PHYTOREMEDIATION GENERALIZED OVERVIEW WITH SPECIFIC FOCUS ON THE REMEDIATION OF URANIUM FROM WATER

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ABSTRACT

The phytoremediation of heavy metals has been studied for approximately two decades. During this short time period, phytoremediation has evolved to include both living and non-living plants for the remediation of both organic and inorganic contaminants. There are several advantages and disadvantages to both types of remediation systems. For example, most living plants cannot survive in high concentrations of salts, heavy metals, or lack of nutrients. In addition the remediation of soils polluted with heavy metals or organic is depth limited, to the root systems of the particular plant. However, many of these concerns are not observed with non-living plant materials. The dead plant systems do not require nutrients and the high concentrations of salts and heavy metals do not affect the health of the system. But, dead plant systems can only be used for the remediation of water systems, whereas phytoremediation using living plants can be applied to both soils and water. This presentation will focus on the application of dead plant material, in a system commonly referred to as phytofiltration. Further more data will be presented on the phytoremediation of uranium from aqueous solution using alfalfa biomass. Studies have shown that biomaterials have the capacity to adsorb heavy metals and metal oxo-cations from aqueous solution. Most of the research in this field has been performed on the more common heavy metals such as copper, nickel, and chromium. However, some studies have shown that biomaterials have the ability to bind uranyl cations from solution with capacities that are comparable or greater than some commercially available synthetic ion exchange resins. By using chemical modification of the alfalfa biomass, Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), and X-ray Absorption Spectroscopy (XAS) we have found that the primary functional group on alfalfa biomass responsible for the binding of uranyl cations from aqueous solution is the carboxyl functionality. Batch pH dependency experiments show a direct relationship between the increase in binding and the increase in pH (up to pH 4.5). In addition, time dependency experiments showed that the binding of uranyl cations from aqueous solution occurs rapidly, within the first five minutes of contact and remains constant up to one

hour. Batch capacity studies showed that native alfalfa biomass has a capacity of approximately 140 mg/g (mg uranium/g of alfalfa), where as hydrolyzed alfalfa biomass has a capacity of approximately 290 mg/g and esterified alfalfa biomass has a capacity of approximately 70 mg/g. In addition, the results of this study also show that amino functionalities and carbon groups play a minor role in the binding of uranyl cations from aqueous solution. XAS experiments showed that the major ligand involved in the binding of uranyl cations from aqueous solution was either a carbon, nitrogen or oxygen ligand, and coordination numbers ranged from 6 to 10 +/- 1.

INTRODUCTION

Over the past few decades, the United States has spent billions of dollars remediating radioactive sites, including the cleanup of decommissioned weapon processing sites. Areas such as the Hanford site are contaminated with a plethora of different contaminants including spent uranium and radioactive lanthanide elements (1). In addition the remediation, of both the radioactive and non-radioactive forms of the lanthanide elements have great potential for cost recovery for industries that use the lanthanide elements. Lanthanide elements are used in television appliances, medical immunoassays, X-ray photography and many other applications (2). As time progresses, problems of recovering and premeditating such elements will only worsen, and to make matters worse, the eventual closure and decommission of nuclear power plants will create a surge in the amount of radioactive waste produced in this country.

Additional wastes, including high concentrations of uranium, have resulted from the use of radioactive materials in mining industries. Not only do uranium mines contain high concentrations of uranium, but fossil fuels, such as coal, also contain high concentrations of uranium. Another problem associated with mining is acid mine drainage, which increases the mobility of metal contaminants through the environment. With the wide spread use of the lanthanide elements, new stocks will either have to be found or the metals will have to be recovered from wastes.

Traditional methods used to extract contaminants from the environment are usually expensive and labor intensive. Traditional techniques for the remediation of toxic contaminates from the environment include soil washing, soil excavation, pump and treat techniques, soil vetrification, and soil roasting. Remediation techniques for the cleaning of contaminate from aqueous solution include ion exchange, reverse osmosis, membrane techniques, coagulation, flocculation, sedimentation, and filtration. These remediation techniques may work well; they are both expensive and inefficient. For example, soil excavation requires the soil to first be excavated and then stored in a landfill. Techniques such as soil washing, soil verification, and soil roasting usually leave the soil devoid of nutrients, known as dead soil. In addition, soil washing techniques, flocculation, and coagulation use harsh chemicals such as high concentrations of mineral acids, sodium hydroxide, or chemical complexing agents that can be hazardous to the environmental and therefore, human health. Furthermore, membrane technologies are not only expensive but also fragile since they tear and clog easily causing water treatment methods using this type of technology usually to require some pretreatment of the solutions. Ion exchange resins include difficulties associated with their use such as high concentrations of hard cations, which make the ion-exchange resin useless. In addition, during the production of many ion-exchange resins, toxic chemicals such as benzene, toluene, and styrene are used to create the

polymeric backbone of the resins (3). The use of such chemicals creates new hazardous waste, which has to be treated and stored. In addition, many of the chemicals used for the creation of polymeric ion-exchange backbones are carcinogenic and not completely removed from the resins, which can be subsequently released from the resin upon use.

