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DESIGN, SYNTHESIS, AND EVALUATION OF POLYHYDROXAMATE  
CHELATORS FOR SELECTIVE COMPLEXATION OF ACTINIDES

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# Design, Synthesis, and Evaluation of Polyhydroxamate Chelators for Selective Complexation of Actinides

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## ABSTRACT

Specific chelating polymers targeted for actinides have much relevance to problems involving remediation of nuclear waste. A major goal of our research program is to develop polymer supported, ion specific extraction systems for removing actinides and other hazardous metal ions from wastewaters. This is part of a broader effort in our laboratories to develop novel and cost effective chelators that have the high selectivity and binding constants needed to remove actinide ions such as plutonium from soils and waste streams. Selected ligands from our ongoing research efforts are being attached to polymeric backbones to create novel chelating polymers. These polymers and a number of other water soluble and water insoluble polymers have been synthesized and are being evaluated for their abilities to selectively remove the target metal ions from process waste streams.

## INTRODUCTION

Virtually every DOE facility in the United States which handles nuclear materials produces some form of radioactive waste. One of the primary radioactive contaminants at these sites is the class of radionuclides known as actinides (Th, U, Pu, Am, etc.), whose extreme toxicity make them potential environmental hazards. Actinides are particularly problematic after they are released into the environment for two reasons. 1) Some actinides form soluble and therefore mobile species which can migrate rapidly into the groundwater. 2) Other actinides form insoluble oxides and hydroxides which are very difficult to solubilize and remove from the environment.

Current processing methods lack clean-up selectivity so that considerable non-radioactive material is collected together with the radioactive actinides. Cost effective and efficient methods are needed to remove soluble actinides from process waste streams to ultralow levels to meet stringent regulatory limits and to decrease waste disposal costs. Technology also needs to be developed to remove insoluble actinides from soils and contaminated equipment in order to reduce the volume of material which must be stored at a nuclear waste repository. A number of different technologies are currently being investigated for this purpose including some that are based on the selective coordination and subsequent removal of actinide ions by synthetic chelators.

The development of new synthetic chelators for actinides has relied heavily on the use of siderophores as model compounds (Gopalan, in press). Siderophores are a class of low molecular weight compounds, usually possessing hydroxamates or catecholates that are synthesized and utilized by microbes for the purpose of iron sequestering and transport (Miller, 1989). The similar charge to ionic radius ratio of  $\text{Fe}^{3+}$  and  $\text{Pu}^{4+}$  (46 and 42 e nm<sup>-1</sup> respectively) led Raymond and

other workers to synthesize modified siderophores, in which four catechol groups containing polar, solubilizing sulfonate groups were incorporated into a structural backbone similar to enterobactin, an iron siderophore (Weitl, 1978; Weitl, 1980). They have also prepared a number of linear catechoylamide derivatives (including sulfonate and carboxylate substituted analogs) and evaluated their actinide (IV) binding. Most of the chelators developed so far have limitations (e.g. solubility, stability or selectivity) that limit their practical usage (Raymond, 1993; Xu, 1992; Uhlir, 1993; Bergeron, 1984).

In designing specific actinide sequestering agents, researchers have tried to take advantage of the higher coordination sites on these metal ions due to their larger size relative to  $\text{Fe}^{3+}$ . Preorganization of the ligand groups around a spacer group so as to provide the appropriate geometry should enhance both actinide ion selectivity and binding. While it is important to consider both cyclic and acyclic backbones for anchoring ligand moieties, in at least some cases the greater stereochemical freedom of linear backbones, may lead to more effective chelation (Hancock, 1989). An additional factor to be considered is the choice of ligand groups. Based on hard acid-hard base interactions, it is clear that multidentate oxoligands such as hydroxamates, iminodiacetates and hydroxypyridinones show promise for the binding of the relatively hard actinide ions present in acidic, aqueous process solutions (Streater, 1990; Dobbin, 1990; Wilkinson, 1987).

Metal ion specific polymeric chelators have received considerable attention over the past 20 years (Sherrington, 1988; Warshawsky, 1987). However, much of the interest has involved separations concerning transition metal ions and very little work has been done for the actinides with the specific exception of uranium (Hirotzu, 1986; Vernon, 1982). Chelating polymers are the basis of a number of successful industrial separations including removing calcium to very low levels from brine and removing radioactive cesium from alkaline waste waters (Kantipuly, 1990; Geckler, 1980; Calmon, 1981).

