



Chelating Polymers and Environmental Remediation

by Nicole E. Zander

ARL-CR-0623

March 2009

prepared by

Dynamic Science, Inc
8433 N. Black Canyon Highway
Phoenix, AZ 85021

under contract

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14. ABSTRACT Although there are many approaches to clean up wastewater and soil contaminated with heavy metals and other industrial pollutants, remediation with chelating polymers is one of the most versatile and inexpensive methods. The polymer ligand's efficiency and selectivity for particular metal ions are two important parameters that can be controlled by ligand type, ligand density, solubility of the polymer, as well as operating pH. An overview of remediating polymers and ligands currently in use as well as an outlook for the future directions of chelating polymer design are presented in this work.					
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1. Introduction and Background

Approximately five million tons of heavy metals from industrial manufacturing are added every year to our nation's wastewater streams, which makes cleanup a high priority. Lead (Pb), mercury (Hg), and cadmium (Cd) in particular, are extremely toxic to the majority of living organisms (1). Conventional cleanup of contaminated soil is done by washing with strong acids or caustics, which results in secondary pollution and large deposits of sludge that often go to landfills (2). Wastewaters are typically remediated through precipitation with chemical agents, adsorption onto activated carbon, ion-exchange resins, or membrane filtration processes (3, 4). Colloidal metals are easily separated by simple filtration techniques, but cationic metals require more complex techniques like reverse osmosis (5). Precipitation results in large amounts of hazardous sludge, while ion-exchange is only effective for solutions with low dissolved solid concentrations (2–5). Membrane separation methods are quite effective but are not feasible solutions for large area remediation due to the high costs associated with these techniques (5).

Recently, the use of chelating polymers for remediation of water and soil has attracted much attention (6). Chelating groups are incorporated into the polymeric side chains or backbone. The choice of the type of ligands, ligand density, structure and solubility of the polymer, as well as pH, govern the metal ion affinity, retention efficiency and selectivity (3, 6, 7). Chelating polymers or polychelators are used for remediation in homogenous reactions with water soluble polymers coupled with ultra filtration, or in heterogeneous reactions of solid polymer beads or semi-permeable membranes (8).

2. Materials and Methods

2.1 Materials

Three main classes of polymers are used for remediation applications (9). The first group consists of basic polymers such as polyethyleneimine (PEI) (a highly branched polyamine), polyvinylamine, and other polymers bearing amino or imino functionalities. The next set includes neutral polymers with oxygen groups such as the polyglycols, polyalcohols, and polyethers. The third group contains acidic polymers such as polyacrylic acid, polyvinylsulfonic acid, and sulfonated polystyrene. The acidic and basic polychelators are polyelectrolytes; thus pH drastically affects their chelation properties.

2.2 Analysis Methods

There are a variety of methods to determine metal ion uptake efficiency, including radioisotope tracing (10); however, atomic absorption spectroscopy, elemental analysis, and infrared

spectroscopy are the most common methods utilized. Atomic absorption and elemental analysis provide qualitative and quantitative information about the free metal ions in the filtrate (the amount of metal ions not complexed with the polymer). This information can be used to determine the relative binding efficiency of the polymeric ligands. Infrared spectroscopy can be used to understand the metal ligand bonding states by the changes in vibrational energies of the bonds. In most cases, complexation of the metal induces shifts of the chelating functional groups to higher energies as their non-bonding electrons form a metal-ligand bond. The degree of complexation of the polymer's ligands can generally be estimated by comparing the complexed polymer and uncomplexed polymer spectra (11–13).

3. Technical Background

3.1 Metal-ligand Affinity

The affinity or strength of the metal-ligand interaction is influenced by many factors including the functionality of the chelating group, the density of chelating groups in the polymer, oxidation state and electronic configuration of the metal, stereochemistry, steric constraints as well as electrostatic interactions (6). As previously discussed, the chelating functionality usually consists of some type of mono-, bi-, or polydentate moiety with nitrogen and/or charged or neutral oxygen donor group that can act as a Lewis base and donate electron density to the metal. The spacing between the functional groups on the polymer can play an important role in how the ligands chelate (3). If the donor groups are close together on the polymer chain, or if there is little steric hindrance between chains, several monodentate ligands can act as a polydentate ligand. Thus, the metal ion can induce local folding or crosslinking of the polymer chains.

