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Water-Soluble Polyacids with Capability to Remove Metal Ions in Homogenous Phase by Using the Liquid Phase Polymer-Based Retention Technique

Bernabé L. Rivas, Antonio Maureira, Eduardo D. Pereira*

Summary: Water-soluble polymers containing carboxylic acid and sulfonic acid groups were investigated as polychelatogens under different experimental conditions in view to study their metal ion binding properties, using the *liquid-phase polymer-based retention* technique. The divalent metal ions investigated were: Co^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+}. When the pH increased above 3, and especially at pH 5, metal ion retention capability increased as the majority of the functional groups are carboxylate, which can form more stable complexes with the metal ions. The retention capability also depended on the structure of the polyacid and the filtration factor, Z.

Keywords: membranes; metal ions; metal-polymer complexes; water-soluble functional polymers

Introduction

The increasing world demand for most known metals, the decrease in the grade of the available ores, and strict environmental regulations have generated great interest to find effective, efficient methods for processing waste solutions containing metal ions, even at very low concentrations. Liquid-liquid extraction, sorption, precipitation, and other methods based on two-phase distributions are generally used to separate inorganic species contained in dissolved matrices, industrial fluids or natural waters. Although many of these methods have been developed and successfully used, their application can cause problems. Some problems are related to heterogeneous reactions and interphase transfer. Heterogeneous two-phases system can be avoided by applying membrane process based separation methods, which are among the most promising techniques to enrich various species from solutions.[1–2]

Two-phase systems can be avoided by using separation methods based on pressure-driven membrane processes in the aqueous homogenous phase.

The efficient and selective separation of inorganic ions can be achieved by using water- soluble, polymeric reagents in combination with membrane filtration. Table 1 shows the most common membranes used in this process.This technique, referred to as liquid-phase polymer-based retention technique (LPR), is based on the separation of ions bound to water-soluble polymers (WSP) with chelating groups (polychelatogens) from non-complexed ions.[3–26] The separation process will be successful, if the polymer reagents employed meet the following requirements:

- High affinity towards the target metal ion,
- inactivity towards the non-target metal ion,
- high molecular mass,
- possibility of regeneration,
- chemical and mechanical stability,
- low toxicity, and
- low cost.

A wide variety of water-soluble polymers have been utilized in LPR process to recover heavy metals. Polymers reagents can be classified in the following three main groups:

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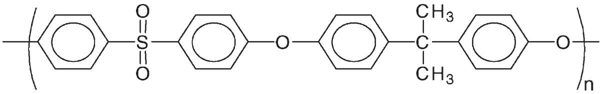
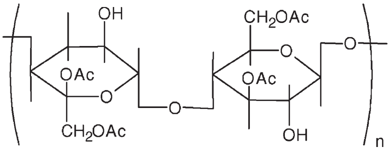
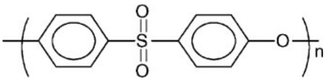
Table 1.
Molecular structure of ultrafiltration membranes.

Name	Molecular structure
Poly(sulfone)	
Cellulose acetate	
Poly(ethersulfone)	

- basic polymers, such as poly(ethyleneimine), poly(vinylamine), poly(allylamine), and other amino or imino group-containing polymers;
- neutral polymers, such as polyglycols, polyalcohols, polyethers, etc., and
- acidic polymers, such as poly(acrylic acid), poly(vinylsulfonic acid), poly(styrene sulfonic acid), and others.

Ultrafiltration is based on the membrane separation of small molecules from high molecular-weight molecules or aggregates. When metal ions are put in contact with a water-soluble polymer inside the ultrafiltration cell, the polymer retains those with high interaction rates with the polymer, which is not able to pass through the ultrafiltration membrane, while other ions are eluted through the membrane during the ultrafiltration run (see Figure 1). To ensure that no macromolecule leaves the ultrafiltration cell, the polymers, prior to being used, are fractionated by the same method using different membranes with known molecular mass cut-off (MMCO). Thus, fractionated and purified, they are then lyophilized and characterized. For LPR experiments, the highest molecular weight fractions are normally used in combination with a low molecular weight cut-off membrane.