Many polymers are commercially available and have the requisite functional handles for subsequent introduction of ligands/chelating moieties which makes their direct use quite attractive. The ideal procedure for polymer modification is preassembling the whole ligand, followed by its attachment in one step. It is our intention to attach some of the synthesized chelating moieties to such polymeric systems, using either substitution or condensation reactions as appropriate.

A number of factors are important to the success of a chelating polymer. Due to the relatively low concentration of actinide ions with respect to other metal ions in many of the waste streams it is critical that the chelating polymer possess both strong binding and selectivity for actinide ions. Also, formation of the complex must be rapid in order to develop viable separation processes. The final crucial factor is the wettability of the polymer. Suitable hydrophilic groups must exist in the polymer to achieve this.

## RESULTS AND DISCUSSION

A new class of tetrahydroxamate chelators have been identified in our laboratories (Figure 1) which exhibit much promise for the binding of actinide ions in solution and which warrant further development. (Gopalan, 1992; Gopalan, 1993). The hydroxamate chelators that we have developed were recently evaluated for their binding of plutonium(IV) at Los Alamos and the results are very encouraging. Our results so far clearly show that both the meta and para tetrahydroxamate chelators 1 and 2 bind plutonium very strongly and show some selectivity for  $\text{Pu}^{4+}$  over  $\text{Fe}^{3+}$ . Also the synthesis of a number of modified analogs (Koshti, 1994; Koshti, 1994) of this class of chelators has been concluded and their evaluation has been initiated. Our results from these studies have in turn encouraged us to develop specific chelating polymers for actinides for applications to radioactive waste water remediation.

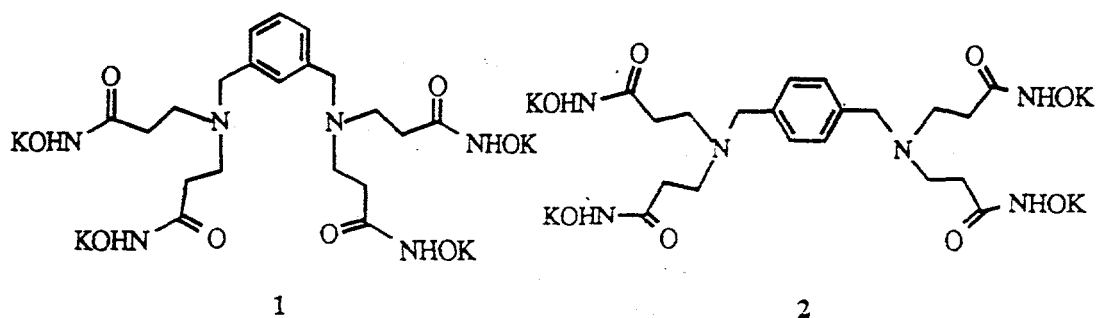


Figure 1. Tetrahydroxamate ligands

### Development of Chelating Polymers for Actinides

The primary objective of this project is to develop a series of polymer supported extraction systems for removing radioactive actinides from wastewater streams. The actinide specific chelating polymers that we are developing can be divided into two classes water soluble and water insoluble. The first class of chelators being developed are water soluble chelating polymers for use with ultrafiltration as a mode of metal ion separation. These polymers have a backbone that is hydrophilic and carry the same ligand moieties previously shown to be effective for actinide ion binding. They will potentially have more rapid exchange kinetics than ion exchange and chelating resins due to the homogeneity of the system. The subject ions will be complexed by the water soluble chelating polymer which is then separated from the aqueous stream by filtration through ultrafiltration membranes. The polymers, which are in the range of 50,000 to 500,000 daltons, are impermeable and are retained by these membranes. This process should allow a great reduction in the volume of plutonium waste requiring storage.

### Synthesis of water soluble polymers

A simple route for the preparation of water soluble hydroxamate polymer 3 and its carboxylate analog 4 from polyethyleneimine has been developed (Figure 2). Polyethyleneimine has a hydrophilic backbone and is available in a wide range of molecular weights from commercial sources.