In an attempt to overcome the aforementioned problems associated with more traditional remediation techniques, scientists and engineers have been investigating the ability of live plants and inactivated biomaterials as remediation alternatives. The use of natural materials to remediate contaminated waters and soils has been investigated for the past thirty years. There have been numerous studies that have investigated the ability of plants to uptake heavy metals and organic contaminates from soil and solutions. These new techniques have been termed bioremediation (4,5).

Bioremediation can be defined as the use of plants to remove, reduce, or remediate contamination from the environment (6). The techniques that involve the use of living organisms include bioremediation, phytoextraction, phytovolatilization, phytostabilization, rhizofiltration, and phytoremediation. Bioremediation can be defined as the use of living organisms, such as microbes and microorganisms, to reduce or eliminate toxic contaminates from the environment; this is very akin to phytoremediation, which uses live plants to reduce concentrations of toxic contaminates from the environment. Phytoextraction however, is a slightly different technique than phytoremediation; phytoextraction can be defined as the use of live plants to extract specific elements from the environment, such as used in phytomining (6). Phytovolatilization is the use of plants to volatilize an organic contaminate, such as trichloroethylene, from the environment whereas rhizofiltration uses the roots, or the rhizosphere, of plants to remove heavy metals from aqueous solution. Finally, phytostabilization is the use of plants to stabilize contaminants from moving through the environment. As previously mentioned, other phytoremediation techniques involve the use of nonliving biomaterials, which include phytofiltration and phytoextraction. Phytofiltration can be defined as the use of dead plant materials to filter out contaminants from solution whereas phytoextraction is the use of dead plant materials to extract specific elements from aqueous solution (7).

Many different researchers have investigated the use of live plants in the remediation process whereas the advantages in using the dead biomaterials include:

i. There are no concerns of toxicity to the dead biomaterial, so the system is not concentration limited;
ii. There are no requirements of trace nutrients for dead biomaterials;
iii. High concentrations of salts and brines do not appear the effect the filtration process;
iv. The inactive biomass acts as an ion-exchange resin and there is no additional cost for harvesting the biomass after it has uptaken the contaminant.

Although the use of dead biomaterials has advantages over the use of living plants there as still some disadvantages:

i. Phytofilitration can only be used for solution extraction unlike the use of live plants, which can be used for both solution and solid media extraction;

ii. The mechanisms and functional groups through which phytofilitration works is not fully understood.

The disadvantages of phytofilitration are minor and can be over come by using different phytoremediation techniques.

The phytoextraction and phytofilitration of heavy metal ions from aqueous solution has become a topic of interest in the past few decades (8,9). Numerous researchers have shown that there are three different mechanisms through which phytoextraction/phytofiltration work. These mechanisms include ion exchange, ligand exchange mechanisms, and reduction mechanisms (10,11,12). Phytoremediation has been shown to have many advantages over the aforementioned classical remediation techniques. The advantages of phytoremediation over classical remediation techniques include the following:

i. There is no need to use harsh chemical agents for the remediation process;
ii. There are no toxic chemicals used in the production of the biosorbents;
iii. Biosorbents have been shown to work effectively in high concentrations of hard cations with little to no effect on sorption processes (3);
iv. For soil treatment, bioremediation actually increases nutrients in the soil and does not destroy the soil structure (6);
v. It generally costs less and is less labor intensive then traditional remediation techniques (6).

However, as with any technique there are disadvantages associated with its usage and the disadvantages include the following:

i. Generally, bioremediation requires longer times to fully remediate a particular site (6);
ii. Bioremediation of soil and solutions with live plants is depth limited by the root system/structure of the particular plant (6).