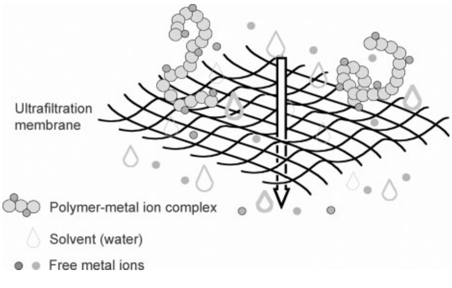


Figure 1.
Ultrafiltration principle.

Different modes of separations by LPR can be used for inorganic ions. The first one is the washing method, which is a batch-like method where a liquid sample containing the polymer and the metal ions to be separated is placed in the ultrafiltration cell at a given pH and ionic strength. This is then washed with a water solution contained in the reservoir that may reproduce the same pH and ionic strength values. Conditions may be found at which the ions of interest are retained and other species are removed. The washing method can also be applied to purify a macromolecular compound by eliminating the microsolutes. The second one is the enrichment method, analogous to a column method. A solution containing the metal ions to be separated is passed from the reservoir through the ultrafiltration cell containing a polymer solution. Both cell and reservoir solutions may be adjusted to the same pH and ionic strength values.

In both cases, a blank experiment (in the absence of the water-soluble polymer) is required to evaluate the interaction of the membrane with the metal ions.

The aim of this paper is to investigate the retention properties of different polyacids containing carboxylic acid and sulfonic acid groups as pendant groups using the *liquid-phase polymer based retention* technique.

Experimental Part

Reagents

The monomers acrylic acid, AA, (Merck), methacrylic acid, MA, (Merck), glycidyl methacrylate, GMA, (Aldrich), and sodium imino diacetate, IDA, (Aldrich) and 2-acrylamido-2-methyl-1-propane sulfonic acid, APSA, (Aldrich) were purified before the polymerization reaction. 2-Hydroxy-(3-methacryloyloxypropyl)amino diacetic acid (HMPADA) was synthesized according to the literature.[27] Poly(acrylic acid), P(AA), poly(methacrylic acid), P(MA), poly[2-hydroxy-(3-methacryloyloxypropyl) amino diacetic acid], P(HMPADA), and poly (2-acrylamido-2-methyl-1-propane sulfonic acid), P(APSA) were synthesized by radical polymerization using ammonium persulfate, APS as initiator (1 mol-%) for 24 hours at 60 °C in an oil bath, with a $N_2(g)$ atmosphere. Poly(α,β-*DL*-aspartic acid), P(Asp) was purchased (Aldrich). All the polymers were purified by passing them through a ultrafiltration membrane with a molar mass cut off (MMCO) of 3000 Daltons (Da). Then, the polymers were fractionated by membranes with different MMCO and the fraction >50000 Da was used for LPR runs. The metal salts studied were: $Co(NO_3)_2$ x 6 H_20, 99%, p.a. Merck; $Cu(NO_3)_2$ x 3 H_20, 99%, p.a. Merck; $Zn(NO_3)_2$ x 6 H_20, extra pure, Merck; $Cd(NO_3)_2$ x 4 H_2O, 99%, p.a. Sodium hydroxide (NaOH, Merck) and nitric acid 70% (HNO_3, Caledon) were used to adjust the solution pH.

