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PREPARATION OF WATER-SOLUBLE POLYMERS MODIFIED WITH SULFUR DONORS FOR RECOVERY OF HEAVY METALS

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ABSTRACT

Polyethylenimine (PEI) was modified with ligands containing sulfur donors to give soluble polymers for binding toxic metal ions. Reaction of purified PEI with mercaptosuccinic anhydride, ethylene sulfide, or methylthiocyanate gave PEI-MSA (25% functionalization), PEI-ET (100% functionalization), and PEI-TU (25% functionalization), respectively. Purification of the polymers was accomplished by diafiltration. The capacities for toxic metal ions (Hg, Cd, and Pb) and transition metal ions (Cu and Ni) were measured for each of the polymers. PEI-ET and PEI-TU showed high affinity for the softer metal ions, Hg and Cd, with loading capacities substantially higher than those for the base polymer PEI. Both polymers had high capacities for Cu. Release of the metal ions from the polymers was accomplished by lowering pH; however,

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small amounts of metal remained bound to the polymers at pH 1. Competition studies showed that PEI-TU and PEI-ET bound Hg and Cu more strongly than Cd and Pb.

Key Words: Toxic metals; Soluble polymers; Sulfur donors

INTRODUCTION

A significant need exists for new materials to recover valuable and toxic metal ions from both the environment and industrial process streams. This interest is driven by 1) increasingly stringent environmental regulations, 2) the need to reclaim valuable resources, and 3) the need to identify new restoration methods. While a number of methods exist for removal of metal ions from wastewaters, the use of water-soluble polymers combined with the membrane-based separation method of ultrafiltration is receiving significant attention (1). This technology, which was initially proposed by Micheals, uses functionalized soluble polymers to bind specific metal ions from aqueous solution (2). Metal-loaded polymers are of sufficient molecular size to be retained by a size-exclusion membrane, and thus the metal ions can be concentrated during the ultrafiltration process for recovery or disposal. The advantages of Polymer Filtration^{TM} (PF) over traditional metal-ion separation techniques, such as ion exchange and solvent extraction, are the following: 1) high metal ion capacity and selectivity, 2) enhanced binding and release kinetics, 3) all aqueous-based processing, and 4) room temperature and low-pressure operation (1,3–10). PF has been applied infrequently on an industrial scale; however, the inherent advantages of the method and the recent advances in the development of strong, stable ultrafiltration membranes will allow this technology to realize much broader application.

The success of any process for metal ion recycling or wastewater treatment stems from the selectivity of the extractant for a target metal ion. With the growing acceptance of PF, interest is growing with regard to the design of new water-soluble polymers to selectively bind specific classes of valuable and toxic metal ions (1,8–11). One of the most significant features of water-soluble polymers as extractants is the ease with which many commercially available polymeric backbones can be modified with specific chelators to affect the desired selectivity for a specific metal ion or for a class of contaminants. The immense database of thermodynamic data allows researchers to create polymers with a wide range of selectivity. The polymers can be prepared by the covalent attachment of the appropriate chelators (1,8–9). Initial work at Los Alamos National Laboratory in polymer design focused on the recovery and separation of actinides for analytical, environmental, and processing applications because good decontamination factors for the actinides could be realized with the PF approach (3–6). A logical extension of this work was the design and evaluation of polymeric systems for toxic or valuable metal-ion recovery from waste or process streams. The focus of the work reported here is the synthesis and characterization of polyethylenimine (PEI) substituted polymers that contain sulfur donors for sequestration of heavy metals such as Hg, Pb, and Cd.

While a number of reports describe the separation of heavy metals from waste streams using soluble polymers, the separations typically relied on unmodified polymers or polymers functionalized with a limited set of ligands. For example, recovery of a wide range of metals has been demonstrated using PEI alone (12–14). While many of the systems previously cited in the literature bind a wide range of metal ions, they are not designed to specifically sequester toxic metals. We were interested in determining if the incorporation of softer thiol donors into PEI would result in systems with more selective metal-ion binding. Soluble polymers with sulfur donors have been described in the literature, and as might be anticipated, these systems show superior binding of heavy metal ions. Geckeler et al. reported on the preparation of several polymeric backbones copolymerized with methylthiourea (1). Retention studies using these polymers showed that a range of metal ions, Cu, Cd, Hg, Co, and Zn, were bound at pH 5. All metals except Hg were released during ultrafiltration at pH 3 (15). Geckeler et al. also reported that functionalization of PEI with 2-chloroethylmethyl sulfide or methylisothiocyanate gave polymers with affinity for noble metals, such as Pd, as well as Hg and Cu (7). In these systems, which contain both hard (nitrogen) donors and soft (sulfur) donors, the retention of metal ions was not strongly influenced by pH. These studies suggest that this combination of donors may result in systems with high affinity for heavy metal ions. The work herein describes the synthesis of several new polymer systems containing sulfur donors and evaluates both the capacity and selectivity of the resultant polymers for the heavy metal ions Hg, Cd, and Pb.

