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Poly(2-acrylamido glycolic acid): A water-soluble polymer with ability to interact with metal ions in homogenous phase

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Abstract

A water-soluble polymer, poly(2-acrylamido glycolic acid) was obtained by radical polymerization and characterized by FT-IR, ^{1}H NMR, and ^{13}C NMR spectroscopy. The metal ion retention properties were investigated through the liquid-phase polymer based retention (LPR) technique at different pHs and filtration factor Z. The affinity of the ligand groups for the metal ions depends strongly on the pH. At lower pH, the retention is lower than 50%, which increased as the pH increased. At pH 5, the polymer showed a high affinity and selectivity for Pb(II), and at pH 7 the P(AGA) formed stable complexes with Cu(II), Co(II), Ni(II), Cd(II), and Pb(II). Of the three potential ligand groups, amide, hydroxyl, and carboxylate groups, the carboxylate groups form the more stable complexes with the metal ions.

Keywords: Water-soluble polymer; Metal ions; Polymer–metal complexes; Acrylamido glycolic acid; Liquid-phase polymer based retention

Removal, separation, and enrichment of hazardous metal ions in aqueous solution play an important role in environment remediation of municipal and industrial water. Among the many separation techniques, membrane separation is an efficient, widely applied separation process that is comparable to other separation techniques in terms of technical and economical feasibility. Many commercial separation problems are being solved by membrane processes, which can be successfully used to treat industrial effluents. Liquid–liquid extraction, sorption, ion exchange, and others are classic methods for pre-concentration and separation of elements in biological, environmental, geological, and industrial fluids.

The efficient and selective separation of metal ions can be achieved by using water-soluble polymers, WSPs, in combination with membrane filtration [1]. This technique termed liquid-phase polymer-based retention (LPR) is based on the separation of metal ions bound to WSP with chelating groups, which is the term used to refer to polychelatogens from non-complexed metal ions [2–4]. This technique has found application in the recovery of metal ions from diluted solutions on both an analytical and technical scale. The general principle of this technique is to add WSP binding reagents to a multicomponent solution so that these agents will form macromolecular compounds only with the target ions. Thus, the size of the metal ion would be increased significantly whereas the size of the non-target species would remain unchanged. If such a solution were then passed through an ultrafiltration membrane, the target metal ion would be separated from the non-target species. In the LPR process, the membrane represents a barrier that retains all ions bound to the polymer reagent, allowing permeation of all unbound ions. The separation process will be successful if the polymer reagent employed meet the following requirements [5]: 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. Considering these requirements, basic, neutral, and acid hydrophilic polymers have been designed and investigated respect to the analytical determination of metal ions

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[6–19]. These WSPs can be synthesized by different routes such as radical, cationic, and spontaneous polymerization, but the most usual synthetic procedures are addition polymerization, especially radical polymerization, and by functionalizing polymer backbone through polymer-analogous reactions. The polychelatogens may be homo- and copolymers, and can contain one or more ligand or coordinating groups. These groups are placed at the backbone or at the side chain, directly or through a spacer group.

The aim of this paper is to synthesize a water-soluble polymer containing three potential ligand groups and study its metal ion retention properties under different experimental conditions through the liquid-phase polymer based retention (LPR) technique.

N-Acrylamido glycolic acid (5.49 g, 0.0334 mol) was polymerized in radical way, using ammonium persulfate (APS) at 1 mol% as initiator, keeping the polymerization solution at 60 °C for 24 h under N_2(g) atmosphere. Similar conditions were previously described [20]. Poly(*N*-acrylamido glycolic acid), P(AGA) was purified with ultrafiltration membranes of 10000 Da of molecular weight cut off (MWCO). To purify the polymer, an aqueous polymer solution of 0.5 g/100 mL was prepared. This solution was ultrafiltrated with a polyethersulfone membrane of 100,000 Da as MWCO. Subsequently, the solution was lyophilized to obtain a dry polymer. The yield is 96%. The polymer was characterized by ^{1}H NMR, ^{13}C NMR, FT-IR, where the monomer's double bond signals [21] are not observed.

The study of poly(2-acrylamido glycolic acid) as polychelatogen was performed using the LPR technique employing the washing method [22]. All the experiments were performed at variable ionic strength.

