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A CRITICAL STUDY ABOUT THE CHELATING POLYMERS AND ENVIRONMENTAL REMEDIATION

ABSTRACTS

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Due to their effect on metal availability and mobility, and in particular because of their persistence in the environment, aminopolycarboxylate chelating agents are under investigation. Chelate adsorption, metal mobilisation, metal exchange, mineral dissolution, reactive transport, photodegradation and chemical degradation are all shown to be significantly affected by chelated metal ions in this study. When determining the reactions of chelating agents in the atmosphere, the different reactivities of the metal complexes have to be noted since they occur in natural waters, primarily in the form of metal complexes. Therefore, understanding the speciation of chelating agents in natural waters is essential to predicting their environmental fate. Despite this significance, only a few measurements of speciation for natural waters have been recorded, and model calculations have been used frequently instead. However these calculations are complicated by slow metal-exchange reactions that result in nonequilibrium speciation and by the presence of natural ligands that compete for available metals with the chelating agents. While there are many approaches to clean up waste water and soil polluted with heavy metals and other industrial contaminants, one of the most versatile and affordable methods is to remediate chelating polymers. The efficiency and selectivity of the polymer ligand for specific metal ions are two significant parameters that can be regulated by ligand form, ligand density, polymer solubility, as well as operating pH. This work provides an overview of remediating polymers and ligands currently in use as well as an outlook for the future directions of chelating polymer design.

Key Words: chelating polymers, metal ions, environmental remediation, nanotechnology

INTRODUCTION

Each year, about five million tonnes of heavy metals from industrial production are introduced to the wastewater streams of our country which makes cleanup a high priority.

In particular, lead (Pb), mercury (Hg), and cadmium (Cd) are highly toxic to most living species (1). Conventional polluted soil cleanup is carried out by washing with strong acids or caustics, resulting in secondary contamination and massive sludge dumps that often go to landfills (2). Wastewater is usually remediated by chemical agent precipitation, activated carbon adsorption, ion-exchange resins, or membrane filtration methods (3, 4). Colloidal metals are easily separated by simple filtration techniques, but more complicated techniques such as reverse osmosis are needed for cationic metals (5). Significant quantities of hazardous sludge result from precipitation, while ion exchange is only efficient for low dissolved solid concentration solutions (2-5). Membrane separation techniques are very successful, but because of the high costs associated with these techniques, they are not realistic solutions for large-scale remediation (5).

The use of chelating polymers for water and soil remediation has gained a lot of attention lately (6). In the polymeric side chains or backbone, chelating groups are integrated. Metal ion affinity, retention efficiency and selectivity are controlled by the choice of ligand form, ligand density, polymer structure and solubility, as well as pH (3, 6, 7). Chelating polymers or polychelatogens are used for the remediation of solid polymer beads or semi-permeable membranes in homogenous reactions with water-soluble polymers coupled with ultra-filtration or in heterogeneous reactions (8).

Metal-ligand Affinity

Many factors affect the affinity or strength of the metal-ligand interaction, including the functionality of the chelating group, polymer chelating group density, oxidation state and metal electronic structure, stereochemistry, steric constraints, and electrostatic interactions (6). As previously discussed, the chelating functionality generally consists of some type of nitrogen and/or charged or neutral oxygen donor group mono-, bi-, or polydentate moiety that can serve as a Lewis base and donate electron density to the metal. The spacing on the polymer between the functional groups will play a significant role in how the ligands chelate (3). Several monodentate ligands may work as a polydentate ligand if the donor groups are close together on the polymer chain, or if there is little steric impedance between chains. Thus, local folding or crosslinking of the polymer chains may be caused by the metal ion.

Furthermore the existence of the intervening groups is also important (3). The folding of the polymer chains is supported by small flexible spacing groups, while rigid or bulky groups preclude such operation. Steric limitations on metal ligation are often dictated by the bulkiness of the functional group itself. The pKa of the polymeric backbone and ligands also has a significant impact on the interaction of the metal-ligand (14). Many of the nitrogen-bearing polymers undergo very poor binding to metal cations at low pH due to amine protonation, resulting in a loss of electron donation ability (9). Increasing the pH above pKa for functional groups of carboxylic acid leads to deprotonation and increased capacity to donate electrons. In addition, charge repulsion on the polymer between similarly charged groups can induce electrostatic repulsion that can also affect the efficacy of the ligation.