Procedure (Washing Method) of LPR Technique

The main features of a LPR system are a filtration cell with a magnetic stirrer containing a membrane filter with a known exclusion rating, a reservoir and a pressure source, *e.g.* a nitrogen bottle. In ideal cases, this system may be considered a steady-state mixed flow reactor. Either a conventional stirred filtration cell or a specially designed tangential-flow cell equipped with a pump can be used. Essential parameters are the molar mass exclusion rate in a wide pH range (1–12), an appropriate permeate flow rate (0.5–12 mL min^{-1}), retentate volume (2–50 mL) and gas pressure, where 300 kPa is a suitable pressure in most cases. The most usual molar mass cut-offs range between 1,000 and 300,000 Da. A nominal exclusion rate of 10,000 Da proved to be convenient for polymers having a molecular mass between 30 and 50 kg mol^{-1}.

A 20.0 mL solution containing $5.0 \cdot 10^{-3}$ meq/L of a water-soluble copolymer and $1.0 \cdot 10^{-4}$ M of metal ions are placed into the solution cell provided with an ultrafiltration membrane with a MMCO of 10000 Da (Millipore, Amicon). The pH is adjusted with dilute HNO_3. A washing solution (water at pH = 3.0, 5.0, and 7.0, depending on the metal ion) is passed through under pressure (3.5 bar of N_2) from the reservoir through the cell solution. As the in- and out flux are rapidly equaled, the initial volume (20.0 mL) is kept constant during the experiment. Ten fractions of 20 mL were collected. Each fraction is collected in graduated tubes, and the corresponding metal ion concentration is determined.

Measurements

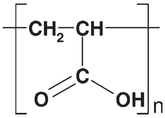
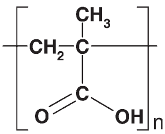
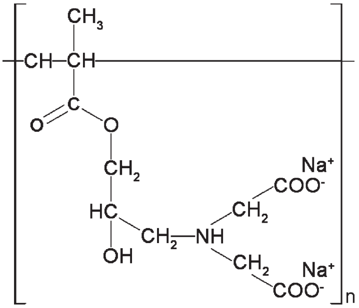
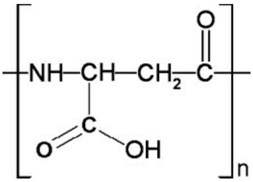
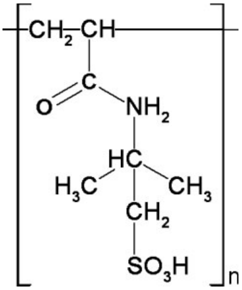
The pH was determined with a Jenco Electronics 1671 pH-meter. For the LPR technique, a membrane filtration system was employed to test the coordinating properties of the polychelatogen. A Unicam Solaar M5 series Atomic Absorption Spectrometer was used to determine the metal ion concentrations in the filtrate.

Results and Discussion

Different water-soluble polyacids containing the carboxylic acid/carboxyate and sulfonic acid groups were synthesized by radical polymerization and studied as a polychelatogen using the LPR technique. The P(AA) and P(MA) contain only carboxylic groups; P(HMPADA) contains carboxylic, hydroxy, ester groups, and tertiary amino functional groups; P(Asp) has carbonyl, carboxylic, and secondary amino groups; and P(APSA) corresponds to a strong polyelectrolyte containing two potential interacting groups as amide and sulfonic acid groups (see Table 2).

The metal ions were selected for their environmental and human impact, especially Cd^{2+} and Zn^{2+}, as well as for their importance in potential applications as metal-polymer metal complexes, particularly those with Cu^{2+}.

Table 2.
Structure of the polyacids as polychelatogens, pKa, and metal ions investigated.

Polymer	Structure	Investigated cations	pK*a*
Poly(acrylic acid) P(AA)		Co^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}	4.80
Poly(methacrylic acid) P(MA)		Co^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}	4.85
Poly[2-hydroxy-(3-methacryloyloxypropyl) amino diacetic acid] P(HMPADA)		Co^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}	–
Poly(*dl*-aspartic acid) P(Asp)		Co^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}	–
Poly(2-acrylamido-2-methyl-1-propane sulfonic acid) P(APSA)		Co^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}	1.0

To quantify the separation process, metal species retention versus the filtration factor is plotted. The binding and elution processes may be formulated as a chemical reaction, where a reversible reaction in combination with an irreversible transfer of metal ions across the membrane is responsible for metal retention (see Figure 2). Retention (R) is defined for any species as the fraction per unit of the species under study remaining in the cell during filtration. The filtration factor (Z) is defined as the volume ratio of the filtrate (V_f) versus volume in the cell (Vo). The metal ion (M) remaining in the cell during filtration is equal to the sum of the metal ion bound to the polymer chain and the metal ion free in the solution.

