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Metal Ion Removal from Aqueous Solution by Liquid Phase Polymer-Based Retention Technique

Bernabé L. Rivas, Eduardo D. Pereira, Pamela Robles, Rocío Cid*

Summary: Water-soluble poly[3-(dimethylamino)propylacrylate] is synthesized by radical polymerization with a yield of 87%. The polymer structure is confirmed by FT-IR and ^{1}H-NMR spectroscopies. The polymer lost only 3% of weight up to 100 °C. The narrowest molecular weight distribution is observed with the fraction between 3,000 and 10,000 Da. P(DAPA) presents a high affinity for the metal ions Pb^{2+} and Cu^{2+}, while the other metal ions are not significantly retained. By increasing the filtration factor, Z, metal ion affinity decreases, indicating a very weak ligand-metal interaction and the possibility of its destruction when washed with water at the filtration cell's pH. For $Z = 10$, the retention values of Pb^{2+} and Cu^{2+} at pH 5 are 76.5% and 48.5%, respectively, while the values for Cu^{2+} and Cd^{2+} at pH 7 are 89.5% and 40.4%, respectively.

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

Introduction

There is a growing interest to use water-soluble polymers (WSPs) in conjunction with ultrafiltration membranes to separate metal ions from aqueous solutions.

Apart from the formation of well-defined complexes, interactions of polymers with metal ions are interesting because of their potential analytical and technological applications in fields like environmental science, wastewater treatment, metallurgy industry, *etc*., as well as their implications in biological systems.

Water-soluble polymer-metal ion interactions take place in a homogeneous medium. To separate metal ions bound and not bound to polymers, one of the most promising techniques used is the application of separation methods based on membrane processes [1–29]. Using the method known as liquid-phase polymer-based retention (LPR) technique, membrane filtration easily allows this separation. Ultrafiltration is found as the most suitable technique for LPR studies. For use in homogeneous metal ion recovery, the appropriate water-soluble polymers may present high water solubility, an easy and cheap synthesis route, an adequate molecular weight and molecular weight distribution, chemical stability, high affinity for one or more metal ions, and selectivity for the metal ion of interest.

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, those presenting high interaction rates with the polymer are retained by the polymer, which is then unable to pass through the ultrafiltration membrane, while other ions are eluted through the membrane. To ensure that no macromolecule goes out the ultrafiltration cell, the polymers are fractionated by the same method, prior to use, using different membranes with known molecular mass cut-offs (MMCO).

Essential parameters to consider include: the MMCO 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 3 bar is a

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

suitable pressure in most cases. The most usual MMCO ranges between 1,000 and 300,000 Daltons (Da). A nominal exclusion rate 5,000 or 10,000 Da proved to be convenient for polymers having a molecular mass between 30 and 50 kg mol^{-1}.

Different modes of LPR separation 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 are placed in the ultrafiltration cell at a given pH and ionic strength. A second method is the enrichment method, which is 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.

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

The aim of this paper is to synthesize a functional water-soluble polymer containing tertiary amino groups as potential ligands for metal ions and to study the metal ion binding capability using the liquid-phase polymer-based retention (LPR) technique.

Experimental Part

Reagents

3-(dimethylamino)propylacrylate, (95% Aldrich, DAPA) was used without further purification. Ammonium persulfate, (Merck) and nitric acid (65%, Merck) were used. NaOH (pellets, 97%, Merck), and NaNO3 (p.a. Merck) were used. Aqueous solutions of NaOH and nitric acid were used to adjust the pH and to wash the membranes. The metal salts (Merck, p.a): $Ni(NO_3)_2 \times 6\ H_2O$, 99%, $Cd(NO_3)_2 \times 4\ H_2O$, 99%, $Cu(NO_3)_2 \times 3\ H_2O$, 99%, $Co(NO_3)_2 \times 6\ H_2O$, 99%, $Cr(NO_3)_3$ standard 1000 ppm, $Pb(NO_3)_2$, 99%, $Ca(NO_3)_2 \times 4\ H_2O$, 99%, $Zn(NO_3)_2 \times 6\ H_2O$, $Mg(NO_3)_2 \times 6\ H_2O$, 99%. The solutions were prepared with twice-distilled water with conductivity was lower than 1 $mS \cdot cm^{-1}$.