In addition, the nature of the intervening groups is also important (3). Small, flexible spacing groups aid in the folding of the polymer chains, while rigid or bulky groups prohibit such activity. The bulkiness of the functional group itself also determines the steric constraints on metal ligation. The pKa of the polymeric backbone and ligands also has a significant effect on the metal-ligand interaction (14). Many of the polymers bearing nitrogen functionalities experience very weak binding to metal cations at low pH due to protonation of the amine; hence loss of electron donation ability (9). Increasing the pH above the pKa for carboxylic acid functional groups leads to deprotonation and increased electron donating ability. Furthermore, charge repulsion between similarly charged groups on the polymer can cause electrostatic repulsion which can impact the ligation efficacy as well.

Next, the size, electronic configuration, and oxidation state of the metal affect the coordination geometry and number. Metals with large ligand field stabilization energies such as d^6 low spin metals prefer octahedral arrangements whereas metals such as Zn^{2+} with d^{10} configurations tend to have tetrahedral geometry (15). In addition, the electronegativity, and hence polarizability, of

the metal affects the strength of the metal ligation. The Pearson scale, a measure of the hardness or softness of a species in terms of electron donation, suggests which types of chelate groups and metal ions will preferentially interact. Based on this scale, noble metals such as copper (Cu), Hg, Pb, and Cd are defined as soft acceptors and preferentially interaction with soft donors such as nitrogen. On the other hand, chromium (Cr) is defined as a hard species and is best ligated by hard oxygen species (5). The interplay of the aforementioned parameters, which affect metal ligation affinity, can be employed for selective binding of metal ions.

3.2 Selectivity

The selectivity or ability of the polymeric ligand to discriminate binding of metal ions is critical for successful remediation because most wastewater and soils contain a complex mixture of metallic ions. Separation of target ions allows for proper waste disposal or recycling of these materials. In addition, many of these waste streams contain competing ligands such as ethylenediaminetetraacetic acid (EDTA) and acid (H^+) which can compete with the chelating polymer to bind target metals or protonate and inactivate the donating ability of the polymer, respectively (4, 14). There are several parameters that can be tailored to selectively remove the target ion even in the presence of competitor ligands. For competing ligands, the pH of the solution can be altered to reduce the affinity of the metal for the competitor ligand. For competing metal ions, ligand substitution kinetics can be taken into account in the design of the chelate group, and experimental conditions such as reaction time and temperature for the target metal ion removal. In addition, depending on the relative size of the target ion, encapsulating ligand functional groups can be utilized to create a size specific cage to trap the target ion (3, 10).

4. Results

4.1 Ligand Composition

As mentioned above, the environmental remediation ability and selectivity of chelating polymers depends strongly on ligand composition and pH. Sauer et al. examined the use of polyethyleneimine functionalized with full and partial molar equivalents of carboxylic acids for homogenous lead extraction from contaminated soils (figure 1) (2).

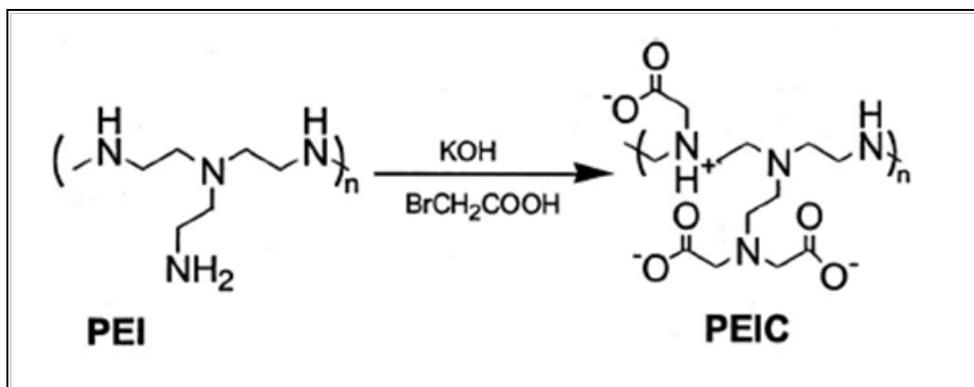


Figure 1. Functionalization of PEI with bromoacetic acid².