EXPERIMENTAL

All chemicals used in these studies were reagent grade and used as received except where specifically indicated. PEI was obtained from BASF (Clifton, NJ) and purified prior to use by diafiltration using an AG Technologies ultrafiltration system with a 3×10^4 MWCO ultrafiltration cartridge. PEI-ET (polyethylenimine-ethyl thiol), PEI-TU (polyethylenimine-*N*-methylthiourea), and PEI-MSA (polyethylenimine mercaptosuccinic acid) were synthesized by published methods using purified PEI (16). Standard metal-ion solutions (as nitrate salts) used for binding studies were obtained from Fisher Scientific. Distilled, deionized (type II) water was used for all experiments.

Analytical Methods

Metal analysis for this study was conducted on a Varian Liberty 220 Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES), following the standard SW846 EPA (Environmental Protection Agency) Method 6010 procedure. Metal standards were matrix-matched to the sample type by adding the appropriate buffer and polymer concentrations. Metal ion analyses were verified with QC-19 quality control standards obtained from Plasma Chem. Mercury analysis was performed by cold vapor atomic absorption spectroscopy using a Perkin-Elmer Flow injection mercury system. Instrument calibration was performed with 10, 25, and 50 ppb standards. Samples were diluted 20–500-fold for analysis. The Hg line at 234.1 nm was used for analysis. Quality assurance measures included a continuous calibration blank, reagent blank, continuous calibration standard, and laboratory control standard. Standards were reanalyzed after each calibration curve and were accepted only when within ± 10% of the expected values.

Binding Studies

Binding capacities were performed by adding an aliquot containing 5 mg of a metal to a solution of 0.04% polymer (10 mg) in 0.1 mol/L $NaNO_3$. Dilute HCl or KOH was used to bring the pH to 6.5–7.0, and the solution volume was brought to 25 mL. The solution was mixed for 4 hours to ensure that equilibrium was obtained. A 5-mL aliquot was taken for analysis (metal ion concentration in solution in ppm $= M_I$), and the remaining solution was subjected to ultrafiltration with an Amicon 50-mL stirred cell and a 10×10^4 M.W. (molecular weight) cutoff filter. Approximately 2 mL of filtrate (metal ion concentration in filtrate in ppm $= M_F$) was collected, and metal analysis was performed to determine metal concentration of both filtrate and initial solution. The metal-binding capacity of the polymer was determined using the following equation:

$$\text{Capacity} = (\text{mmol of metal/g Polymer}) = \frac{(C_i - C_p) \times V}{1000 \times P \times A}$$

C_i (ppm) is the initial concentration of metal ion in the solution; C_p (ppm) is the concentration of metal ion in the permeate; V (mL) is the volume of initial solution; P (g) is the amount of polymer used; and A is the atomic weight of metal ion. If no metal was detected in the filtrate, the experiment was repeated with higher metal-ion concentrations until the polymer was saturated.

To determine metal ion retention, the calculated amount of metal that would be bound by 20 mg of polymer was added to a 50-mL volumetric flask that contained the polymer. The solution was brought to 50-mL volume with 0.1 mol/L $NaNO_3$ solution. The solution was allowed to equilibrate for 4 hours, then five 10-

mL aliquots were taken and placed in 15-mL centrifuge tubes and the pH adjusted from 1 to 5 using HCl or KOH as needed. A 1-mL aliquot was taken and diluted to 10 mL for initial analysis (M_I), and the remaining solution was subjected to ultrafiltration through the use of an Amicon 10-mL stirred cell with a 10×10^4 M.W. cutoff filter. After analysis of the initial and final metal ion concentrations, metal retention was determined by the following equation:

$$\% \text{ Retention} = \frac{(M_\mathrm{I} - M_\mathrm{F})}{M_\mathrm{I}} \times 100$$

For metal ion selectivity, a mixture of metal ions, each at 10 ppm, was placed in a 1% wt/vol polymer solution containing 0.1 mol/L $NaNO_3$. Individual 10-mL aliquots were adjusted to pH values from 1 to 7, and the solutions were allowed to equilibrate. The solutions were then filtered using an Amicon 10-mL stirred cell with a 10×10^4 M.W. cutoff membrane filter, and the filtrate analyzed for the metal concentrations.