Measurements

The molecular weight and molecular weight distributions of the polychelatogens were analyzed by gel permeation chromatography (GPC) using a Perkin Elmer series 200 with a differential refractive index (DRI) detector and PL-aqua gel-OH columns. Water and polystyrene were solvent and standard, respectively. The FT-IR spectra were recorded on a Magna Nicolet 550 spectrophotometer. The 1H-NMR spectra were recorded in D2O using a Bruker Multinuclear AM 250 spectrophotometer. The thermal stability was studied under nitrogen atmosphere with a Polymer Laboratories Thermal Analyzer STA 625. The heating rate was 10 °C/min.

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.

Polychelatogen poly[3-(dimethylamino)-propylacrylate], P(DAPA) Synthesis

10.0016 g (0.0636 mol) of 3-(dimethylamino)propylacrylate, (DAPA) and 0.1481 g (6.36×10^{-4} mol) of ammonium persulfate (1 mol-%) are dissolved in 10 mL of twice-distilled water. The polymerization flask was kept under nitrogen at 70 °C for 24 h. The polymer is lyophilized. Yield: 87 %. P(DAPA) was purified and fractionated by ultrafiltration membranes with different MMCO, Millipore Amicon (100,000 Da, polyethersulfone, diameter 76 mm, 10,000 Da, polyethersulfone, diameter 76 mm, 3,000 Da, polyethersulfone, diameter 76 mm) and characterized by FT-IR and ^{1}H-NMR spectroscopies.

FT-IR (cm^{-1}) at 3424.24 (N–H); 2957.11 (C–H); 1722.97 (C=O); 1572.6l (N–H); and 1275.31 ($–CH_2–$).

^1H-NMR (D2O, ppm) at 1 ($CH_2–CH_3$), 1.7 ($–CH_2–CH–$, $–CH_2–CH_2–$), 2.3 ($–N–(CH_3)_2–$, 2.5 ($–CH_2–N–$)

TGA (scan rate: 10 °C min^{-1}, under N_2, mass of polymer: 4.461 mg). The weight-loss (%) at different temperatures (°C) are: 100: 3.0; 200: 14.1; 300: 41.2; 400: 63.6; 500: 88.8, and 550: 91.1.

GPC analysis by a PL Aquagel OH column, with 0.2 M $NaNO_3$, temperature: 20 °C (see Table I).

Fractions between 3,000 Da and 10,000 Da, and >100,000 Da were used to investigate the metal ion retention properties.

The metal nitrates of, Cu(II), Ni(II), Co(II), Ca(II), Mg(II), Pb(II), Cd(II), Zn(II), and Cr(III) (Merck, analytical grade) were used as received. The experimental conditions are indicated in Table II.

Procedure (Washing Method)

20.0 mL of a solution containing $5.0 \cdot 10–3$ eq/L of a water-soluble polymer, 0.010 or 0.10 M of $NaNO_3$, and $1.0 \cdot 10-4$ M of metal ions were placed in the solution cell with a ultrafiltration membrane with MMCO of 10,000 g/mol (Millipore, Amicon). The pH was adjusted to 5.0 with dilute HNO_3. A washing solution (0.010 M or 0.10 M of $NaNO_3$ in water at pH = 3.0, 5.0, and 7.0, depending on the metal ion) was passed through under pressure (3 bar of N_2) from the reservoir through the cell solution. All the experiments were carried out at constant ionic strength (see Table I). As the in- and out flux are rapidly equalled, the initial volume (20.0 mL) is kept constant during the experiment. Ten fractions of 10 mL were collected and then ten more of 20.0 mL. Each fraction was collected in graduated tubes, and the corresponding metal ion concentration was determined.