Binding of the metal cation induces precipitation of the polymer-metal complex which can be filtered to remove the metals from solution. The fully functionalized and partially functionalized polymers were compared for efficiency of lead extraction with varying amounts of excess of the PEI based on binding capacity (figure 2).

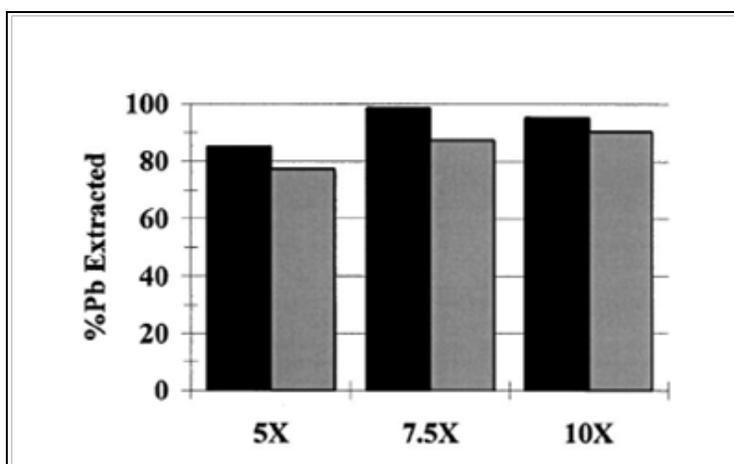


Figure 2. Percent of Pb extraction from contaminated soil using excess PEI (Black bar = fully functionalized, grey bar = partially functionalized) (2).

Figure 2 shows there is an increase in the Pb^{2+} removal with 5 to 7.5 fold excess PEI, but little change between 7.5 and 10 fold excess. The fully functionalized polymer more effectively binds the Pb^{2+} , but the difference is fairly small indicating the partially functionalized polymer's amine sites also form strong complexes with the Pb^{2+} . The researchers also found that the partially functionalized PEI had more selectivity for Pb^{2+} over the competing calcium (Ca^{2+}) found in large quantities in the soil. They claimed the softer nitrogen donors in the partially functionalized system preferentially bound Pb^{2+} over Ca^{2+} , whereas the fully functionalized system only had hard oxygen donors available for complexation with Ca^{2+} . The reason for the better overall performance of the fully functionalized system for Pb^{2+} removal can most likely be

attributed to the higher number of donors as two oxygen atoms were added to each primary and secondary nitrogen in the polymer chain ends and backbone, respectively .

Selectivity can also be achieved by adding cage-like chelating groups to the polymer that sterically controls the size of the metal ion that can be ligated. Bell et al. synthesized insoluble block copolymer nanoparticles consisting of a polystyrene core and a thin shell of poly((2-acetoacetoxy)ethyl methacrylate (10). One particle ligated via the thiolate functionality, while the other also had a macrobicyclic amino-captan cage ligand attached (figure 3).