Next the coordinating geometry and number are influenced by the scale, electronic configuration, and oxidation state of the metal. Metals with high stabilising energies of the ligand field such as d6 low spin metals prefer octahedral structures, whereas metals with d10 configurations such as Zn2+ tend to have tetrahedral geometry (15). In addition, the strength of the metal ligation is influenced by the electronegativity, and thus polarizability, of the metal. The Pearson scale, a measure of a species' hardness or softness in terms of electron donation, indicates which types of groups of chelates and metal ions will interact preferentially. Noble metals such as copper (Cu), Hg, Pb and Cd are classified as soft acceptors based on this scale and interact preferentially with soft donors such as nitrogen. Chromium (Cr), on the other hand, is known as a hard species and is best linked to hard oxygen species (5). For selective binding of metal ions, the interplay of the aforementioned parameters which affect metal ligation affinity, can be used.

RESEARCH METHODOLOGY

For remediation applications, three major polymer groups are used (9). The first group consists of simple polymers such as polyethyleneimine (PEI) (highly-branched polyamine), polyvinylamine, and other amino or imino-containing polymers. The next collection contains neutral polymers with oxygen groups such as the polyglycols, polyalcohols, and polyethers. Acidic polymers such as polyacrylic acid, polyvinylsulfonic acid and sulfonated polystyrene are found in the third group. Polyelectrolytes are the acidic and essential polychelatogens; hence, their chelation properties are dramatically influenced by pH.

Analysis Methods

There are a range of methods to determine the efficiency of metal ion uptake, including radioisotope tracing (10), although the most common methods used are atomic absorption spectroscopy, elemental analysis, and infrared spectroscopy. Qualitative and quantitative information about the free metal ions in the filtrate is given by atomic absorption and elemental analysis (the amount of metal ions not complexed with the polymer). To assess the relative binding efficiency of the polymeric ligands, this knowledge can be used. Infrared spectroscopy can be used to understand the bonding states of the metal ligand through the shifts in the bonds' vibrational energies. In most cases, metal complexation causes shifts of the chelating functional groups to higher energies as a metal-ligand bond is formed by their non-bonding electrons. Generally, by comparing the complexed polymer and uncomplexed polymer spectra (11-13), the degree of complexation of the polymer ligands can be estimated.