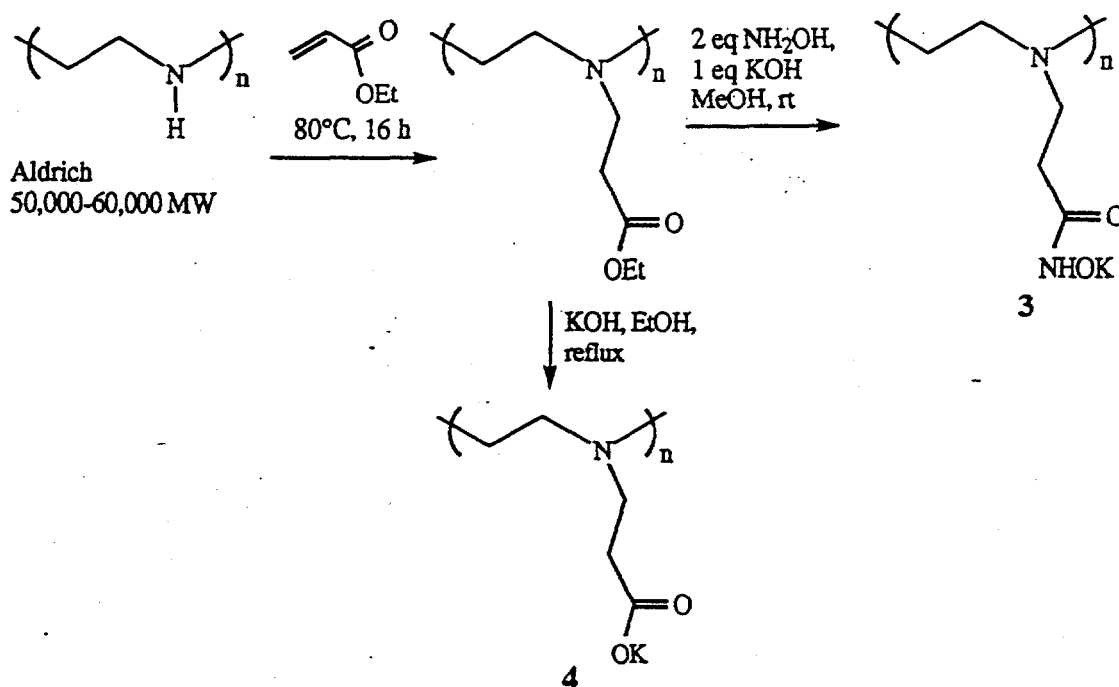


Figure 2. Synthesis of water soluble polymeric chelators 3 and 4.

We have also synthesized a water soluble hydroxamate polymer **5** and its carboxylate analog **6** from commercially available polyallylamine. The synthetic route for this new chelating polymer is described in Figure 3.