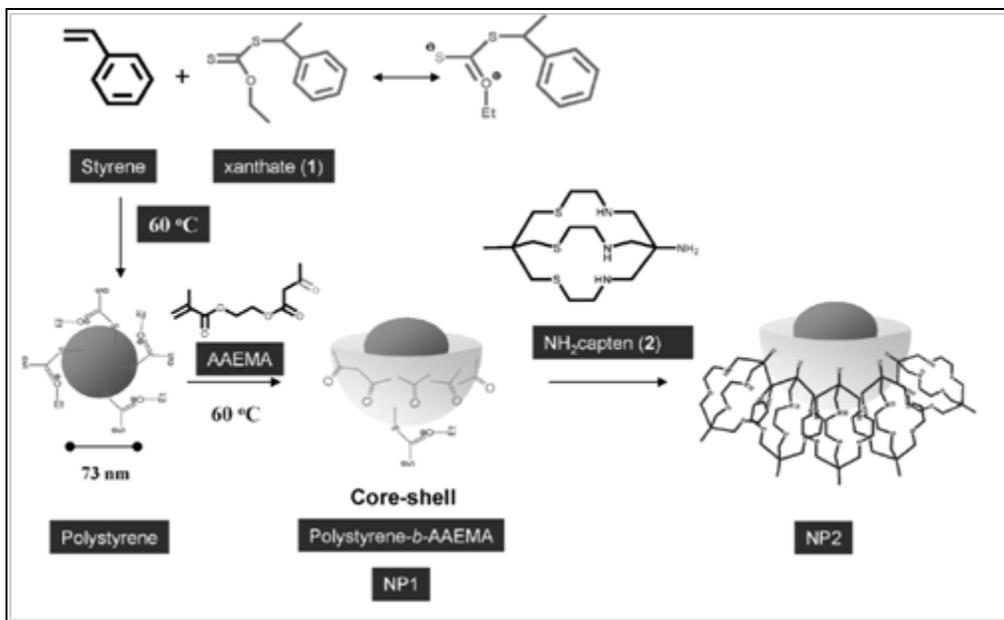


Figure 3. Procedure for the preparation of nanoparticles with different surface functionality. NP1 has xanthate ligand and NP2 has a macrobicyclic amino-captan ligands (10).

The competitive binding of cobalt in the presence of Cd, Pb, and Hg was tested at a low fixed cobalt (Co) concentration with increasing excess of the other metals. The results, displayed in figure 4, show that even at 1000 fold excess of competitor ions, the binding efficiency of Co²⁺ was not affected. It is important to note that the aforementioned experiments were conducted at the optimal binding time and temperature for Co²⁺ (25 °C, 10 min). At these conditions, the binding of the other larger metals with the ester groups is kinetically slower. When the same experiment was conducted at 40 °C for 1 h, the selectivity of Co²⁺ over the other metals is greatly reduced. This is mostly likely not because the heavy metals are binding to the macrobicyclic ligand, but rather to the ester groups in the polymer backbone. It is interesting to note that the NP1 achieved good selectivity of Hg²⁺ over Co²⁺ when tested at the former conditions.

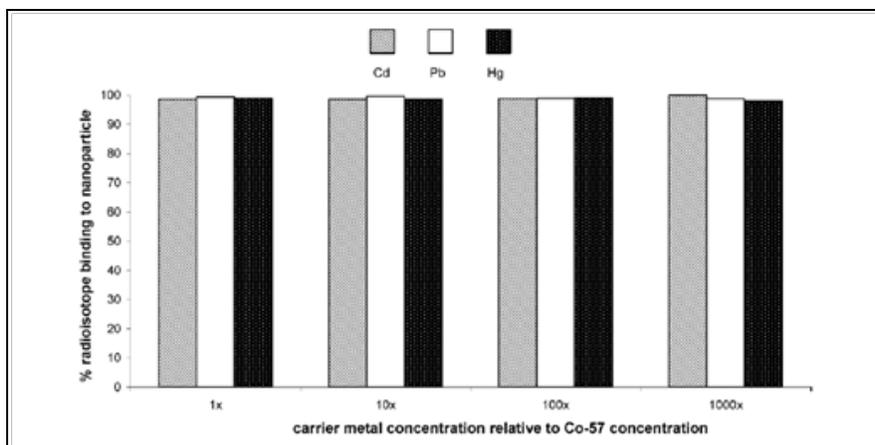


Figure 4. Competitive binding experiments of Co in the presence of Cd, Pb and Hg with increasing concentrations (1, 10, 100, 1000 fold excess) (10).

Efficiency and selectivity of metal ligation can also be affected by polymeric structure including functional group density, rigidity, and bulkiness of pendant groups. Mocioi et al. explored functional group proximity as a means to influence the efficiency of metal complexation (3). They examined a variety of polymers with amine and carboxylic acid moieties and their respective complexation with Cu^{2+} . Possible complexation geometries are shown in figure 5. The B and C polymers shown in figure 5 (a) have a very rigid coordination geometry where the Cu ion is trapped in the triethylenetetraamine cage, and is also coordinated by the nitrogen donation. The polymer system shown in figure 5 (b) represents a much more flexible arrangement with four polymer chains coming together to form metallic crosslinks. The coordination is less effective in the latter system due to the flexibility between chains and the electron donation coming from two oxygen donors instead of amine donors, as steric hindrance due to the aromatic rings attached to the nitrogen donors would prevent coordination of the metal ion with four nitrogen groups.