RESULTS AND DISCUSSION

Figure 1 shows the structures of the functional groups bound to PEI. This set of functional groups was specifically selected for incorporation into the PEI backbone. These structures can be used to evaluate the binding of the soft metal ions Hg, Cd, Ag, and Pt as well as slightly harder metals, such as Pb.

Loading Capacities for Metal Ions on Polymers

Table 1 compares loading capacities for each of the PEI-based polymers and the bare PEI backbone for a series of transition and toxic metal ions. In general, the introduction of sulfur donors into the polymers increased their capacity for the soft metal ions over that of PEI at neutral pH for most of the systems examined. PEI-ET had the highest affinity for Pb and Cd (2.4 and 2.7 mmol metal/g polymer)

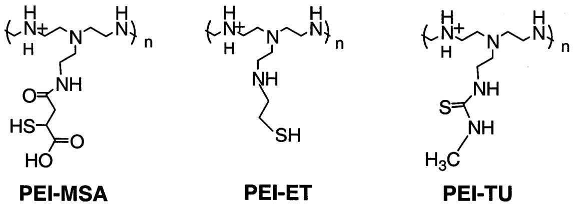


Figure 1. Structures of modified polymers PEI-MSA, PEI-ET, and PEI-TU.

Table 1. Metal-Ion Loading Capacities of PEI and Sulfur Derivative Polymers

	Molar Capacity (mmol metal ion/g polymer)			
Metal Ion	PEI	PEI-MSA	PEI-ET	PEI-TU
Cu^{+2}	11.8	7.1	7.4	11.6
Ni^{+2}	4.9	2.0	3.9	4.3
Pb^{+2}	1.4	1.9	2.4	1.9
Cd^{+2}	2.0	1.6	2.7	2.6
Hg^{+2}	2.5	—	3.2	4.8

All capacities were measured at pH 6.5–7.0 at 25°C using a 0.04 wt% polymer solution in 0.1 mol/L $NaNO_3$.
—Data not available.

with increases of 70 and 35%, respectively, over that of PEI. We were not surprised that the modification of the polymers with soft donors reduced the observed capacities for the harder metals, Cu and Ni. This observation is consistent with the strong affinity of Cu and Ni for nitrogen-containing ligands and the well-documented use of PEI as a sequestering agent for Cu and Ni (12–14).

Mercury binding was substantially increased over that of PEI with both PEI-ET and PEI-TU. The Hg capacity of 4.8 mmol Hg/g for PEI-TU is similar to that reported by Strathmann, who measured a slightly lower capacity for Hg (3.8 mmol/g polymer) for a thiourea-functionalized PEI at pH 1 (13). Strathmann reported no pH dependence of the capacity. The capacities in Table 1 were measured at pH 7. Release studies with PEI-TU showed that the Hg was tightly bound to the polymer and that most of the metal (approximately 95%) remained bound to the polymer at pH 1. This corresponds to a capacity of roughly 4.5 mmol Hg/g polymer at pH 1. A similar trend was seen for PEI when HNO_3 was used as the acidifying agent: The Hg capacity dropped from 2.5 mmol metal/g polymer at pH 7 to 1.1 mmol Hg/g PEI at pH 1. The significantly larger decrease in capacity for Hg on PEI at pH 1 (a decrease of 55%) is consistent with a higher affinity of PEI-TU for Hg over PEI. The variance between the results reported herein and those of Strathmann most likely result from differences in the degree of polymer modification. Functionalization levels for the PEI-TU were 20–25% determined by analysis of sulfur content was consistent with modification of most of the primary amines in PEI. However, the capacity differences could be attributed to the presence of different counter ions in solution. These studies with PEI-TU were done in the presence of chloride, which is known to coordinate Hg (17) and could impact the observed loading capacities for Hg as well as metal release from the polymer.

