *Macromol. Chem. Phys.* **2001**, *202*, 882.
[20] B. L. Rivas, P. Ovando, S. Villegas, *J. Appl. Polym. Sci.* **2002**, *83*, 2595.
[21] B. L. Rivas, S. A. Pooley, E. Aceitón, *J. Appl. Polym. Sci.* **2002**, *84*, 1251.
[22] B. L. Rivas, B. Ruf, *J. Appl. Polym. Sci.* **2003**, *88*, 1230.
[23] B. L. Rivas, B. Quilodrán, E. Quiroz, *J. Appl. Polym. Sci.* **2003**, *88*, 2614.
[24] B. L. Rivas, A. Castro, *J. Appl. Polym. Sci.* **2003**, *90*, 700.
[25] B. L. Rivas, S. Villegas, *J. Appl. Polym. Sci.* **2003**, *90*, 3556.
[26] B. L. Rivas, S. Villegas, B. Ruf, *J. Appl. Polym. Sci.* **2006**, *102*, 5232.
[27] B. L. Rivas, C. Muñoz, *J. Appl. Polym. Sci.* **2007**, *104*, 1769.
[28] S. Vijayalakshmi, R. Sankar, S. Subramanian, S. Rajagopan, T. Kaliyappan, *J. Appl. Polym. Sci.* **2007**, *104*, 797.
[29] L. Uzun, A. Kara, N. Tüzmen, A. Karabakan, N. Beşirli, A. Denizli, *J. Appl. Polym. Sci.* **2006**, *102*, 4276.
[30] Ch. Sun, R. Qu, Ch. Ji, Q. Wang, Ch. Wang, Y. Sun, G. Cheng, *E. Polym. J.* **2006**, *42*, 188.
[31] B. L. Rivas, M. Jara, E. Pereira, *J. Appl. Polym. Sci.* **2003**, *89*, 2852.