RESULTS AND DISCUSSION

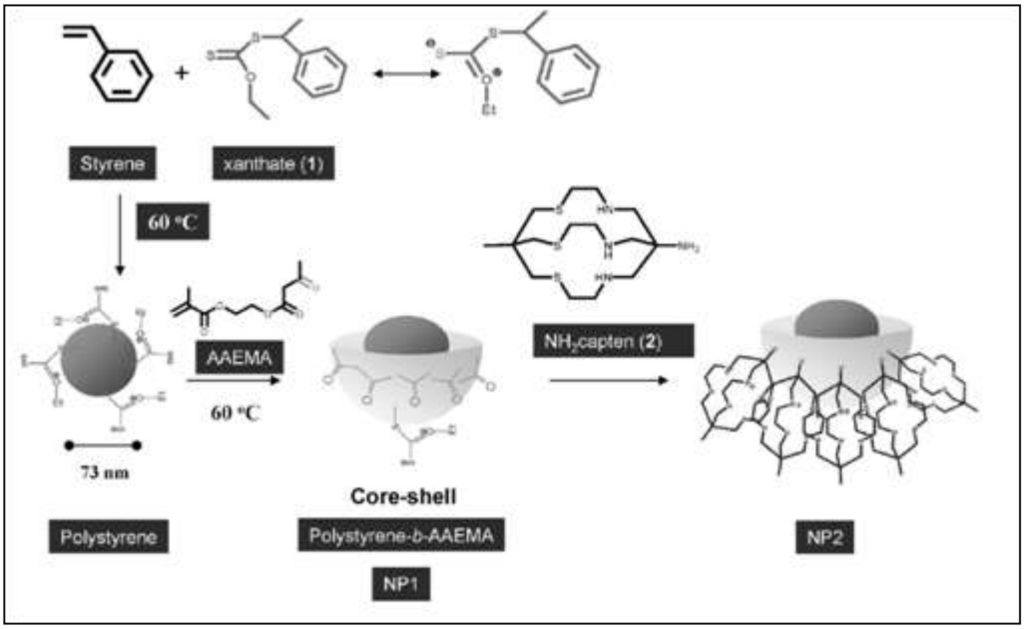
Ligand Composition

The environmental remediation potential and selectivity of chelating polymers depends strongly on the composition of the ligand and pH, as described above. Sauer et al. investigated the use of functionalized polyethyleneimine with complete and partial molar equivalents of carboxylic acids for the extraction of homogenous lead from polluted soils. Metal cation binding causes the polymer-metal complex to precipitate, which can be extracted to remove the metals from the solution. For the efficiency of lead extraction, the fully functionalized and partially functionalized polymers were compared with varying amounts of excess PEI based on binding power. With 5 to 7.5 fold excess PEI, there is a rise in Pb2+ elimination, but little improvement between 7.5 and 10 fold excess. The completely functionalized polymer binds the Pb2+ more effectively, but the difference is fairly small, suggesting that the amine sites of the partially functionalized polymer also form strong Pb2+ complexes. The researchers also observed that Pb2+ was more selective for the partially functionalized PEI than the competing calcium (Ca2+) found in large amounts in the soil. They reported that the softer nitrogen donors preferentially bound Pb2+ over Ca2+ in the partially functionalized system, while the completely functionalized system only had hard oxygen donors available for Ca2+ complexation. As two oxygen atoms were added to each primary and secondary nitrogen in the polymer chain ends and backbone, the reason for the better overall performance of the fully functionalized device for Pb2+ removal can most likely be attributed to the higher number of donors.

By adding cage-like chelating groups to the polymer that sterically regulates the size of the metal ion that can be bound, selectivity can also be achieved. Insoluble block copolymer nanoparticles composed of a polystyrene centre and a thin poly(2-acetoacetoxy)ethyl methacrylate shell were synthesised by Bell et al (10). Thiolate functionality ligated one particle, while the other also had a macrobicyclic amino-captain cage ligand attached to it (figure 1).

In the presence of Cd, Pb, and Hg, the competitive binding of cobalt was measured at a low fixed cobalt (Co) concentration with a growing excess of other metals. The findings, shown in figure 4, show that the binding efficiency of Co2+ was not impaired even at 1000 times the excess of competitor ions It is important to remember that the above experiments were performed at the optimum binding time and temperature for Co2+ (25 ºC, 10 min). The binding of the other larger metals with the ester groups is kinetically slower at these conditions. The selectivity of Co2+ over the other metals is considerably reduced when the same experiment was performed at 40 C for 1 h. This is most likely not because the heavy metals bind to the macrobicyclic ligand, but to the polymer backbone ester groups. It is important to note that when evaluated under the former conditions, NP1 achieved good selectivity of Hg2+ over Co2+.

Figure 1. Procedure for the preparation of nanoparticles with different surface functionality. NP1 has xanthate ligand and NP2 has a macrobicyclic amino-capten ligands.



The pH Effects

The pH of the polymer, and hence the protonation state for acidic and basic polymers, plays a decisive role in regulating the chelation properties in accordance with the composition and density of the ligand. The effect of pH transition on metal ion retention of poly(2-acrylamido glycolic acid) was studied by Rivas et al (9). The effects of the retention of various metal ions at three different pHs are shown in Figure 6. Metal ion retention increased with pH in all situations, although the magnitude varied with the individual metal. The polymer is in a totally protonated state at low pH, so the nitrogen atoms are positively charged and do not supply the metal cations with electron density. Moreover, carboxylic acids are also protonated, making them less powerful donors. It is important to note that at the lower pH values, the retention of Cu2+ and Pb2+ is much higher. The softer donors of nitrogen are still often protonated at pH 3 and 5; thus the complexation must be with the harder functionality of oxygen, while the former metal ions are usually known as soft ions.

PEI is especially vulnerable to alterations in pH. Since quaternary ammonium groups are unable to donate electron density, they are unable to form metal ion complexations. The elimination efficiency of PEI is therefore somewhat negligible at pHs much lower than the pKa of PEI (8-10) (figure 2).