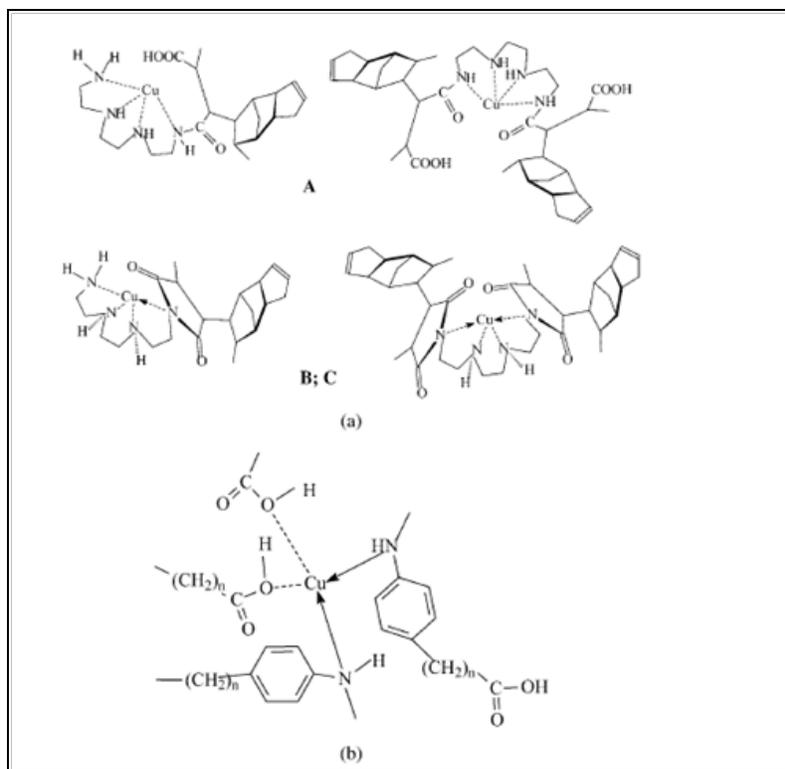


Figure 5. Complexation geometries of coordination polymers (3).

4.2 The pH Effects

In concert with ligand composition and density, the pH of the polymer, and hence protonation state for acidic and basic polymers, plays a definitive role in controlling the chelation properties. Rivas et al. studied the effect of changing the pH on metal ion retention of poly(2-acrylamido glycolic acid) (9). Figure 6 displays results for retention of various metal ions at three different pHs. In all cases, metal ion retention increased with pH, although the extent varied with the particular metal. At low pH, the polymer is in a fully protonated form; thus the nitrogen atoms are positively charged and cannot donate electron density to the metal cations. In addition, the carboxylic acids are also protonated and are less effective donors. It is interesting to note that the retention of Cu^{2+} and Pb^{2+} is much higher at the lower pH values. At pH 3 and 5, the softer nitrogen donors are still mostly protonated; therefore, the complexation must be with the harder oxygen functionalities, although the former metal ions are typically classified as soft ions.

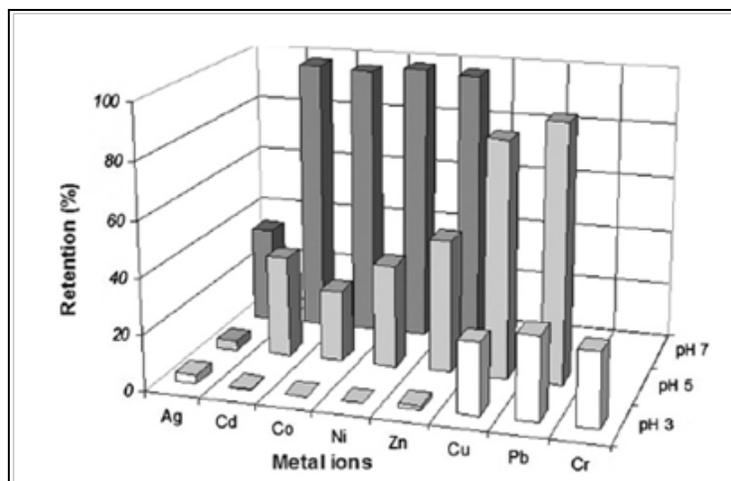


Figure 6. Metal ion retention of poly(2-acrylamido glycolic acid) at pH 3, 5, and 7 (14).