Table II.
Experimental conditions for LPR experiments. Volume from 1000 ppm prepared from nitric acid metal salts.

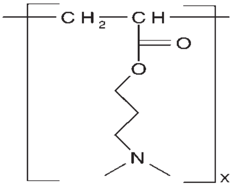
Metal ion	Volume	Final concentration	pH
	µL	ppm	
Co^{2+}	290	14.5	3, 5, 7
Ni^{2+}	290	14.5	3, 5, 7
Ca^{2+}	200	10.0	3, 5, 7
Mg^{2+}	120	6.0	3, 5, 7
Pb^{2+}	1,040	52.0	3, 5
Cd^{2+}	560	28.0	3, 5, 7
Zn^{2+}	330	16.5	3, 5, 7
Cr^{3+}	260	13.0	3
Cu^{2+}	320	16.0	3, 5, 7

Results and Discussion

Poly[3-(dimethylamino)propylacrylate], P(DAPA) is a very interesting water-soluble polymer due to the presence of the tertiary amine groups which should present metal ion affinity.

Synthesis and Characterization of poly[3-(dimethylamino)propylacrylate], P(DAPA).

The functional water-soluble polymer was synthesized by radical polymerization and fractionated by ultrafiltration membranes. The structure is shown below.



P(DAPA)

The polymer structure was corroborated by FT-IR and ^1H-NMR spectroscopies. The

Table I.
Molecular weight and molecular weight distribution of P(DAPA).

Polymer	Fraction (Da)	Area (%)	$\overline{M_w}$	$\overline{M_n}$	$\overline{M_w}/\overline{M_n}$
P(DAPA)	>100K	94.5	55,500	29,600	1.87
	10K < PM < 100K	92.7	16,800	15,900	1.05
	3K < PM < 10K	50.9	2,600	1,400	1.86

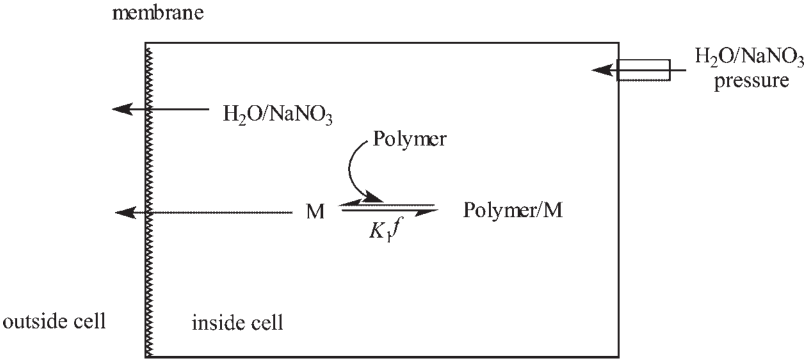


Figure 1.
Principle of ultrafiltration process.

thermal stability is high only up to 100 °C, after that it presents important weight losses, where at 300 °C, only 60% of its original weight remains (see experimental part). The results obtained for molecular weight and molecular weight distribution indicate that the fraction between 3,000 and 10,000 Da presents the narrowest molecular weight distribution (see Table I).