As the in- and out-flux are rapidly equalled, the initial volume (20.0 mL) is kept constant during the experiment. Vigorous stirring was maintained to minimize concentration polarization and fouling. Ten fractions of 20 mL were collected. Each fraction was collected in graduated tubes, and the corresponding metal ion concentration was determined for Atomic Absorption using a Unicam Solaar M5 series Spectrometer.

The metal ion retention ability of the water-soluble polymer depends strongly on the pH. Retention (R) is defined for any species as the fraction per unit of the species under study remaining in the cell during filtration. The metal ion (M) remaining in the cell during filtration consists of the sum of the metal ion bound to the polymer chain and the free metal ion in the solution.

The retention profiles for the following metal ions: Ag(I), Co(II), Ni(II), Cu(II), Pb(II), Cd(II), Zn(II), and Cr(III), were studied by LPR technique at pH 3, 5, and 7, and changing the filtration factor Z from 0 to 10. Z is defined as the ratio of the volume in the filtrate (V_f) to the volume of the cell solution (V_o).

To obtain the retention profiles, a WSP : metal ion ratio of 40:1.0 is used, corresponding to 0.2 mmol : 0.005 mmol. This ratio obeys to ensure an excess of the ligand groups respect to the metal ion. At the investigated pH, the metal ions are basically as free form, avoiding the presence of species as $M(OH)^{n+}$ and $M(OH)_n$. The effect of the pH may be regarded in several ways. For weak polyelectrolytes, very low pH values are associated to a low ionic strength, and in consequence, competition to condense on the polymer surface between H^+ and divalent metal ions is established. Thus, for ultrafiltration experiments performed at pH near 1, elution of divalent metal ions takes place from the polymer domain, while significant binding is found at pH above 3. As the pH increases, the metal ion retention increases, but there is an important pH effect that differs from the behaviour observed for strong sulfonic acid groups. This difference means that the ligand-metal ion interaction is basically different for carboxylic acid groups, which form stable complexes with the carboxylate groups.

Fig. 1 shows the retention profile for P(AGA) with the fraction of 10,000 Da. At low pH, by increasing the filtration factor, Z, the affinity for the metal ions decreases, indicating that the ligand–metal ion interaction is very weak and that it can be destroyed by washing with water at the same pH of the filtration cell. To a 0.01 M polymer solution (0.02 mol), 32.6 mg of polymer P(AGA) were necessary.

Thus, at pH 3 and $Z = 6$, the all metal ion retention is lower than 50%; at pH 5, this behaviour is maintained for all metal ions except for Pb(II) whose retention is higher 90%. The affinity of the ligand for the metal ion does not depend on the filtration factor. Pb(II) was not studied at pH 7 to avoid the precipitation. At pH 7, it interacted more strongly with Cu(II), Co(II), Ni(II), Cd(II), and Zn(II). The retention is higher 95% and the interaction is very strong since it does not change as Z increases.

This polymer is protonated with all the functional groups as carboxylic acid at pH 3, is partially deprotonated at pH 5, and is completely deprotonated only at pH 7. The metal ions show a similar behaviour because hydroxy cation species, as $Cu(OH)^+$, $Pb(OH)^+$, and $Cd(OH)^+$ are present in solution at pH 5 and 7.

The time required to achieve 100% retention depends on the membrane's molecular weight cut off (MWCO), the polymer's molecular weight, and the pH. Although it was not determined for these measurements in particular, in general the time is approximately 2 h (after $Z = 10$) for a membrane with a MWCO 10000 Da. The polymer can be regenerated by protolysis and electrolysis of the polymer–metal ion complexes.

The retention behaviour for these metals by this water-soluble polymer P(AGA) is different with respect to water-insoluble P(AGA). Thus, Cu(II) retention for the crosslinked P(AGA) is lower (<60% at pH 5) than for WSP [23]. At pH 7, the behaviour is similar for Cu(II) (48%), Cd(II) (41%), Ni(II), (50%), and Pb(II) (60%), which were studied at trace concentration [24]. The lower metal ion retention of the crosslinked P(AGA) with respect to the water-soluble P(AGA) is due to the presence of two-