Mercury binding by PEI-MSA was also examined; however, consistent loading capacities could not be obtained. While data from individual runs with multiple samples were consistent, capacities measured with different batches of

PEI-MSA or with the same batch of PEI-MSA measured at different times varied substantially. This behavior may be the result of polymer cross-linking through disulfide linkages. PEI-MSA lost solubility (as well as capacity for metal binding) over time if not stored in solution under an inert atmosphere. Another possibility is that Hg, with its readily accessible +1 oxidation state, could assist in the formation of disulfides. This behavior was not seen for the other metals evaluated (Cd, Pb, Cu, or Ni). In fact, PEI-MSA, which contains both hard (carboxylate) and soft (thio-ether) donors, bound more Pb (a borderline soft metal) than did the base polymer PEI. Capacities for the other metals examined with PEI-MSA Cu, Cd, and Ni, were well below those determined for PEI.

Each of the polymers was evaluated for the binding of the noble metals Pt, Au, and Ag. Unfortunately, experiments designed to measure capacities for Au, Ag, and Pt gave insoluble materials in the evaluated pH range of 1–7. Analysis of the solids by ICP-AES indicated that the metals had precipitated as metal sulfides. Experiments with polymers in the presence and absence of Ag showed that the carbon content of solutions did not vary upon reaction with metal, suggesting that residual polymer remained in solution; this polymer remaining in solution could readily complex unprecipitated metals. The amount of metal remaining in solution varied after contact with the different polymers. For example, for Ag with PEI-ET, 25−40% of the metal precipitated out at each pH value. As a result of these observations, no further evaluation of the polymer systems with the noble metals was done.

Release of Individual Metal Ions from Polymers

Metal ion retention studies were designed to identify the conditions required for release of bound metal ion and the regeneration of polymers. Figure 2 shows the release curves for Cd and Pb bound to PEI-MSA, PEI-TU, and PEI-ET upon acidification of the metal-loaded polymers. For PEI-ET and PEI-TU, approximately 80% of the Pb and Cd were released at pH 6; however, both polymers had small residual amounts of both Pb and Cd bound ($< 10\%$) at pH 1. This behavior suggests that at low metal loadings these flexible polymers can orient to form binding pockets that form highly stable chelates with these metals. PEI–MSA showed similar release behavior; even at pH 1, 15% of the Pb and 22% of the Cd remained bound to the polymer. Attempts to release these metals from all of the polymers by addition of higher concentrations of acid resulted in the degradation of the polymers through loss of sulfur (with the generation of H_2S). While this behavior limits the regeneration of the polymers, it indicates that these systems will be well suited for polishing dilute heavy-metal waste streams in which reuse of the polymers is not imperative.

Figure 3 shows Hg release curves for PEI-ET at 3 different metal-ion loadings: 10%, 50%, and 100% of capacity. As can be seen from this figure, a significant difference was found between the release curves for the metal-ion loading lev-

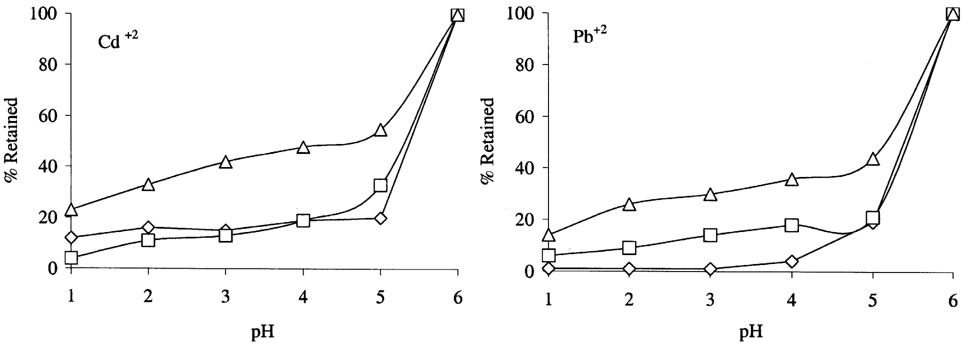


Figure 2. Retention of Pb and Cd on PEI-ET (◇), PEI-TU (□), and PEI-MSA (△) as a function of pH. Release studies were done with HNO_3, and initial metal ion concentrations were adjusted to fully load 20 mg of polymer. Cadmium concentrations were 50 ppm on PEI-MSA, 90 ppm on PEI-TU, and 110 ppm on PEI-ET. Lead Concentrations were 90 ppm on PEI-MSA, 150 ppm on PEI-TU, and 195 ppm on PEI-ET.