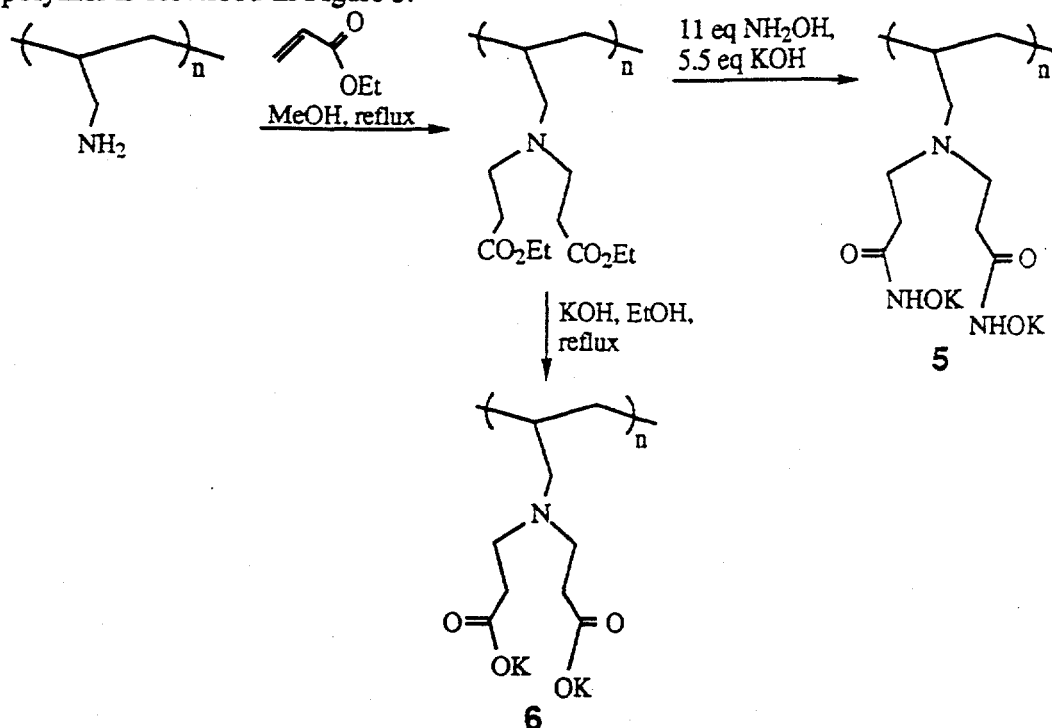


Figure 3. Synthesis of water soluble polymeric chelators **5** and **6**.

#### Evaluation of water soluble polymers

Chelating polymers for use in ultrafiltration metal ion separation technology must exhibit adequate solubility and stability at the pH range of interest. The water solubility of some of the synthetic polymers developed so far has been of some concern. In general, they are soluble at both low and high pH and precipitate under mildly acidic conditions. Some strategies to improve the water solubility of these polymers are currently under investigation. These strategies include adding more hydrophilic groups and changing the extent of functionalization.

Despite the moderate solubility of these polymers, we have been able to obtain some preliminary results on the ability of these polymers to remove various target metal ions from solution. The general protocol for the analysis of these water soluble polymers is as follows. Two to four grams of the polymer to be evaluated is dissolved in approximately 250 mL of distilled deionized water. The solution is then subjected to diafiltration (Amicon LP-1) to yield a polymer product with a relatively narrow molecular size distribution (greater than 30,000 amu). Following diafiltration, the water is removed from the retained polymer solution by rotoevaporation and the amount of polymer quantified. The resulting residue is dissolved in distilled deionized water and the pH adjusted with concentrated HCl to a pH of approximately 1.8. At this stage any insoluble particulates are removed by vacuum filtration. The purified polymer is then redissolved in distilled deionized water to produce a 25 mg/mL stock solution for use in the metal binding studies.

The metal ion binding/extraction efficiency of these polymers is evaluated as follows. 5 mL of the purified polymer stock solution, 5 mL of 0.5M ionic strength adjuster, 5 mL of a 50 ppm eight metal ion test solution (Al, Cd, Cr, Cu, Fe, Ni, Pb, Zn), and 10 mL of distilled deionized water are combined. The pH of the polymer containing solution is then adjusted from 1-7 and 10 by the addition of small amounts of dilute acid or base. Solutions are inspected visually to ascertain the solubility of the polymer under the given conditions. Each of the solutions is separately ultrafiltered using Centriprep 10 (Amicon Corp.) 10,000 NMWC ultracentrifuge cartridges. The permeates obtained from this treatment are collected and analyzed for the metal ions of interest by inductively coupled plasma spectroscopy (Varian Liberty 220). The absence of metals in the permeate is attributed to chelation by the water soluble polymer after correction for any precipitation of these metal ions that may have occurred.



During the analysis of these polymers it is important to determine the extent to which the target metal ions are removed by a polymer unrelated precipitation process (probably as their hydroxides) or by chelation with the polymer. Hence, a control experiment was done in which the pH of the metal ion solution was varied and the percentage of the metal ions in solution determined. The results of this study are shown in Figure 4. These results clearly show that removal of the metal ions from the solution by precipitation is an important process particularly at pH 5 and above. These factors must be taken into account in establishing the efficiency of our synthetic polymers. This also compels us to develop water soluble metal ion chelating polymers that can function at pH 4 or below.

Both the polyethyleneimine and the polyallylamine hydroxamate polymers have been examined using the above protocol. The PEI-hydroxamate 3, is soluble from pH 1 to 4. At pH 1 very little of the metal ions are complexed by the polymer. At pH 3, this polymer is effective in removing almost all of the iron and copper present in the standard metal ion solution. A significant amount of aluminum is also removed. However, very little of metal ions such as cadmium, chromium and nickel are removed under these conditions. The metal ion selectivity of this polymer is somewhat less at pH 4 but even under these conditions it is effective in removing the harder metal ions such as iron in preference to zinc or cadmium. The data for this polymer is shown in Figures 5.