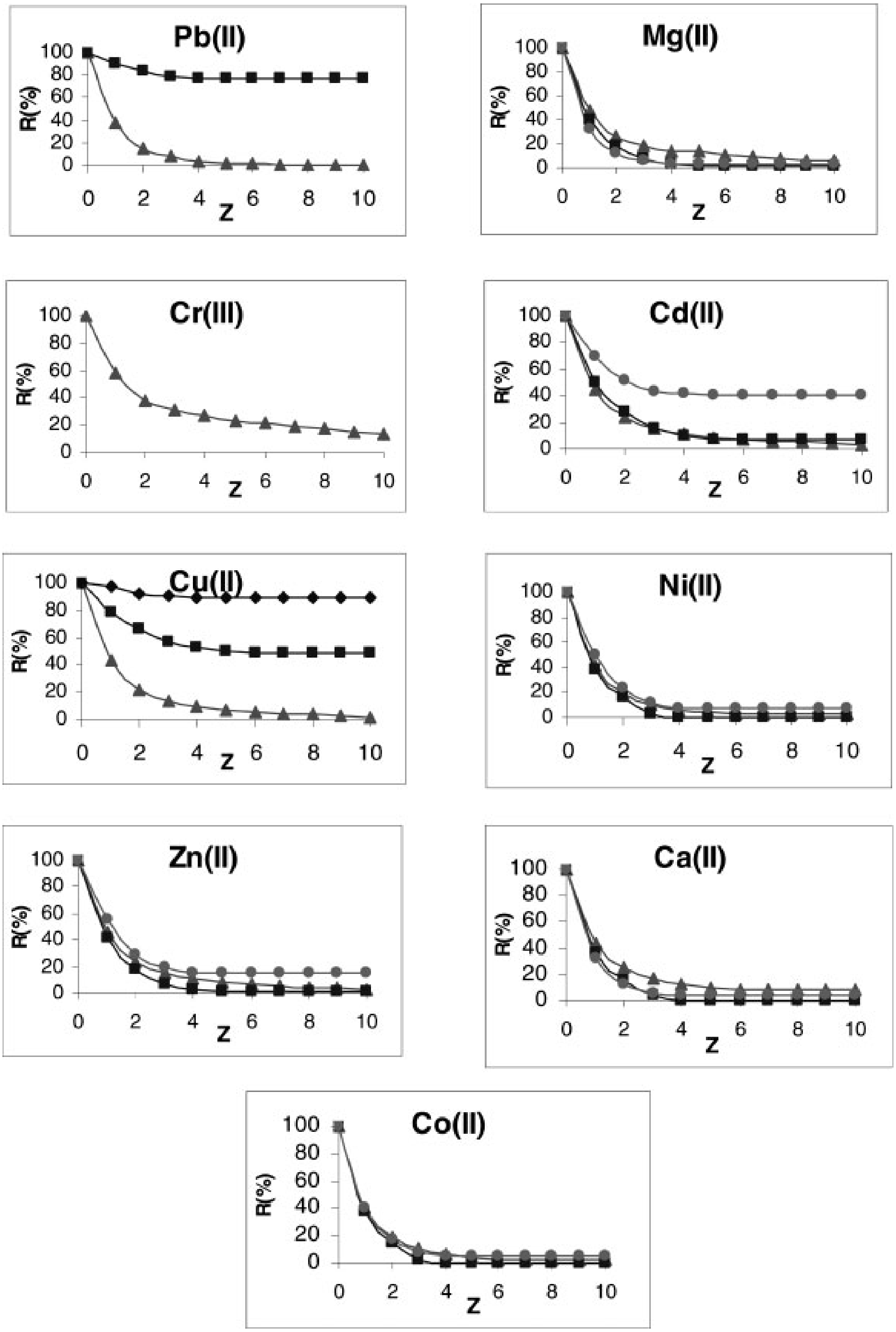
Metal ion retention properties of poly([3-(dimethylamino)propylacrylate], P(DAPA) were studied by LPR technique.

Once the P(DAPA) is characterized, the metal ion binding capability was evaluated using the LPR technique for the following nine metal ions: Co^{2+}, Ni^{2+}, Ca^{2+}, Mg^{2+}, Pb^{2+}, Cd^{2+}, Zn^{2+}, Cr^{3+}, and Cu^{2+} at pHs 3, 5, and 7, while changing the filtration factor Z from 0 to 10. Additionally, the washing method was also employed. To quantify the separation process, metal species retention is graphed with respect to the filtration factor. The binding and elution processes may be formulated as a chemical reaction, where reversible reaction in combination with an irreversible transfer of metal ions across the membrane is responsible for metal retention. To separate the components of a small volume sample in analytical chemistry (relative preconcentration), the liquid sample is placed in the polymer-containing cell solution and then washed with water (washing method). The pH is adjusted to a value at which the ions of interest are retained and the other species are removed. The washing method can also be applied to purify a macromolecular compound by eliminating the microsolutes when a constant volume is maintained in the cell.

