Water-Soluble Polymers and Their Polymer-Metal Ion-Complexes as Antibacterial Agents

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Summary: Natural and synthetic polymers with heteroatom, such as oxygen, nitrogen, sulfur or phosphorous, potentially can efficiently remove metal ions from aqueous solutions. The ability of synthetic polymers derived from imino diacetic acid, acrylamido glycolic copolymer, and the natural polymer alginic acid to remove metal ions from dilute solution in conjunction with ultrafiltration membranes was studied. The maximum retention capacity was determined and its polymer-metal ion-complexes were studied as possible antibacterial agents.

Keywords: alginic acid; antibacterial; metal ions; ultrafiltration membrane; water-soluble polymers

Introduction

Water-soluble polymers (WSP) cover a wide range of macromolecular systems including biopolymers such as DNA and synthetic polymers such a poly(acrylic acid). Due to its different structures, spatial conformation, and atomic composition give to this class of polymers a wide range of applications.

Polyelectrolytes may be distinguished from chelating polymers (polychelatogens) according to their structures and atomic composition. Polyelectrolytes have charged groups or easily ionizable groups in aqueous solution, such as sulfonic or phosphonic acids; while the latter bear functional groups with the ability to form coordination bonds. The most investigated ligands present at the polychelatogen structure are amines, carboxylic acids, amides, alcohols, aminoacids, pyridine, thiourea, imino, *etc*.

Removal, separation, and enrichment of hazardous metal ions in aqueous solutions play an important role for remediation of municipal and wastewater. At least 20 metals are classified as toxic and half of these are emitted into the environment in quantities that constitute human health risks. The toxic heavy metal cations contained in industrial effluents coming from plants using or producing heavy toxic metals and heavy toxic metal compounds are the main sources of the heavy toxic metal pollution. Specifically, metal-bearing wastewaters include discharges from electrolysis copper plating (for printed circuits, plating on plastics, *etc*.) and metal finishing industries as well as the washing effluents from metal-contaminated soil. Therefore, metal ion recovery is a key challenge from both an environmental and economic point of view. Treatment methods for such wastewaters depend greatly on the particular complexing reagents and metal ions used as well as their concentrations. In general, they are grouped into three categories: chemical, physical, and electrochemical.[1–9]

From many separation techniques used industrially, membrane separation is an efficient and widely applied separation process that is comparable to other separation techniques in terms of technical and economic feasibility. Liquid-liquid extraction, sorption, precipitation, ion exchange, and others are classic preconcentration and

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separation methods for elements in geological, biological, environmental, and industrial fluids. These two-phase distributions or heterogeneous reactions with diffusion-controlled processes present several disadvantages, such as long contact times or the use of additional separations processes. These disadvantages can be avoided with the use of water-soluble polymeric reagents in combination with membrane filtration.[10,11] This technique termed *liquid-phase polymer-based retention technique* (LPR) is based on the separation of ions bound to WSP from those non-bound by mean electrostatic groups or chelating groups can be achieved by two methods. The *washing method* is a batch-like method where a liquid sample containing the polymer and the metal ions to be separated is placed in the ultrafiltration (UF) cell at a given pH and ionic strength. Subsequently, solutes, in contact with WSP and UF membrane are washed with a water solution contained in the reservoir that may reproduce the same pH and ionic strength values. The second one, the *enrichment method*, is analogous to a column method. A solution containing the metal ions to be separated is passed from the reservoir through the UF cell containing a polymer solution. Both cell and reservoir solutions may be adjusted to the same ion strength and pH. The separation process will be successful if the polymer reagent employed meet requirements such as: 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.

Furthermore, this method is used to synthesize polymer-metal ion complexes (PMC), which have emerged as a new generation of materials with tremendous potential in fields such as superconducting materials, ultrahigh strength material, liquid crystals, catalysts, and biocompatible polymers.[12–15] Different polymer acids such as: poly(acrylic acid), P(AA), poly(methacrylic acid), P(MAA), poly(vinyl sulfonic acid), P(VSA), poly(styrene sulfonic acid), P(SSA), and poly(2-acrylamido-2-methyl propane sulfonic acid), P(APSA)[16–21] have demostrated a good efficiency for this propose. Alginic acid is a natural polymer derived from brown algae. In acid aqueous medium, it can be found in gel form, and with the presence of Ca(II) and Mg(II) ions it forms gel in water. This polymer consists in two uronic acids, *D*-mannuronic and *L*-guloronic acids, disposed as blocks in different ratios, alternating or random form. Due to this variability, its pKa value ranges between 3.5 to 5.0.[22–24]

The aim of this work is to analyze the potential use of synthetic and natural WSPs as poly(hydroxymethyl propyl imino diacetic acid), P(HMPADA), poly(2-acrylamido glycolic acid), P(AGA), poly(2-acrylamido glycolic acid-*co*-2-acrylamido-2-methyl propane sulfonic acid), P(AGA-*co*-AMPS), and alginic acid (AA) to remove metal ions from aqueous solution, determining the functional groups involved in the formation of the polymer-metal ion complex using infrared spectroscopy and studying their application as antimicrobial agents.

Materials

Imino diacetic acid (Aldrich Co.), 2-glycidyl methacrylate 96%, (Aldrich Co.), 2-acrylamido glycolic acid, 2-acrylamido-2-methyl propane sulfonic acid, (Aldrich Co.), alginic acid from brown algae was obtained from Sigma. Ammonium persulfate (AP, Fluka) was used without further purification All metal ions were purchased from Merck: $Cu(NO_3)_2 \times 3H_2O$, 99%, p.a.; $Zn(NO_3)_2 \times 6H_2O$, extra pure; $AgNO_3$, 99.8%, p.a.; $Cd(NO_3)_2 \times 4\ H_2O$, 99%, p.a. Sodium hydroxide (NaOH, Merck), nitric acid 70% (HNO_3, Caledon) were used to adjust pH.

Polymer Synthesis

P(HMPADA), P(AGA), P(AGA-*co*-APSA) were synthesized from their corresponding monomers by radical polymerization using