Interactions of metal ions with water-soluble polymers are mainly due to electrostatic forces and the formation of coordinating bonds. Other weak interactions may appear such as trapping metal ions in the bulk of the polymer phase.

The features of coordination between polymers and metal ions can be described by the usual coordination theories, but some special aspects should also be considered. When intra-chain complexes are predominant, the existence of a polymer domain with near constant ligand concentration is normally recognized since the distances between them keep them within a narrow range for a given polymer chain. As a result, the chelating reaction appears as a one-step reaction. For relatively low ligand amounts in the solution, completely complexed metal ions may coexist with free, non-complexed ones. The reactivity of the complexes can be strongly affected by the polymer ligand that exists outside the coordination sphere and surrounds the metal complex by means of special chemical environment and steric effects.

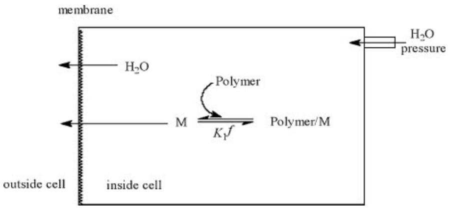


Figure 2.
Polymer-metal interaction in the filtration cell.

Interactions of metal ions with water-soluble polymers are mainly due to electrostatic forces and the formation of coordinating bonds. Other weak interactions may appear such as trapping metal ions in the bulk of the polymer phase.

The interactions between polyacids and metal ions are very dependent on the ionic strength, and low interaction rates are found when the ionic strength is high. Consequently, at pH 1, where the concentration of the monovalent H^+ ions is high, low interaction rates are always found. The interaction rates increase rapidly with increasing pH, and high retention values are found for divalent and trivalent metal ions at pH above 3.

In contrast, when interactions occur by formation of coordinating bonds, the nature of the metal ions and the effect of the pH may induce differences in the retention profiles of like-charged metal ions and selectivity is often informed. Polymers containing carboxylic acid groups (such as P(AA), P(MA), P(HMPADA), and P(Asp)) behave as weak polyelectrolytes and present high retention values at pH above 3. They also have chelating properties, and interactions with Cu^{2+} are normally found to be more intense than with other divalent metal ions.

The effect of the pH may be considered in several ways. For a strong polyelectrolyte, very low pH values are associated to high ionic strength, and in consequence, a competition of H^+ with divalent metal ions to condense on the polymer surface is established. Thus, in ultrafiltration experiments performed at pH near to 1, elution of divalent metal ions occurs from the polymer domain; while at pH 3, significant binding is found as can be seen in Figure 2. A weak polyelectrolyte, such as polycarboxylic acids, presents high retention ability at pH above 4.5 where most carboxylic units are deprotonated. The pKa for the polymer ranged from 4.4 and 4.8, and thus metal ion retention increases at pH 5 and pH 7.

The filtration factor Z is also a qualitative measurement of the strength between the ligand group and the metal ions. Thus, when these interactions are weak, it is only necessary to pass it through pure twice-distilled water to break this interaction. However, if these interactions are strong, they will be maintained and it is necessary to employ another method to recover the polychelatogen (see Figure 3).