The principle of the LPR technique is shown in figure 1.

To obtain the retention profiles, a P(DAPA):metal ion 40:1.0 relationship is used and corresponds to 0.2 mmol: 0.005 mmol. At the investigated pH, the metal ions are basically found in free form, avoiding the presence of species as $M(OH)^{n+}$ and M(OH)n.

The metal ion retention ability of the water-soluble polymer depends strongly on the pH and filtration factor, Z. As the pH increases, metal ion retention increases, but decreases as the Z value increases (see figure 2). This result is because the majority of amine groups are non-protonated at a higher pH. As a result, the electron pair is more available to bind metal ions and the methyl groups do not play an important role in metal ion retention from a steric hindrance point of view. It is suggested that the ester group does not interact with the metal ions. P(DAPA) shows a high affinity for the metal ions, Pb^{2+} and Cu^{2+}. The other metal ions are not significantly retained. By increasing the filtration factor, Z, metal ion affinity decreases, indicating a very weak ligand-metal interaction and the possibility of its destruction by washing with water at the filtration cell's pH. Thus, for a $Z = 10$, the retention values of Pb^{2+}



Pb(II)

Mg(II)

Cr(III)

Cd(II)

Cu(II)

Ni(II)

Zn(II)

Ca(II)

Co(II)

Figure 2.

Retention profiles of poly[3-(dimethylamino)propylacrylate]; P(DAPA). Fraction > 100.000 Da at pH 3 (▲); 5 (■); 7 (●).

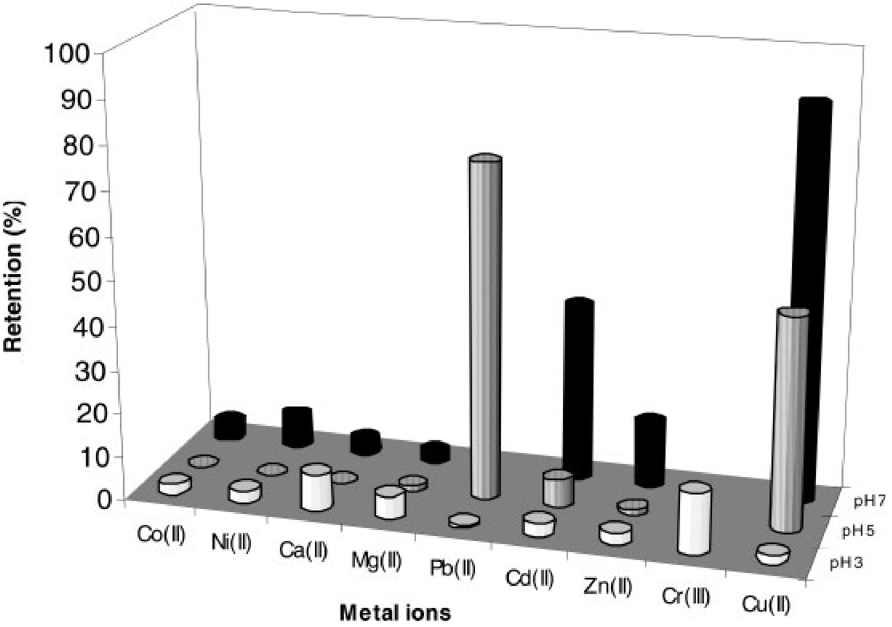


Figure 3.
Metal ion retention of poly[3-(dimethylamino)propylacrylate]; P(DAPA), Fraction > 100,000 Da at Z = 10 and pH 3, 5, and 7.

and Cu^{2+} at pH 5 are 76.5% and 48.5%, respectively, while the retention values for Cu^{2+} and Cd^{2+} at pH 7 are 89.5% and 40.4%, respectively (see figure 3).