Various researchers have shown success in removing heavy metal ions including uranium and the lanthanide elements from aqueous solutions using biological processes (1,13,14). Kelley *et al.,* have used aquatic plants to remove europium from aqueous solutions. After the Chernobyl accident in the 1990's, willows and Indian mustard were used for some of the remediation process and they did have some success in removing the radioactive contamination (15,16). An example of phytofilitration includes the utilization of *Sargassum* seaweed and *Myxococoxcus xanthus* in adsorbing uranium ions from aqueous solutions (13,14,17). It has also been shown that certain microbes have the ability to reduce uranium(VI) to uranium(IV) (16). From our laboratory, we have shown that alfalfa biomass can be used to remediate europium(III) ions from aqueous solutions (18).

Although the mechanism of biosorption has been investigated in the literature there is still not a complete understanding of the mechanism involved. Furthermore, the sorption of the lanthanide and actinide elements to different biomaterials has not been investigated so vigorously or as intensively as the sorption of the more common heavy metal ions.

This work is relevant to a number of different industries and environmental issues. First and foremost, the work is applicable to the remediation of the lanthanide and actinide ions from aqueous and environmental solutions. The body of the work presented in this dissertation entails the investigation of a clean, cost effective, and efficient sorbent to remove metal ions from aqueous solutions. Perhaps even more important to industries such as the petrochemical industry, this research may provide a inexpensive methods for the recovery of rare earth metals used effectively in many catalysts. In addition, this work may provide an effective means to recover the lanthanide elements from waste solutions, thus reducing the reliance of obtaining these metal ions from mining. By providing more cost efficient means of metal recovery more industries may implement the technology in reducing their current waste streams.

Objectives

Biosorption of heavy metals ions has been studied in recent years. However, it is still an emerging field of study. Biosorption may provide a cost and time effective means to remediate contaminated water.

Various researchers have shown success in removing heavy metal ions including uranium and the lanthanide elements from aqueous solutions using biological processes (1,13,14). Previous research in the field of biosorption has indicated that there are several possible ligands involved in the biosorption process, but further research is required. The specific objectives of this work are as follows:

I.) We are proposing to determine how uranium ions are binding to alfalfa biomass.
II.) Determine the effects of pH on binding
III.) Determine the effects of time on binding,
IV.) Determine the capacities of specific metal ion binding.
V.) Determine the ligands on the alfalfa biomass responsible for metal ion binding, through the use of chemical modification techniques and different spectroscopic techniques.
VI.) Overall, to determine the mechanism(s) of the biosorption of the specified actinide ions binding to the alfalfa biomass.

The goal of this research is to understand the mechanism(s) of how bio-based sorbents function in the sorption actinide ions from aqueous solution. These studies will add to the wealth of knowledge regarding bio-sorbents. In addition, these studies may aid in the development of new sorption materials for the removal of actinide ions from aqueous solution.

Methodology

Alfalfa Biomass Collection

The Malone cultivar of Alfalfa (*Medic ago sativa*) was collected from controlled field studies at New Mexico State University, Las Cruces, NM. The alfalfa biomass was harvested and treated as previously reported (19)

Chemical Modification of the Alfalfa Biomass

A number of different chemical modifications were performed on the alfalfa biomass to investigate the involvement of different functional groups on uranyl binding. The first chemical modification performed on the biomass was an esterification. The esterification was performed as previously published in the literature (21,22). Basically, the esterification involved the conversion of carboxylic acid groups on the alfalfa biomass to methyl ester groups. The second modification performed to the alfalfa biomass was a hydrolysis, in order to study the addition of oxygen functional groups to the alfalfa biomass (21). The third chemical modification performed was a modification to the sulfhydrl groups on the biomass, to investigate the effect of removing sulfur groups on the biomass on uranyl binding (22). In this modification the sulfhydrl groups were converted to thiopyrdine functionalities. The two final modifications to the biomass were to modify the amino groups, using succination and acetylation, which were performed as previously published (22). The subsequent effect of each chemical modification on binding was investigated using different chemical and instrumental techniques.

ICP-OES (Inductively Coupled Plasma Optical Emission Spectroscopy) Sample analysis

All ICP-OES analyses were performed using an Optima 4300 DV spectrometer (PerkinElmer Instruments). The instrument was optimized for uranium analysis by performing a BEC (background equivalent concentrations) test. The parameters used for all uranium analyses were as follows: a torch power of 1500 W, flow rate of 1.25 mL/min, nebulization of 0.65 L/min, a 45 second read delay, and read time ranging between 10 s and 20 s.