The polyallylamine hydroxamate polymer 5, has also been evaluated. Unfortunately this polymer is only soluble at pH 1 and 2. At pH 1, this polymer is effective in removing about 30% of the iron present in solution and is highly selective for this metal ion. At pH 2, this polymer is effective in removing over 80% of all the iron along with some of the chromium present in the standard eight metal ion solution. It is important to emphasize that very little precipitation of the metal ions occurs below pH 4 and the removal of the metal ions is primarily due to their complexation with the polymeric chelators. At pH 4, 30% of the iron is removed by a simple precipitation mechanism and this has been taken into account in evaluating the efficiency of our polymers.

The carboxylate analogs 4 and 6 of the above hydroxamate polymers have also been evaluated. The solubility of these polymers is somewhat limited to narrow acidic pH ranges. The PEI-carboxylate 4, is able to remove about 20% of the iron at pH 1. At pH 5 this polymer surprisingly removed almost all of the metal ions present in solution with very little selectivity (Figures 6a and 6c). The PAA- carboxylate 6, removed about 60% of the iron present at pH 2 and was quite selective for this metal ion. At pH 5, this polymer removed major percentages of the metal ions (73% or above, see Figures 6b and 6c) with the exception of nickel (only 40%).

### Synthesis of other polymers

The second type of polymers that are being synthesized are water insoluble polymers that contain preorganized ligand groups for selective actinide ion binding. These insoluble polymers should chelate the metal ions in the affinity chromatography manner in a polymer packed column. The trapped actinides can then be eluted off the column and concentrated to a minimum volume. We hope the column itself can be regenerated for repeated use. If this is not desirable, the saturated column can be dried to result in low volume, solid waste destined for long term storage. Several water insoluble polymers have been prepared (Figure 7) and are currently being evaluated for their ability to remove target metal ions.

The preparation of the water insoluble dihydroxamate polymer 7, and some initial analysis of this material was achieved sometime ago (Gopalan, 1995). We have also examined its binding properties with plutonium. When a sample of this insoluble polymer in 0.1 M nitric acid was contacted with a dilute sample of  $\text{Pu}^{4+}$  solution, about 98% of the  $\text{Pu}^{4+}$  was removed from the solution after 30 minutes of contact time. This is indeed a promising result and strongly encourages further development of this class of polymeric chelators.