The time required to achieve 100 % retention depends on the membrane's molar mass cut off (MMCO), the polymer's molecular weight, and the pH. Although the time was not determined for these measurements, in general for a membrane with a MMCO 10,000 Da, the time is approximately 1 h (after $Z = 10$). The polymer can be regenerated by protolysis and electrolysis of the polymer-metal ion complexes, although this was not performed in the present work. The membranes are washed after the process and re-used.

Metal ion Retention Affinity of poly[3-(dimethylamino)propylacrylate], P(DAPA) for Pb^{2+} and Cu^{2+} by LPR (Enrichment Method).

In the enrichment method, a polymer solution is placed inside the ultrafiltration cell and a metal-ion solution is placed in the reservoir. When the reservoir solution is passed through the polymer solution, the macromolecules uptake metal ions until saturation is achieved. Using this procedure, the polymer's maximum retention capacities can be calculated, defined as the maximum retention amount of metal ions bound to the polymer per unit polymer. Plotting the metal species concentration in the filtrate versus Z allows this calculation (see figure 4). A control experiment, in the absence of the polymer (blank), is needed. The concentration in the filtrate increases until it reaches the reservoir solution's concentration since it is controlled by diffusion. When the water-soluble polymer is present in the cell solution and an irreversible uptake of metal ions is performed, a curve parallel to the plot of the blank experiment will appear at a higher Z value. In those cases, the maximum retention capacity (MRC) can be calculated by:

$$MRC(mg\ metal\ ion/g\ repeat\ unit) = \frac{V_{sat}(L)\ C(mg/L)}{polymer\ mass(g)}$$

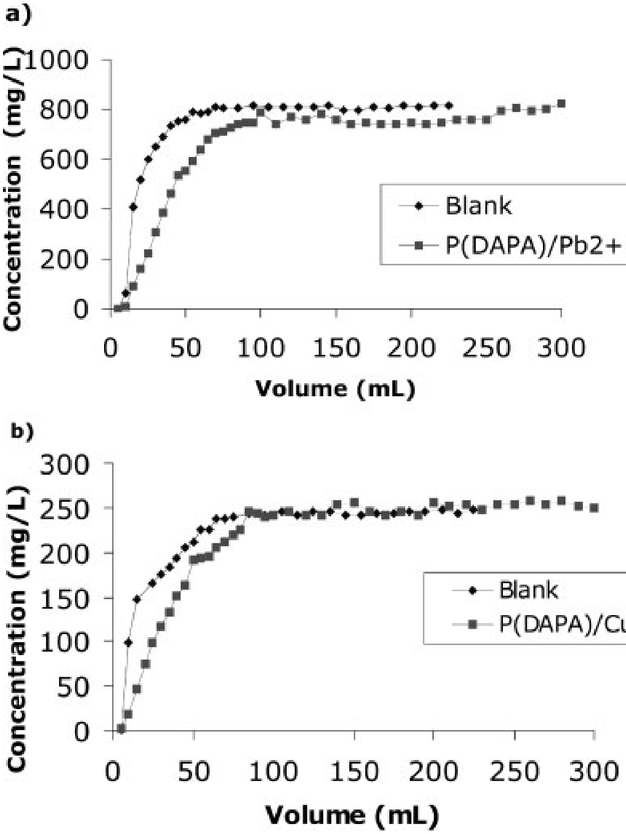


Figure 4.
Maximum retention capacity (MRC) of poly[3-(dimethylamino)propylacrylate], P(DAPA), for a) Pb^{2+} and b) Cu^{2+} at pH 5.

where V_{sat} is the volume required to reach polymer saturation, C is the concentration of metal ion solution in the reservoir, and polymer mass is the quantity of polymer placed in the cell.