pH Profiles

The pH profile investigations were performed as published in the literature (20). Basically, a 400 mg sample of the native alfalfa, chemically modified alfalfa, carboxyl resin (Diaion WT01S (purchased from Supelco (Bellefonte PA)), amino resin (Diaion CRB02 (purchased from Supelco (Bellefonte PA)), and powdered activated carbon (purchased from Fisher Scientific) were washed once in dilute nitric acid and twice in deionized water. Between each washing cycle the samples were centrifuged and the supernatants were discarded and the adsorbent was saved. Subsequent to washing the adsorbent were pH adjusted. to pH 2.0, 3.0, 4.0, and 4.5, using dilute nitric acid (0.01M) and dilute sodium hydroxide (0.01 M). To the pH adjusted adsorbent a 4.0 mL aliquots of pH adjusted UO_2^{2+} from either $UO_2(NO_3)_2$ or $UO_2(CH_3COO)_2$ were added and subsequently equilibrated on a rocker for one hour. After equilibration the samples were subsequently centrifuged at 3000 rpm for five minutes and the supernatants were saved for ICP-OES analysis. All these experiments were performed in triplicate for statistical purposes. In addition, all ICP-OES analysis had calibration coefficients of 0.98 or better.

Time Dependency Studies

The adsorbent samples were washed and extracted the same as in the pH profile studies; however, only the optimal binding pH of 4.5 was used for this investigation. The samples were washed and pH adjusted to pH 4.5 using dilute sodium hydroxide (0.01 M), the samples were extracted into in 4.0 mL aliquots, centrifuged at 3000 rpm for five minutes; 4.0 mL aliquots of 1.0 mM UO_2^{2+} solutions (from either $UO_2(NO_3)_2$ or $UO_2(CH_3COO)_2$) were added to the adsorbent samples, and equilibrated on a rocker under varying time intervals. The time intervals under investigation were as follows: 5.0, 10.0, 15.0, 20.0, 30.0, and 60.0 minutes. These reactions

were performed in triplicate for quality control and statistical purposes. At each time interval, as with the pH profiles, 4.0 mL control samples of the UO_2^{2+} solutions (from both $UO_2(NO_3)_2$ and $UO_2(CH_3COO)_2$) were extracted in triplicate, equilibrated on a rocker as the samples. After equilibration, the samples were centrifuged at 3000 rpm for five minutes, the supernatants were decanted, and saved for ICP-OES analysis. All calibration curves for the ICP-OES analysis had correlation coefficients of 0.98 or better.

Capacity Studies

The samples were prepared as previously mentioned, by washing, centrifuging, and pH adjusting to pH 4.5 the optimal binding pH as observed from the pH profile studies. This study was performed in triplicate for each of the biomasses, and resins, for statistical and quality control purposes. To the pH adjusted samples 4.0 mL of pH adjusted 3.0 mM solutions of UO_2^{2+} were added to the adsorbent samples. The adsorbents samples and the UO_2^{2+}solutions were equilibrated on a rocker for 15 minutes and centrifuged at 300 rpm for 5 minutes and the supernatants were saved for ICP-OES analysis. The sorbent samples then had fresh 4.0 mL aliquots of the UO_2^{2+} solutions added, equilibrated, and centrifuged again, this cycle was repeated ten times to fully exhaust the binding sites on the sorbents. All the supernatants were saved for ICP-OES analysis and calibration coefficients of 0.98 or better were obtained for all analyses.

XAS Sample Preparation and Data Collection

The sorbent samples, 200 mg masses, were washed and pH adjusted to pH 2 (the lowest binding pH observed from the pH profiles) and pH 4.5 (the highest binding pH observed from the pH profiles) as previously mentioned. To the pH adjusted 200 mg sorbent samples 40 mL aliquots of UO_2^{2+} either from $UO_2(NO3)_2$ or $UO_2(CH_3CO_2)_2$ were added. The sorbent samples and UO_2^{2+} solutions were then subsequently equilibrated on a rocker for one hour and centrifuged, saving the solid for XAS analysis.

The solid sorbent samples were then lyophilized by first immersing the sample in liquid nitrogen for 45 minutes to completely freeze the samples; then the samples were placed in a Labconco Freeze Dry System (Freezone 4.5) until all the water was removed from the samples. The uranium loaded sorbent samples were then packed into 1 mm aluminum sample plates with Kapton© tape windows, for analysis at Stanford Synchrotron Radiation Laboratory (SSRL)

The samples were analyzed using the Uranium LIII edge on beam line 2-3 using uranium oxide as an internal calibration standard. The sample spectra were recorded at room temperature using a Lytle fluorescence detector. The operational conditions of the beam line were as follows an average current of 80 mA, a Si(220) double monochromator, a 1.0 mm slit, and an energy of 3 GeV. The model compounds, $UO_2(NO_3)_2$ and $UO_2(CH_3CO_2)_2$, were diluted using boron nitride to give a 1 absorption unit change at the absorption edge and measured in transmission mode. In addition, the beam line was detuned by 50% to reject higher order harmonics for both sample and model compound measurements. Further more to improve signal to noise ratios averages of three scans were for data analysis.