Determination of Maximum Retention Capacity (MRC) by LPR Technique (Concentration Method)

To obtain polymer-metal complexes, the liquid-phase polymer based retention (LPR) technique by concentration method was used. This method consists in passing a metal ion solution, with known concentration, through a solution of water-soluble polymer (20 mL), keeping a constant volume. To only develop the enrichment (or concentration) method, the water-soluble polymer is placed into the ultrafiltration cell and the metal ion solution is placed in the reservoir. Equal concentrations of metal ion and polymer are used in the reservoir and ultrafiltration cell, respectively. When metal ions pass through the ultrafiltration cell, the macromolecules uptake the metal ions until saturation and the non-retained metal ions are collected in assay tubes and quantified by AAS. The same polymer fraction (>100 kDa) and ultrafiltration membrane of 10 kDa were employed in this study. A blank experiment with metal ions and without polymer is needed to determine the effect of the ultrafiltration membrane in metal ion retention. The amount of metal ion bound to the water-soluble polymer was calculated by calculating the difference between the concentration curve slope and the blank curve.

The MRC are calculated by the relationship:

$$MRC = {}^{MV}/_{Pm}$$

where MRC is expressed as milligrams of metal ion retained per gram of polymer (or expressed in mole), M is the metal ion concentration in mg/L, V is the filtrate volume passed through the membrane free of metal ion (in L), and Pm is the mass of polymer in g.

Assuming a quantitative retention of different metal ions, the enrichment factor (E) was determined according to the following relationship:

$$E = {}^{P \times C}/_{M}$$

where P is polymer concentration (g/L), C is maximum capacity of the polymer (mg/g), M is initial concentration of the metal salt (mg/L).

Figure 4 presents the concentration curves for Cu^{2+} at pH 5.0, where it can be observed that only P(HMPADA) and P(AMPS) are maintained as water-soluble complexes, although P(AA) and especially P(Aps) form precipitates at low metal ion concentration. Table 3 shows obtained results for MRC and E.

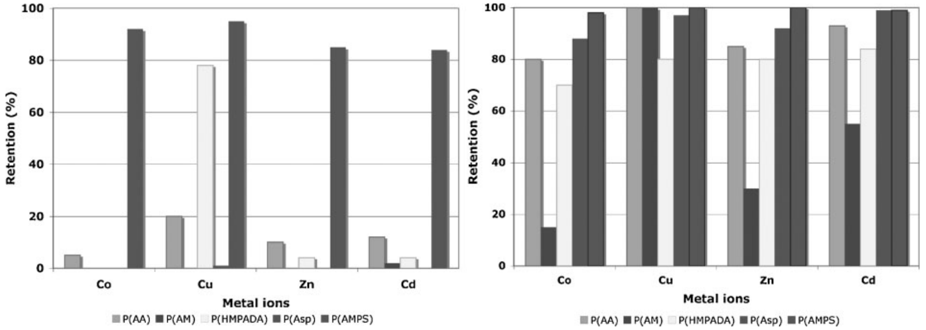


Figure 3.
Retention (%) for different polymer at Z = 10, a) pH 3.0, b) pH 5.0.

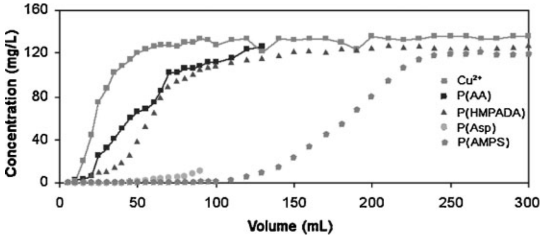


Figure 4.
Maximum retention curves for Cu^{2+} at pH 5.0 with different polymers.

Polymer-metal ion interaction mechanism

The capacity of water-soluble polymer complexing reagents is influenced by various factors, mainly steric and statistical. Usually there is not only intramolecular, but also intermolecular complexation because the coordination number of metal ions is greater than two. The dependence of capacity on the concentration of the polymer solution differs from polymer to polymer. Generally, steric hindrance diminishes the capacity if a certain concentration of solution is exceeded, and is strongly related with the dissociation degree of the polychelatogens. Thus, for P(AA) P(MA), P(HMPADA), P(Asp) at pH 5, most of the ligand groups are present as free carboxylates. Therefore, these groups form polymer-metal complexes, which are shown in Figures 5a and 5b. P(APSA) is deprotonated at a lower pH than that carboxylic acid.