This concentration method (enrichment method) is designed for metal recovery from dilute technological solutions and for absolute preconcentration of elements in analytical chemistry.

The maximum retention capacity for Pb^{2+} and Cu^{2+} ions was determined at pH 5 based on the washing method results. The results are summarized in Tables III and IV and figure 4. The highest MRC value (0.15 mmol of metal/mol repeat unit) was obtained for Pb^{2+}, while Cu^{2+} obtained 0.09 mmol metal/ mol repeat unit. The filtrate volume for both runs was 300 mL, which was sufficient for the saturation of

Table III.
Experimental conditions and MRC values of Pb^{2+} for P(DAPA) at pH 5.

Pb^{2+} Concentration	828 mg/L
Amount of P(DAPA)	0.1258 g
Saturation Volume	0.0374 L
MRC values	246 mg of metal/g repeat unit of P(DAPA) 2.38 meq of metal/ g repeat unit of P(DAPA) 0.15 mmol of metal/mol repeat unit of P(DAPA)

Table IV.
Experimental conditions and MRC values of Cu^{2+} for P(DAPA) at pH 5.

Cu^{2+} Concentration	254 mg/L
Amount of P(DAPA)	0.1258 g
Saturation Volume	0.0225 L
MRC values	45.4 mg of metal/g repeat unit of P(DAPA) 1.43 meq of metal/g repeat unit of P(DAPA) 0.09 mmol of metal/mol repeat unit of P(DAPA)

the polymer ligands with a metal ion concentration of 4 mM.

Polymer-Metal Ion Interaction

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

The coordination features between polymers and metal ions may be described by the usual coordination theories, although some special aspects may be considered. When intra-chain complexes predominate, the existence of a polymer domain with near constant ligand concentration is normally recognized since the distances between them are kept in a narrow range for a given polymer chain. And consequently, the chelating reaction appears as a one-step reaction. For relative low amounts of ligand in the solution, completely complexed metal ions may coexist with free, uncomplexed ones.

For P(DAPA), the ligand-metal ion interaction is strongly related with the dissociation degree of the polychelatogen. Therefore, at pH 5, most of the ligand groups are present as free amine (see figure 5).

CONCLUSIONS

A water-soluble functional polymer containing tertiary amine ligand groups by radical polymerization was synthesized. Poly[3-(dimethylamino)propylacrylate] P(DAPA) shows a high affinity for the divalent cations Pb^{2+} and Cu^{2+}. These metal ions would form stable complexes

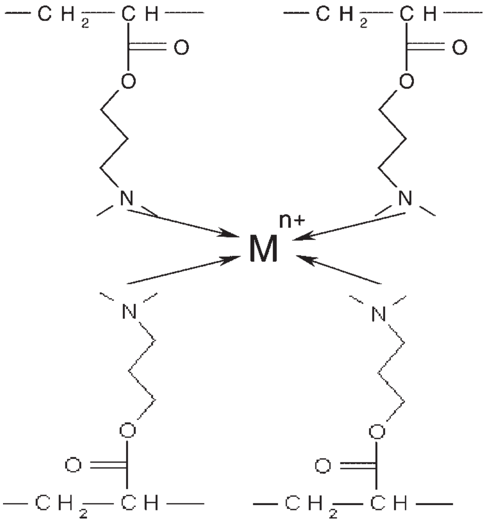


Figure 5.
Suggested polymer-metal ion interaction

though the free electron pairs from the tertiary amine groups. The other metal ions are not significantly retained. By increasing the filtration factor, Z, the affinity for the metal ion decreases. Thus, for $Z = 10$, the retention values of Pb^{2+} and Cu^{2+} at pH 5 are 76.5% and 48.5% respectively, while the retention values for Pb^{2+} and Cd^{2+} at pH 7 are 89.5% and 40.4%, respectively.

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