PEI is particularly susceptible to pH changes. Since quaternary ammonium groups cannot donate electron density, they are unable to form complexations with the metal ions. Thus, at pHs much less than the pKa of PEI (8–10), the removal efficiency of PEI is fairly insignificant (figure 7).

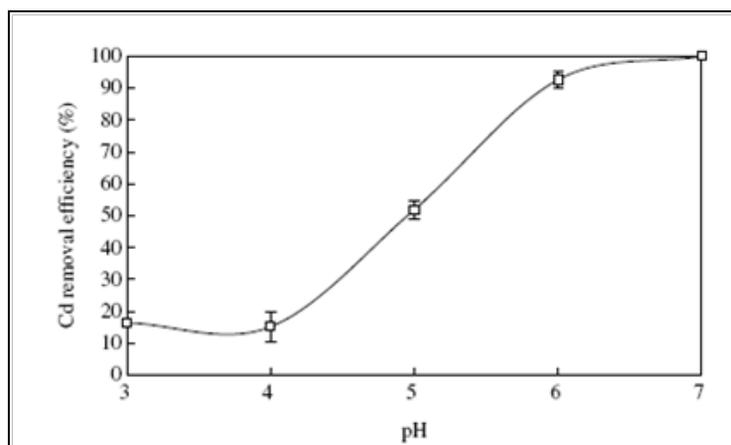


Figure 7. Effect of pH on PEI Cd removal efficiency (14).

Figure 7 shows, at low pH (<5), Cd^{2+} removal efficiency is less than 20%, but rises to nearly 100% at pH 7 when the polymer is in its mostly unprotonated form. Li et al. took the PEI/pH study one step further and examined the impact of pH on PEI removal efficiency in the presence of the competing small molecule ligands EDTA, nitrilotriacetic acid (NTA), and citric acid (14).

Figure 8 displays the results from this study at various pHs with the small molecule ligand to metal ratio fixed at 1:1 and a constant PEI concentration. EDTA appeared not to be pH sensitive and contrary to previous research, the removal of Cd^{2+} was quite high at the lower pHs. The researchers speculated that the complex $\text{Cd}(\text{EDTA})^{2-}$ formed and could interact electrostatically with PEI-H^+ , allowing for efficient removal of Cd^{2+} . At higher pHs, since PEI is no longer protonated, the PEI removal efficiency decreases indicating that EDTA is a better chelator than PEI for Cd^{2+} . The NTA and citric acid ligands did not aid or detract in the Cd^{2+} removal at low pH. Possibly the CdNTA (or CdCitric) complexes did not form or they simply interacted less strongly with the PEI-H^+ than the $\text{Cd}(\text{EDTA})^{2-}$ complex.

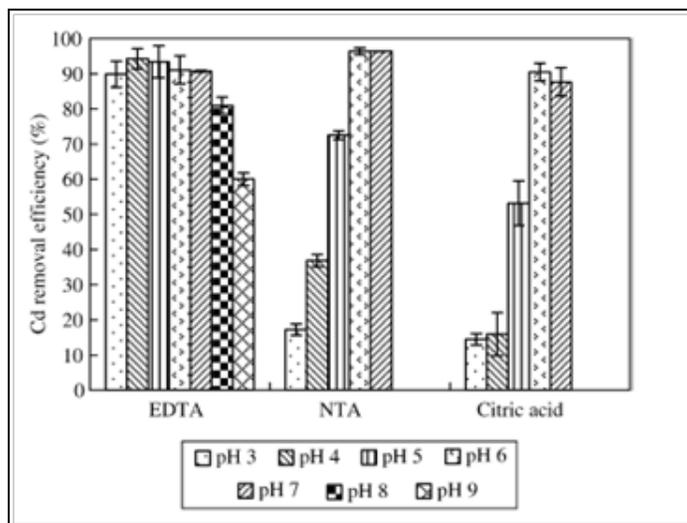


Figure 8. Effect of pH on removal of Cd by PEI in the presence of EDTA, NTA, and citric acid ligands.