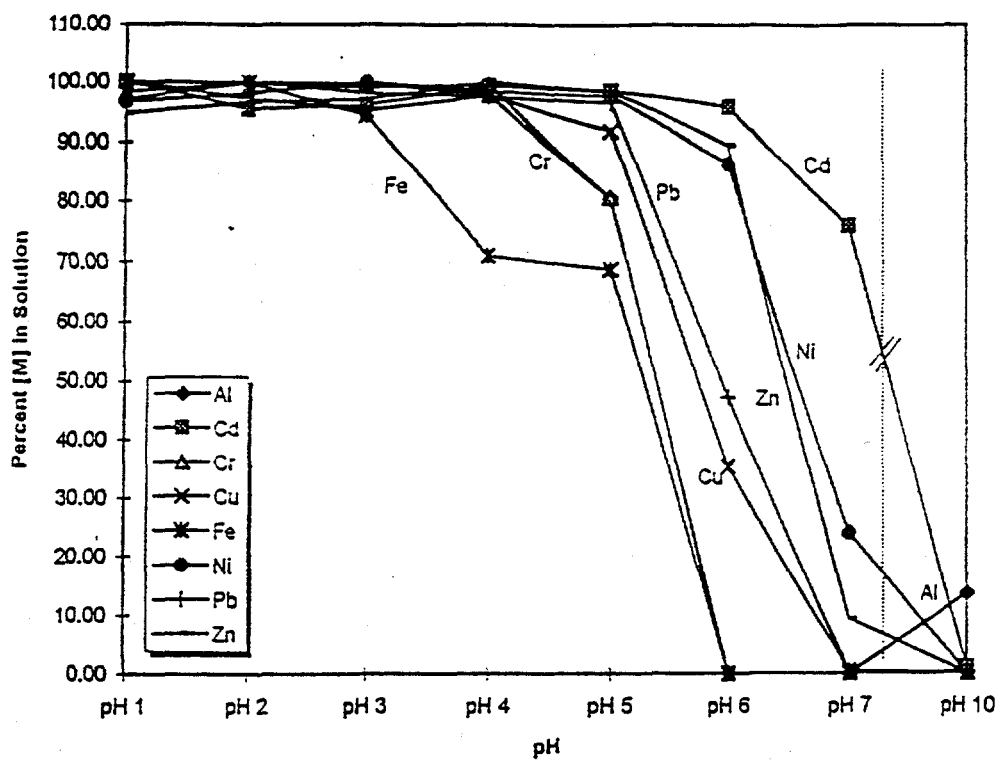


Figure 4. Percent metal ion in solution as a function of pH in the absence of polymer.

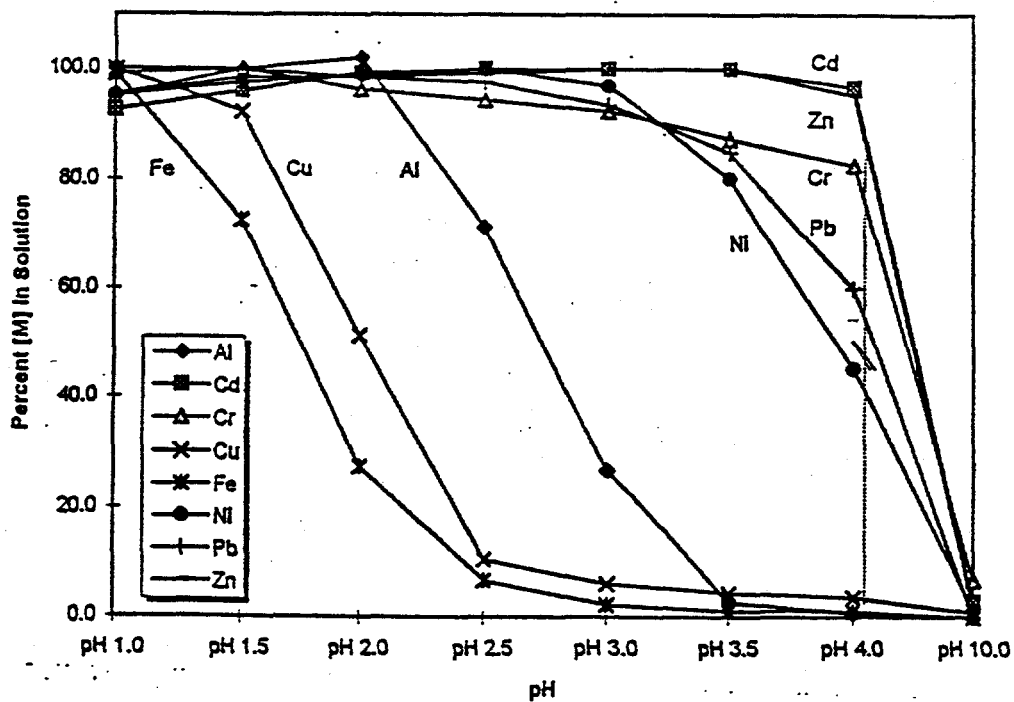


Figure 5. Percent metal ion in solution as a function of pH in the presence of polymer 3.

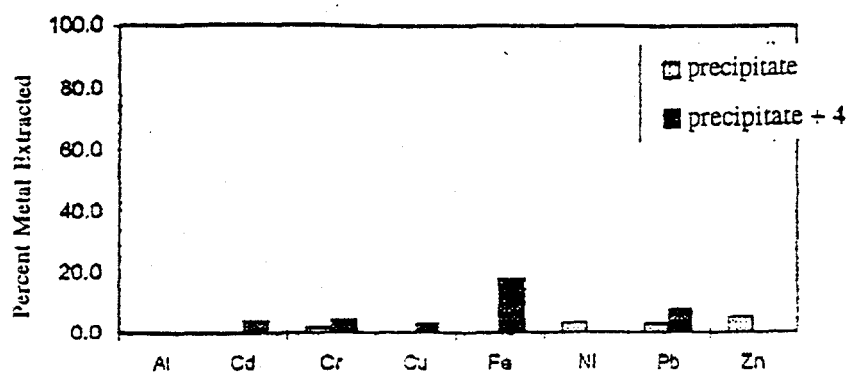


Figure 6a. Percent metal ion extracted with polymer 4 at pH 1.