Figure 2. Effect of pH on PEI Cd removal efficiency

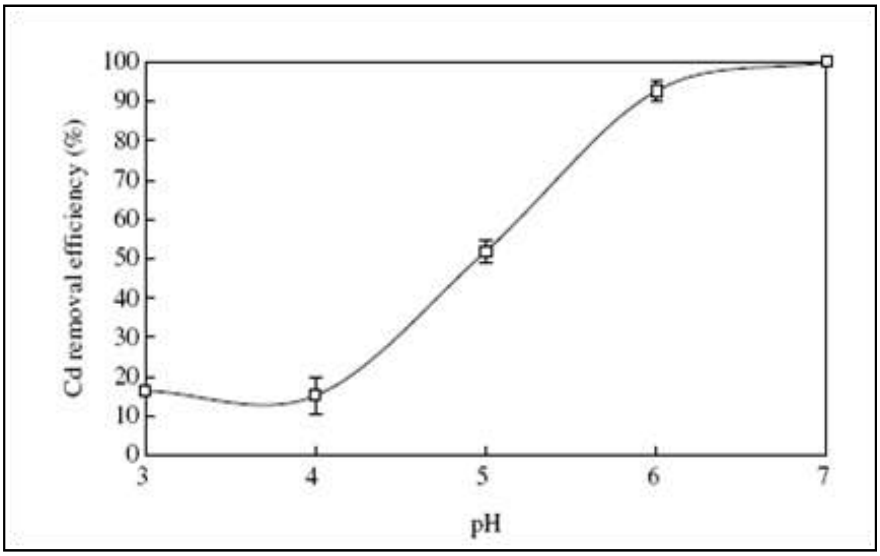


Figure 2 shows that the efficiency of Cd2+ removal is less than 20 percent at low pH (<5), but increases to almost 100 percent at pH 7 when the polymer is in its mostly unprotonated shape. Li et al. took the PEI/pH analysis one step further and investigated the influence of pH on the efficiency of PEI removal in the presence of the opposing EDTA, nitrilotriacetic acid (NTA) and citric acid small molecule ligands.

Regeneration

The capacity to recycle the chelating polymer for reuse is another significant aspect to consider. This is important not only for high-cost products, but also for cheap systems, since it limits the cost of waste disposal and reduces the impact on the environment. The metals are often recovered by regeneration so that they can be disposed of properly or refined for reuse. To regenerate the chelating groups of polymers, there are three main methods: chemical, electrochemical, and thermal. Of the three, the easiest and most cost-effective approach to chemistry is (16). Protolysis can regenerate acidic and basic polymers, altering the solution's pH in order to cleave the polymer-metal bond. Transcomplexation is another strategy that requires adding another ligand with a greater binding affinity for the metal to free the ions from the groups of polymer chelates. Redox reactions such as the reduction of Cr3+ with sodium sulphide to form chromium hydroxide (Cr(OH)3) that precipitates from the aqueous solution are a third chemical regeneration technique (16). For the removal of Hg2+, Chang et al. tested the regeneration of a chitosan biopolymer with acid and discovered strong adsorption abilities over three cycles (Figure 11) (17). Due to the competitive binding of H+ with the polymer, Sauer et al. observed complete recuperation of Pb2+ from the PEI polymer at pH 1.

CONCLUSIONS

The impacts on metal ion removal efficiency and selectivity of ligand composition, density, polymer structure, and pH have been studied. Especially effective in removing target metals from the solution, Ligand functionalities with rigid cages that permitted the two mechanisms of metal cation trapping and coordination were found. Highly branched polymers, such as polyethyleneimine, with a large number of functional groups available for complexation, were also useful in remediation, given that the pH was sufficiently high to ensure that most amine groups were not protonated. The nature of ligands with hard (oxygen) or soft (nitrogen) donor species helped to make metal ions of noble metals more selective than metals of higher ionic character. Polymer regeneration has been shown to be very effective, thus allowing the financial and environmental costs associated with these remediation systems to be reduced. While current chelating polymers are extremely efficient in remediation efforts, these systems have significant disadvantages. For synthesis, many synthetic polymers need toxic solvents. Moreover in order to extract the metal cations from the solution, water soluble polymers need an ultrafiltration step after complexation (1). Conventional insoluble polymer beads and membranes often have low surface-to-volume ratios and are therefore often not as effective as their water-soluble equivalents as remediation agents. In addition, many of the above polymers are ineffective at acidic pHs; thus, would be not be able to remediate the majority of industrial wastewater streams (7). The future of polymeric environmental remediation appears to be influenced by the increasing interest in nanotechnology as well as biomaterials and biomimetic systems. Due to their high number of chain ends and thus chelating groups, highly branched polymers such as nanoscale dendrimers can continue to be explored for homogenous filtration applications. Because of their high surface areas and filtration power, the use of nanofibers and polymer nanoparticles for heterogeneous filtration is increasing. In order to improve performance and selectivity, hybrid technologies such as the addition of catalytic titanium nanoparticles or other photoreactive materials, zeolites, and carbon nanotubes to polymer fibres and membranes will be explored in the years to come. Furthermore the inclusion of metal binding proteins in synthetic or biopolymeric matrices may theoretically allow higher selectivity and ease of thermal or chemical regeneration due to the narrow pH and temperature range of biological system activities (1). The use of natural biopolymers such as chitosan, a carbohydrate, is also expected to increase. Smart or stimulation-responsive polymers are another field of increasing interest for filtration applications. These polymers react with significant conformation changes to very slight changes in environmental conditions such as pH, temperature, electric field, or ionic strength, which could help to ease the regeneration of these systems. Nanoparticles and nanoscale entities are still very expensive at this moment in time. Thus, while there is a strong increase in their usage for remediation, an explosion in nanotechnology is not anticipated until the cost is in line with traditional technologies.

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