Fu et al. also examined the removal of metals with EDTA (CuEDTA) in the presence of *N,N*-bis-(dithiocarboxy)piperazine (BDP). The dithiocarboxy group acted as a bridging ligand to polymerize the metal and form precipitates *in situ*—so called coordination precipitation polymerization (figure 9) (4).

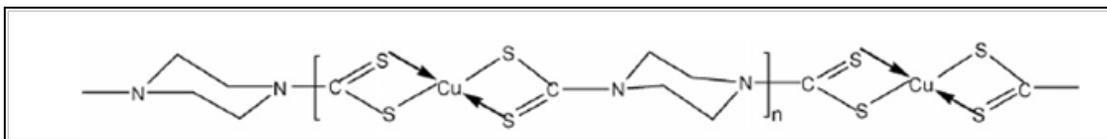


Figure 9. Copper precipitation by coordination precipitation polymerization with a dithiocarboxy polymer.

The results show that BDP was able to effectively precipitate the Cu^{2+} from the CuEDTA solution with little dependence on pH. The small pH effect seen at $\text{pH} < 4$ can be attributed to partial decomposition of the BDP in the presence of strong acid (figure 10).

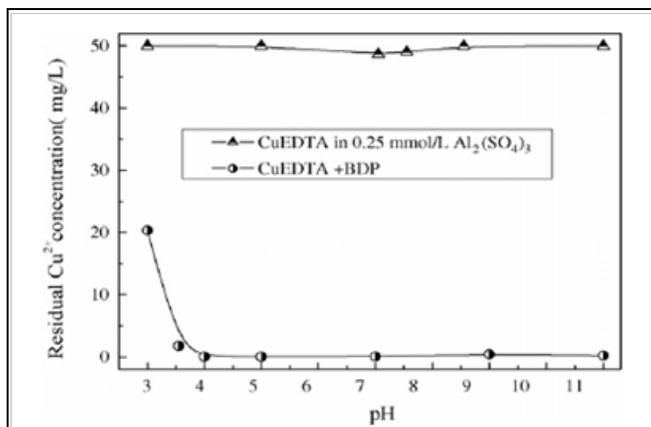


Figure 10. The pH dependence of residual Cu^{2+} concentration in a 50 mg/L solution of CuEDTA (4).

4.3 Regeneration

Another important factor to consider is the ability to regenerate the chelating polymer for reuse. Not only is this important for high cost materials, but also for inexpensive systems since it limits waste disposal costs and reduces the environmental impact. Regeneration also recovers the metals so they can be disposed of properly or purified for reuse. There are three major methods to regenerate polymer's chelating groups: chemical, electrochemical, and thermal. Of the three, chemical is the simplest and most cost-effective approach (16). Acidic and basic polymers can be regenerated by protolysis—changing the pH of the solution in order to cleave the polymer-metal bond. Another method is transcomplexation which involves adding another ligand with a stronger binding affinity for the metal to release the ions from the polymer chelate groups. A third chemical regeneration method involves redox reactions such as the reduction of Cr^{3+} with sodium sulfide to form chromium hydroxide ($\text{Cr}(\text{OH})_3$) which precipitates out of the aqueous solution (16). Chang et al. tested the regeneration of a chitosan biopolymer with acid for the removal of Hg^{2+} and found good adsorption capabilities over three cycles (figure 11) (17). Sauer et al. observed full recovery of Pb^{2+} from the PEI polymer at pH 1 due to the competitive binding of H^+ with the polymer.