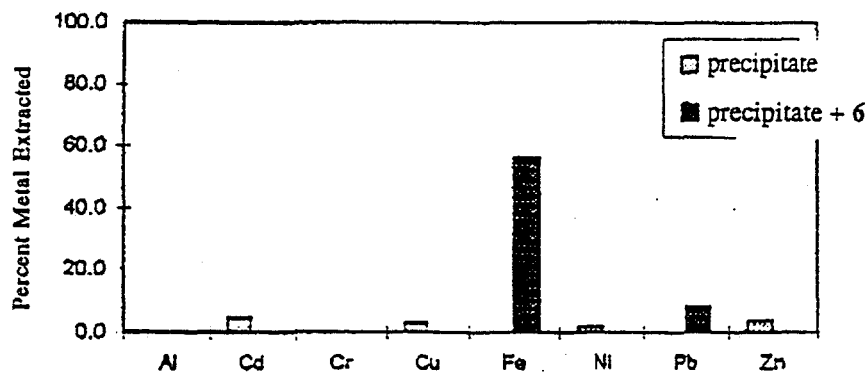


Figure 6b. Percent metal ion extracted with polymer 6 at pH 2.

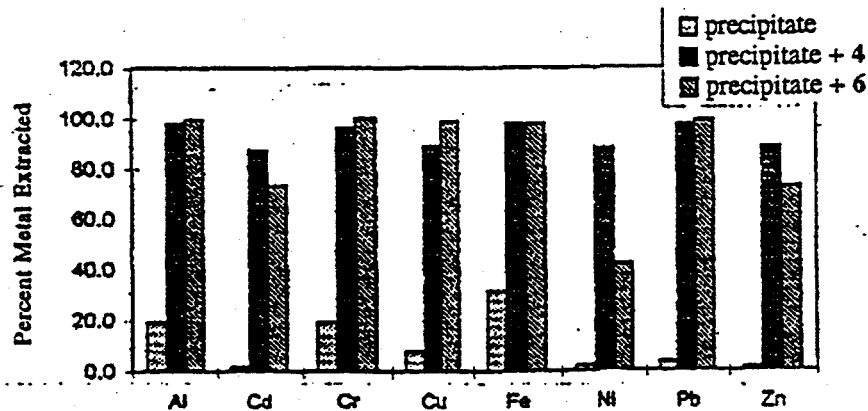


Figure 6c. Percent metal ion extracted with polymers 4 and 6 at pH 5.

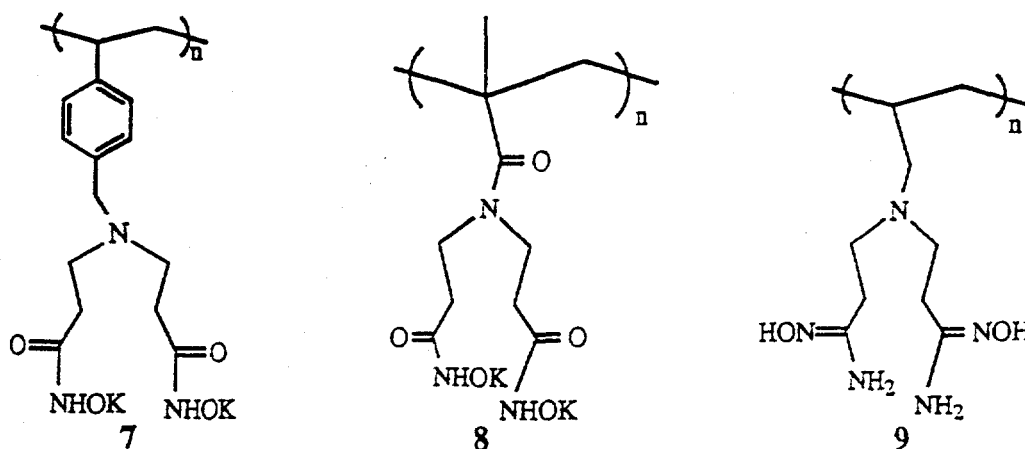


Figure 7. Representative water insoluble polymeric chelators.