XAS Data Analysis

The EXAFS data analysis was performed using WINXAS software V 2.0 using standard data analysis techniques (23). All the spectra of individual samples were calibrated using the internal uranium oxide standard and averaged. The samples were background corrected using a 1 degree polynomial fitting of the pre-edge area. The EXAFS were then subsequently extracted from the absorption spectra by converting the spectra into K space based on the first inflection point of the sample edge. A spline of seven knots of the spectrum was taken between 2.0 and 14.4 $Å^{-1}$ using a k weight of 2 of the sample spectrum. The sample spectra were then Fourier transformed in a modified Hanning window filtering the first and last 10 percents of the spectra. The spectra were then back transformed into K space and fitted using FEFF V8.00 (24). The bond lengths and nearest neighboring atoms were calculated using FEFF with crystallographic inputs created using ATOMS, from crystallographic data of uranyl compounds (25).

Results and Discussion

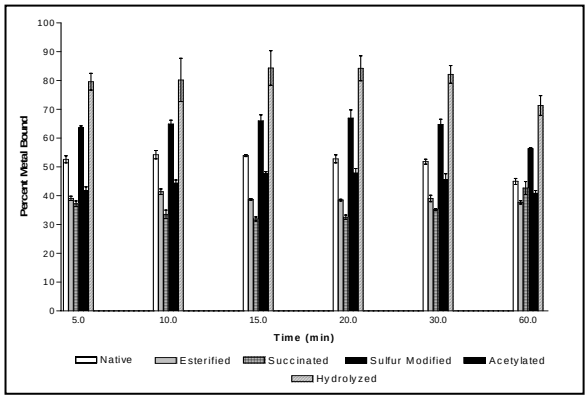
The pH profiles for the biomass and the synthetic resins show a common general trend (data not shown). The general trend between all the sorbents is an increase in binding from pH 2.0 to pH 4.5 for both the uranyl acetate and the uranyl nitrate. This general trend the increase in binding with an increase in pH has been observed for cations reacted with biomaterials. In this study the binding of the native biomass was observed to have been approximately 10% at pH 2, which doubles to approximately 20% at pH 3, the binding subsequently increases to 30% at pH 4, and approximately 45% at pH 4.5. All the biomass samples had this similar binding trend although the different biomasses and resins had different increases in the binding according to increases in the pH.

The hydrolyzed and sulfhydryl modified alfalfa biomass had the highest percentage of uranyl ion binding at 70 and 60 percent for $UO_2(NO_3)_2$ and $UO_2(CH_3O_2)_2$, respectively, whereas, the acetylated and esterified alfalfa biomasses had the lowest percentage of uranyl ion binding at approximately 30 to 40 percent. The data indicates that the carboxyl groups on the biomass are directly involved in the binding of the uranyl cation due to the large increase in percent metal bound after hydrolysis. The increase in binding observed after the sulfhydryl modification may be indicative of a surface charge interaction, indicating an indirect involvement of sulfur in the binding mechanism. The sulfur on the alfalfa biomass will be neutral or positively charged, in the pH ranges studied here. By blocking the sulfhydryl group this charge is reduced or eliminated on the biomass, allowing the uranyl ions to get close to the biomass and bind.

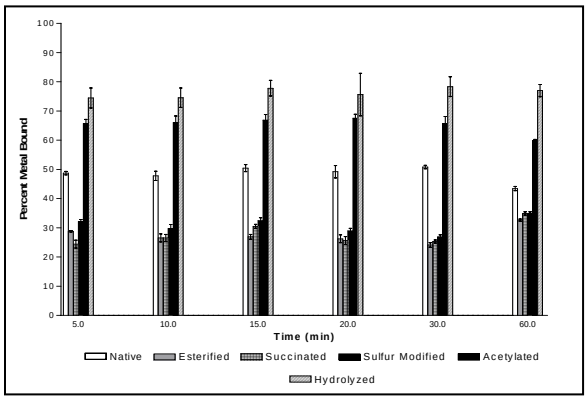
The results of the amino resin pH profiles, binding of approximately 60%, indicate that amino groups play an important role in the binding of uranyl cations from aqueous solution. This resin shows a binding trend that closes resembles the biomass. However, the carboxyl resin showed increased in the binding trend, the maximum binding was approximately 70% that closely resembled the binding by the modified and native alfalfa biomass based on the pH where increases in binding are observed. The largest increase in binding for the biomass samples and the carboxyl resin occurred at pH 3.0. The activated carbon showed the lowest binding at approximately 20 to 30%, indicating the carbon possibly has some minor role in the binding of the uranyl cations from solution. The observed increase in binding by the alfalfa biomass after the hydrolysis reaction shows the importance of the carboxyl groups in the binding mechanism. The other modifications also show the importance of specific functional groups on the biomass