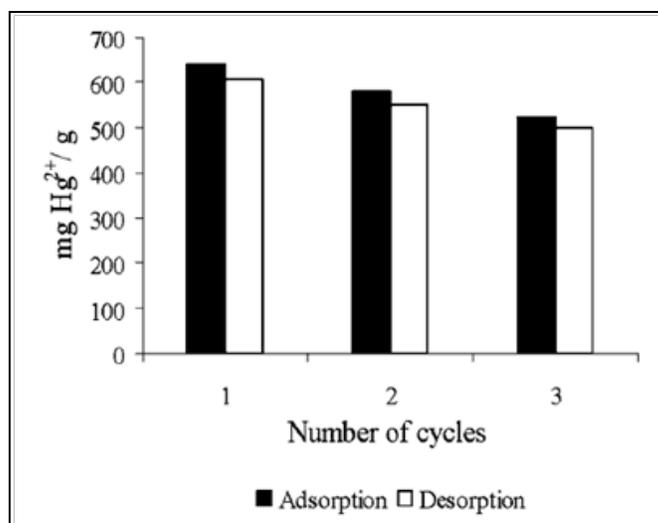


Figure 11. Adsorption/desorption cycles of chitosan biopolymer to evaluate regeneration ability (17).

5. Conclusions and Outlook

The effects of ligand composition, density, polymer structure, and pH on metal ion removal efficiency and selectivity have been examined. Ligand functionalities with rigid cages that allowed the two mechanisms of metal cation entrapment and coordination were found to be particularly effective in removing target metals from solution. Highly branched polymers, such as polyethyleneimine, with a large number of functional groups available for complexation was also efficient for remediation provided the pH was high enough to ensure most of the amine groups were not protonated. The design of ligands, with hard (oxygen) or soft (nitrogen) donor species, aided in selectivity of metal ions of noble metals over metals with more ionic character. Regeneration of the polymers was found to be very efficient thereby providing the ability to reduce financial and environmental costs associated with these remediation systems.

Although current chelating polymers are extremely effective in remediation efforts, there are significant drawbacks to these systems. Many of the synthetic polymers require toxic solvents for synthesis. In addition, the water soluble polymers require an ultrafiltration step after complexation in order to remove the metal cations from solution (1). The conventional insoluble polymer beads and membranes often suffer from low surface area to volume ratios; thus are often not as effective remediation agents as their water soluble counterparts. In addition, many of the aforementioned polymers are ineffective at acidic pHs; therefore, would be not be able to remediate the majority of industrial wastewater streams (7).

The growing interest in nanotechnology as well as biomaterials and biomimetic systems appears to be shaping the future of polymeric environmental remediation (18). Highly branched polymers such as nanoscale dendrimers will continue to be explored for homogenous filtration applications due to their high number of chain ends and hence chelating groups. The use of nanofibers and polymer nanoparticles for heterogeneous filtration is growing due to their high surface areas and filtration capacity. Combination technologies such as the addition of catalytic titania nanoparticles or other photoreactive materials, zeolites, and carbon nanotubes to polymer fibers and membranes in order to increase efficiency and selectivity will be explored in the years to come (18). In addition, incorporation of metal binding proteins into synthetic or biopolymeric matrices could potentially enable higher selectivity and ease of thermal or chemical regeneration due to the narrow pH and temperature range of activities of biological systems (1). Also, the use of natural biopolymers such as the carbohydrate chitosan is expected to increase (17). Another area of growing interest for filtration applications is smart or stimuli-responsive polymers. These polymers respond to very slight changes in environmental conditions such as pH, temperature, electric field, or ionic strength with large conformational changes which could aid in the ease of regeneration of these systems (19). At this point in time, nanoparticles and nanoscale entities are still quite costly. Therefore, although the growth in their use for remediation is evident, an explosion in nanotechnology is not expected until the cost is commensurate to conventional technologies.

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List of Symbols, Abbreviations, and Acronyms

BDP	<i>N,N</i> -bis-(dithiocarboxy)piperazine
Cd	cadmium
Cr	chromium
Cu	copper
Ca	calcium
EDTA	ethylenediaminetetraacetic acid
H ⁺	acid
Hg	mercury
NTA	nitrilotriacetic acid
OH	hydroxide
Pb	lead
PEI	polyethyleneimine

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