Moreover, according to Pearson's soft and hard acids and bases (HSAB) principle,[28] carboxylate groups are soft bases, whereas sulfonate groups are relatively hard bases. The HSAB concept predicts the character of the bond between metal ions and functional groups. For example, the interaction between hard metal and hard ligands are predominantly ionic in nature, whereas soft metal-soft ligand complexes are more covalent in character. While Cu^{2+} ions are soft acids, Cd^{2+} can be regarded as a borderline ion of slightly less character than that Cu^{2+}. Thus, this information suggest that metal ion removal by P(AMPS) occurs predominantly by the ion exchange mechanism (see Figure 5a), whereas removal by P(AA), P(MA), P(HMPADA) and P(Asp) are due to a covalent interaction between the functional groups of polymer metal ions as well as the electrostatic interaction (see Figure 5b).

Conclusions

pH has a strong effect on the metal ion retention ability. The four weak polyacids (P(AA), P(MA), P(HMPADA), P(Asp)) investigated as polychelatogens presented the highest retention properties for Cu^{2+}, forming the most stable complexes. At low pH, the polychelatogen structure was observed to exert an important effect on metal ion retention capability. With respect to the metal ions, predominant species may be present as a function of the pH.

It can be concluded that the metal ion removal by P(AMPS) occurred predominantly by ion exchange mechanism,

Table 3.
Maximum retention capacity and enrichment factor (E) of Cu^{2+} with different polymers.

Sample	pH	mg metal ion/g polymer	meq metal ion/g polymer	E
P(AA)	5.0	21.5	0.34	1.51
P(HMPADA)	5.0	17.2	0.30	1.45
P(Aps)	5.0	*	*	*
P(AMPS)	5.0	84.2	1.34	3.34

*it was not calculated due to precipitation of polymer.

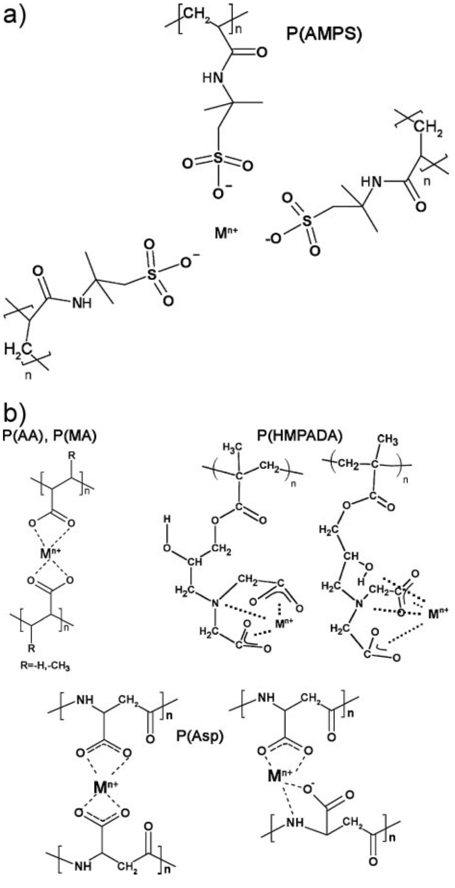


Figure 5.
Possible polymer-metal ion interaction mechanism for a) sulfonate group (electrostatic interaction), b) carboxylate and amido groups (complex formation).

whereas for poly weak carboxylic acids, a covalent interaction between the functional groups of polymer metal ions occurred in addition to the electrostatic one. Since hydroxy-complex precipitation is a phenomenon that should be avoided in LPR studies, Cu^{2+} ions cannot be studied at relatively high concentrations above pH 5.

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