els examined. These differences result from a distribution of Hg binding sites within the polymer. For example, when this polymer was loaded to capacity for Hg, not all Hg could bind at sites with equivalent geometry or donor atom arrangements. During the regeneration process, variations of the Hg affinity in these sites were manifested in the gradual release of the metal from the polymer (approximately 20% of the metal was still bound at pH 2). When Hg was loaded on the polymer at 10% of full capacity, the Hg bound to higher affinity sites. In this instance, nearly 80% of the Hg was bound at pH 2. Similar release patterns were also seen for Cu loaded at various levels on PEI-ET. Of all the metals examined, Hg was the only one that cleanly released from PEI-ET when the solution pH was lowered with HCl to 1. While this observation could suggest that the affinity of PEI-ET for Hg

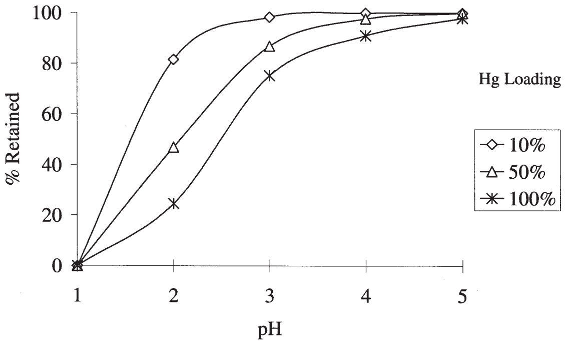


Figure 3. Hg release from PEI-ET as a function of metal loading.

is lower than that for the other metals, this is not consistent with the capacity data: The Hg capacity of PEI-ET was significantly higher than the capacities for Pb and Cd. Competition studies also do not support the conclusion that PEI-ET affinity for Hg is lower than for other metals. Instead, the use of the nonoxidizing HCl as the releasing acid (to minimize stability problems with the S-containing polymers) likely affected the behavior of Hg with this polymer. The strong propensity of Hg (relative to Pb and Cd) to form highly stable chlorides in solution assisted the release of Hg from PEI-ET, and thus at pH 1, full regeneration of the polymer was seen. This effect was not seen for PEI-TU, which binds Hg more strongly than does PEI-ET. Even when the PEI-TU polymer was loaded to maximum capacity, only limited Hg release was observed upon lowering the pH. Analysis of ultrafiltration permeates showed that Hg levels were below the detection limit of 50 ppb.

Selectivity of Polymers for Toxic Metal Ions

The selectivity of polymers for the target metals was determined by monitoring metal binding of a mixed-metal solution. Unlike the metal release studies, which were done with polymers loaded at higher levels, these experiments were done with a very large excess of polymer to ensure availability of high affinity sites for all metals and to minimize the charge buildup resulting from metal ion binding. In addition, we sought to demonstrate the utility of these polymers for the recovery and separation of dilute mixtures of metals that are commonly found in industrial waste streams. Thus, for each of the individual competition experiments, more than 200 times more polymer was present than for the release studies.

Figures 4 and 5 show the selectivity series observed for PEI-ET and PEI-TU. Under conditions of excess polymer, both of these polymers had the highest affinity for Hg and Cu. Separation of these 2 metals from Ni, Cd, and Pb could be readily accomplished with either polymer at pH 1. Less discrimination between Pb, Cd,

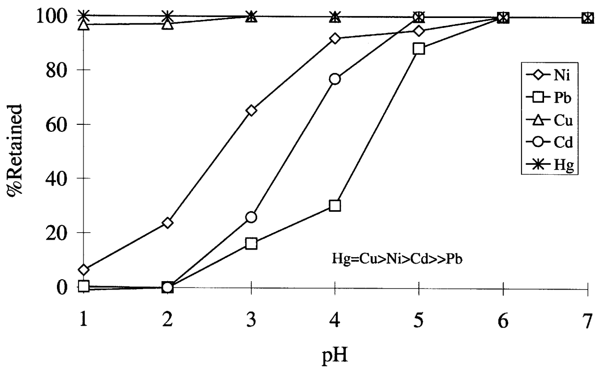


Figure 4. The metal-binding selectivity series for PEI-ET with Ni, Pb, Cu, Cd, and Hg.