The polyallylamine amidoxime polymer 9, developed in our laboratories shows some interesting characteristics particularly for the binding of the uranyl ion. An aqueous solution of uranyl ions was contacted with this insoluble polymer at different pH values. It is encouraging to note that at pH 2, greater than 85% of the uranyl ion was removed from solution with almost quantitative removal observed at pH 4. These results are shown in Figure 8.

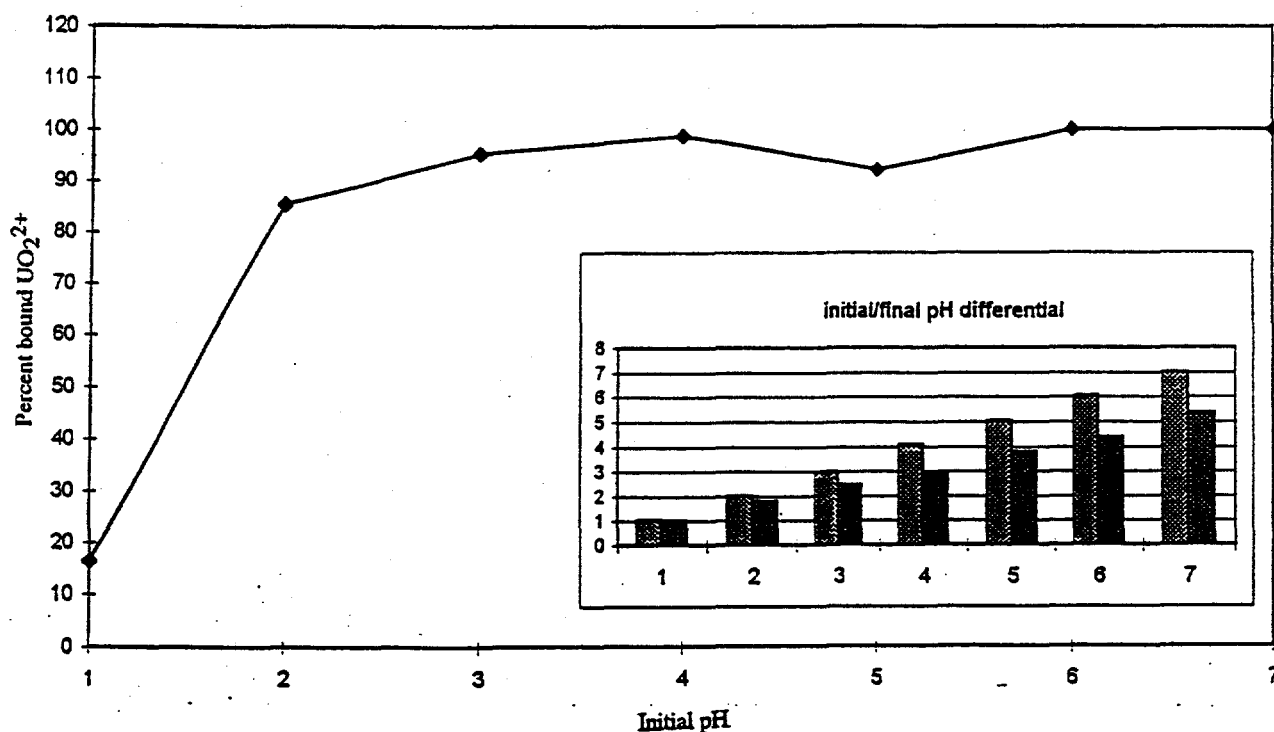


Figure 8. Percentage of  $\text{UO}_2^{2+}$  bound to polymer 9 as a function of pH.

In conclusion, our initial results seem to clearly justify the desirability of incorporating hydroxamate chelators, developed at NMSU, into polymeric matrices and their further development for environmental applications. We believe that by incorporation of more complex and preorganized chelators into polymers one can synthesize new polymeric materials having both the desired selectivity and high binding required for actinide remediation.

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