in the binding mechanism. The esterification of the biomass showed a decrease in the binding from 45% with the native alfalfa to 35% after the esterification. The amino modifications to the biomass showed approximately a 10% decrease in the binding after the acetylation and no change was observed for the succination modification. The data indicates that both the amino and carboxyl groups are important in the binding of uranyl from solution by alfalfa biomass.

The results of the time dependency studies for the biomass sorbents and the synthetic resins are shown in Fig. 1 and Fig. 2, respectively. The time dependency studies show that the binding occurs within the first five minutes of contact time and remains constant for up to 60 minutes for the native, chemically modified alfalfa biomass samples. However, the carboxyl resin and the amino resin show a slight increase in the observed binding with increased time. The binding of the activated carbon adsorbent with the uranyl nitrate has a slight decrease in the binding after the first 15 minutes, and remains constant thereafter, where as with the uranyl acetate there is a slight increase in binding with time. The slight differences in binding observed with time can be explained through a competition mechanism since the acetate in solution from the uranyl acetate is competing with the adsorbent for complexation of the uranyl cation, which is why there is a slight increase with the percent metal bound with increasing time, while the nitrate does not really compete with the adsorbents.



A



B

Fig. 1 A. Time dependency for the binding of $UO_2(CH_3COO)_2$ reacted with native and chemically modified alfalfa biomass between pH 2 and pH 4.5.
B. Time dependency for the binding of $UO_2(NO_3)_2$ reacted with native and chemically modified alfalfa biomass between pH 2.0 and pH 4.5.

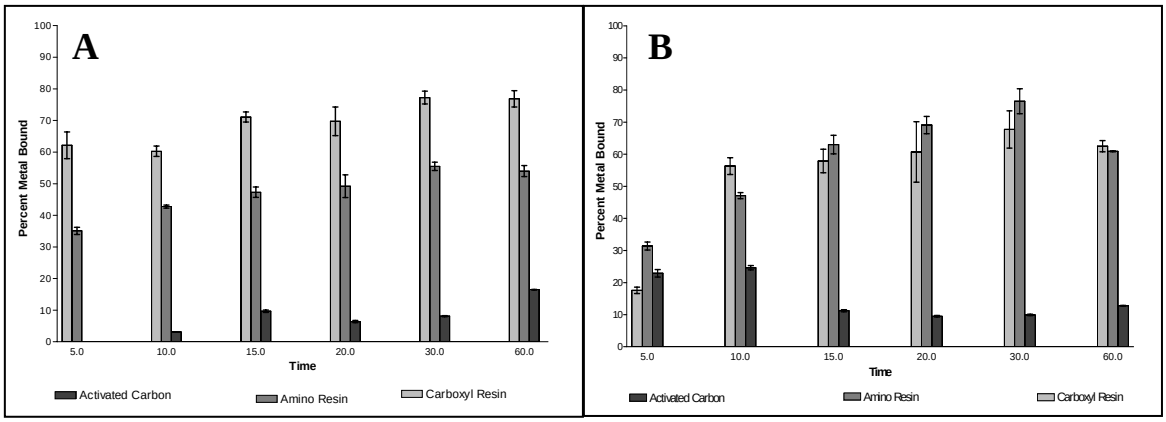


Fig. 2 A. Time dependency for the binding of $UO_2(CH_3COO)_2$ reacted with ion-exchange resins, graphite, and activated carbon between pH 2 and pH 4.5.
B. Time dependency for the binding of $UO_2(NO_3)_2$ reacted with reacted with resins, graphite, and activated carbon between pH 2 and pH 4.5.