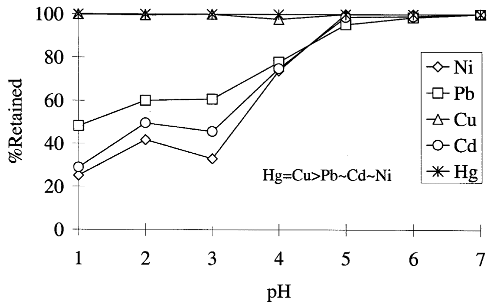


Figure 5. The metal-binding selectivity series for PEI-TU with Ni, Pb, Cu, Cd, and Hg.

and Ni binding was evident, perhaps in part as a result of the large excess of polymer used in these studies. With the large excess of PEI-ET (>200 fold), Hg was bound to the polymer at pH 1. Release studies described earlier clearly illustrate that Hg binding varies as a function of polymer loading. In this set of studies, where the metal ion loading was extremely low, a stable Hg-polymer complex seemed to form and was not disrupted at pH 1. The highest affinity for Hg and Cu was observed PEI-TU. However, all metals tested bound strongly to this polymer and no metal ion tested was completely removed from the polymer at pH 1. For the PEI-TU, with the softer thiourea donor, the selectivity order changes from that determined for PEI-ET. For this polymer, Ni binding was suppressed relative to Pb and Cd.

Figure 6 shows the selectivity series for PEI-MSA. Unlike PEI-TU and PEI-ET, this polymer, which has a mix of hard and soft donors, exhibited higher affinity for Pb and Cd over Cu and Ni. The release curve for this system indicated that a clean separation of Ni from the softer metals Pb and Cd could be achieved at pH 3. These studies were further verified by dual metal competition. In general, the coordination environment around the individual metals varied with degree of functionalization and metal loading as well as the orientation of functional group

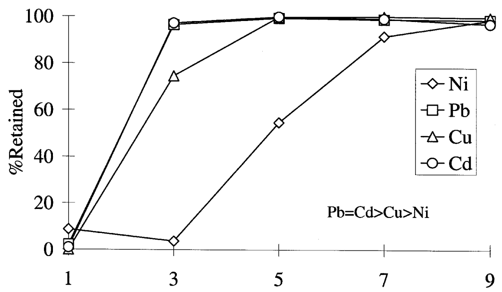
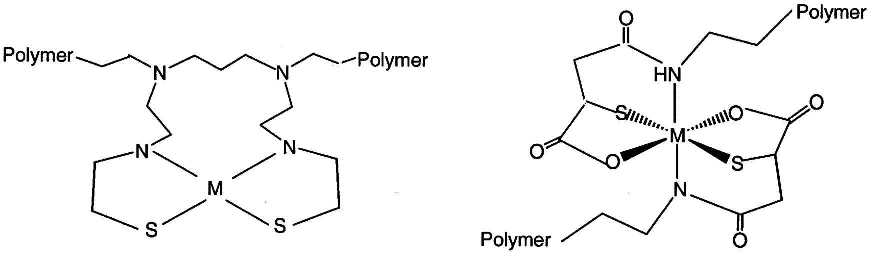


Figure 6. The metal-binding selectivity series for PEI-MSA with Ni, Pb, Cu, and Cd.



PEI-ET Metal Complex

PEI-MSA Metal Complex

Figure 7. Proposed structures for metals such as Hg, Cu, and Cd bound to PEI-ET and Cd, Pb, and Ni bound to PEI-MSA.

arms on the base polymer nitrogens. Figure 7 shows some possible structures for the polymer-metal complexes for PEI-ET and PEI-MSA.

CONCLUSIONS

The modification of PEI with sulfur donors was readily accomplished using simple addition reactions. The resulting polymer systems were highly soluble in aqueous solution and had high capacities for the toxic metals Hg, Pb, and Cd, as well as Cu. Attempts to examine the binding of the noble metals Au, Pt, and Ag were of limited success. Analysis of these systems showed that precipitation of metal sulfides occurred at near neutral pH. Some polymer instability was also seen for PEI-MSA under oxidizing conditions. Selectivity for Hg binding over Pb and Cd was observed for the thiourea-functionalized polymer PEI-TU. PEI-ET, an ethylthiol derivative of PEI was also found to bind the target metal ions Hg, Pb, and Cd. PEI-TU had the highest affinity for the toxic metal ions, which remained bound to the polymer at pH 1. This suggests that PEI-TU holds promise for the recovery of toxic metals from mildly acidic wastewater streams.

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