The binding capacities of the native and chemically modified alfalfa biomass for the uranyl cations showed results similar to the pH profiles. The native alfalfa biomass showed a binding capacity for the uranyl cations of approximately 140 mg/g, approximately half of the binding capacity of *T. versicolor* 290 mg/g and almost the same as that of *P. chrysosporium* at 150 mg/g (26). The hydrolyzed biomass showed the highest binding capacity at approximately 290 mg/g (for both the uranyl nitrate and uranyl acetate), this binding results in approximately a 200 percent increase in the binding compared to the native biomass. However, the esterified biomass had the smallest binding capacity of the biomass samples at approximately 70 mg/g, which is approximately 50 percent of the binding capacity of the native biomass. The ability of the esterified alfalfa biomass to still bind the uranyl cations from solution can be attributed to the presence of other functional groups such as carbon and amino groups. From the results of the carbon and amino resins approximately 20 to 30 percent of the binding of the biomass samples can be attributed to these groups. The activated carbon bound approximately 40 mg/g showing that carbon is involved in the binding of the uranyl cations as has been suggested by other authors (27). The succinated and acetylated biomasses bound approximately 97 and 122 mg/g, respectively, which was approximately a decrease 20 to 30 percent. This decrease in the binding compared to the native biomass shows that amino groups are involved in the binding the uranyl ions. The synthetic adsorbents however showed comparable binding capacities to the alfalfa biomass. The carboxyl resin binding capacities at approximately 210 and 220 mg/g and the amino resin showed capacities of 239 and 273 mg/g (for the uranyl acetate and uranyl nitrate). The capacity of the sulfur modified alfalfa biomass showed an increase in binding in the presence of the uranyl acetate 166 mg/g and no major was observed for the binding of uranyl nitrate 142 mg/g.

The observed differences in the binding of $UO_2(NO_3)_2$ and $UO_2(CH_3COO)_2$, can be explained through a competition; between of the complexation of the counter ion and the biomass for the uranyl ions. The presence of the acetate ion in the reaction solution appears to be competing for the uranyl cations with the biomass as shown by lower capacities in presence of the acetate ions.

The data shows the importance of the carboxyl cations in the binding of the uranyl cations to the alfalfa biomass. In addition, the data also that amino groups and carbon play a minor role in the binding mechanism. Furthermore the slight increases in the binding observed in the binding after the sulfhydrl modifications also show that sulfur groups on the biomass have some role in the binding process. But the sulfur more than likely plays a indirect role in the binding. The sulfur groups on the biomass would control the surface charge of the biomass and thus indirectly controlling the binding by not allowing the cations to get close enough to the biomass to bind.

X-ray absorption spectroscopy showed a number of interesting results in the binding of the uranyl cations to the biomass and the synthetic sorbents. The XANES (x-ray absorption near edge spectroscopy) show that the uranyl cations stayed in the same oxidation state as they were in their original complexes. In addition, the geometry of the complex, which is also indicated by XANES, showed changes from the octahedral arrangement observed in the model compounds.

The EXAFS studies on the uranium bound to the native biomass, modified biomass, and the synthetic resins also corroborated the results of the XANES studies. The EXAFS showed the presence of the axial oxygen atoms at 1.80 Å in all the sorbent samples and the model compounds as has been observed by other authors (28-30). The largest differences in the EXAFS were shown in the equatorial oxygen atoms, which ranged from three to eight oxygen atoms. The presence of six oxygen atoms in the samples indicates an octahedral geometry for the uranyl cations, yet a coordination number of eight is more stable for the uranium cation. The presence of six oxygen atoms bound to the uranium cation indicates that a ring type structure is present in the samples (2). These ring type structures have been observed for uranium complexed to nitrate in the presence of oxygen containing organic ligands. In addition, these complexes have nitrate ligands and organic ligands present in the uranium compound (2). The EXAFS of the sorbents showed the presence of six to eight oxygen ligands split between two different binding shells. This was indicated by the difference in the bond lengths 1.80 Å, the two axial oxygen ligands, and four to six equatorial oxygen ligands at approximately 2.3 to 2.5 Å. The possible structures for the uranyl cations bound to the biomass are presented in Fig. 3.

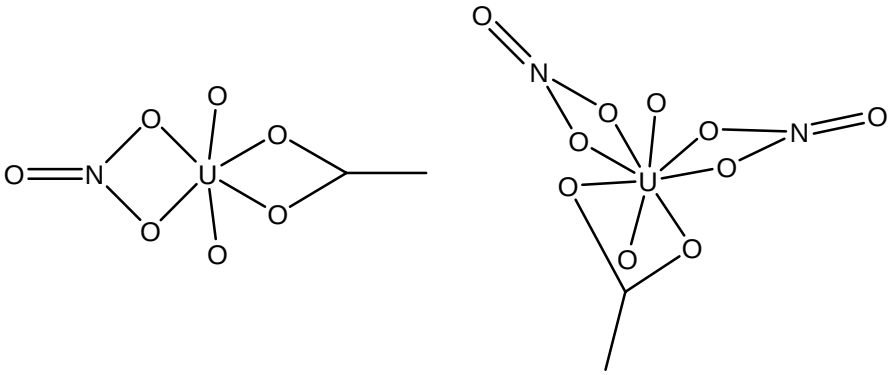


Fig. 3 The possible types of structures for the uranyl cation binding to the alfalfa biomass the nitrate ligands can be interchanged for water or acetate ligands

The structures shown in Fig. 3 produces a system where there are two equally distant axial oxygen atoms, and six equatorial oxygen atoms at mixed bond lengths due to the variation in the coordinating ligands. The structure is suggested because of the difference in the ligand distances found from the fitting results. The different ligand attached to he biomass could be a number of different ligands which including the biomass ligands and either nitrate, acetate, or coordinated water ligands. The fitting results of the EXAFS indicate coordination of a six to eight oxygen atoms from both the solution and the biomass.

Cost Comparison of Using Commercial Resins and Alfalfa Biomass to Remove Lanthanide and Actinide Elements from Aqueous Solution:

A brief cost comparison between the different adsorbents used in the studies performed in this dissertation (excluding the activated carbon) was performed. The Activated carbon is excluded for two reasons: first, it only worked with the uranyl cations but it still was not a viable option; second, it did not adsorb any of the lanthanides to any great extent. The resins that are compared with the raw alfalfa are the weak cation-exchange resin (Diaion WT01S purchased from Supelco) and the amino resin (Diaion CBR02 purchased from Supelco).

The cost of purchasing the Diaion WT01S from Supelco in a bulk purchase is $25,000/137.7 kg ($181.5/kg). The cost of purchasing the Diaion CBR02 from Supelco is $2,500/ 112 kg ($22.3/kg). Therefore a ton of the Diaion WT01S resin costs $182,348, while a ton of the Diaion CBR02 resin costs $22,321 , and a ton of alfalfa costs $200 (personal communication with the providers).

The binding capacities presented throughout the dissertation show that alfalfa has a comparable capacity to the different ion-exchange resins. The ratios of metals bound to the native alfalfa and the ion-exchange resins are given in the Table I.

Table I Ratios of the lanthanide and actinide elements binding to the native alfalfa and the ion-exchange resins.

Element	Alfalfa Capacity kg/ton	Diaion WT01S Capacity kg/ton	Diaion CBR02 Capacity kg/ton
Uranium (Nitrate)	144.0	210.3	273.8
Uranium (Acetate)	138.3	216.5	239.2

As can be seen in Table I the resins do bind better than the alfalfa biomass by approximately a factor of two to three. A comparison of the cost of removing one kilogram of the particular metal based on the cost of the different adsorbents is presented in Table II.

Table II The cost of removing one-kilogram of each of the different metal ions using the alfalfa biomass or the ion-exchange resins.

Element	Alfalfa ($)	Diaion WT01S ($)	Diaion CRB02 ($)
Uranium (Nitrate)	1.40	868.32	81.52
Uranium (Acetate)	1.45	837.64	93.32

As can be clearly seen in Table II alfalfa is much more cost effective in removing 1 kg of uranium from water compared to the commercial adsorbents. Thus alfalfa has the potential to be used as an adsorbent for removing lanthanide and actinide elements from aqueous solution.

CONCLUSIONS

The data obtained from this study indicate an ion exchange type mechanism for the binding of the UO_2^{2+} to the different adsorbents. The pH profiles, capacity, and the XAS data suggest the ligand responsible for the binding of the UO_2^{2+} cations to the adsorbents is likely an oxygen or nitrogen ligand. The data shows that carbon does play a minor role in the binding process. The sulfhydryl modification of the biomass indicates that surface charge plays an important role in the binding, and that the sulfur ligands on the biomass are more than likely indirectly involved in the binding process. The data from the XAS studies indicate that oxygen or nitrogen ligands on the adsorbents is extremely important in the adsorption of the UO_2^{2+} cation to different adsorbents, and the suggested mechanism of adsorption is a loss of one of the original coordinating groups of the UO_2^{2+} cations (i.e., a nitrate group or a acetate group), to form a complex with the adsorbent. These data indicates that the biosorbents adsorb the UO_2^{2+} cations from solution through an ion-exchange process, as is observed with the ion-exchange carboxyl resin. This is supported by the change in percent adsorption with changing pH. Furthermore, the capacities of the native biomass to sorb UO_2^{2+} cations from solution suggest that alfalfa biomass may be an inexpensive and viable means to remediate UO_2^{2+} from environmental solutions.

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