

Remediation of Soils and Wastes Contaminated with Uranium and Toxic Metals

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The presence of radionuclides and toxic metals in soils and wastes due to nuclear related activities is a major environmental concern. To restore the contaminated sites, both the radionuclides and toxic metals must be removed. We have developed a comprehensive method to remediate contaminated soils and wastes with the removal and recovery of uranium and toxic metals. The overall process consist of three steps: extraction, biodegradation, and photodegradation. Radionuclides and toxic metals are removed from contaminated soils and wastes by extracting them with citric acid, a natural multidentate complexing agent. Citric acid forms different types of complexes with the transition metals and actinides that may involve the formation of bidentate, tridentate, binuclear, or polynuclear complex species. Several metal–citrate complexes were readily biodegraded by *Pseudomonas fluorescens*, resulting in the bioprecipitation and recovery of the metals, whereas uranyl citrate, which is recalcitrant to biodegradation, upon exposure to light was photodegraded with the precipitation of uranium as $\text{UO}_3 \cdot x\text{H}_2\text{O}$. For example, uranium was removed from contaminated soils and sludge with >85% efficiency. Biodegradation followed by photodegradation of the citric acid extract resulted in >99% recovery of the extracted uranium. In addition, significant amounts of Al, Ca, Co, Cr, Cu, Mg, Mn, Ni, Pb, Sr, Th, and Zn were also removed during biodegradation of the extract. In this process, the toxic metals and uranium are recovered in separate fractions in concentrated form for recycling or disposal.

Introduction

The end of the Cold War resulted in the closure of many facilities that produced nuclear and chemical weapons worldwide, but it also left behind a legacy of environmental contamination. Large volumes of wastes containing toxic metals and radionuclides are generated by nuclear- and fossil-fueled power plants, by metal fabrication industries, and by facilities producing nuclear weapons. The principal contaminants of concern are the radionuclides U, Th, Pu, ^{60}Co , ^{90}Sr , ^{135}Cs , and ^{99}Tc and the toxic metals Ba, Cd, Cr, Cu, Ni, Pb, and Zn. Because these problems are pervasive at the local, regional, and national scale and the cost of remediating such contaminated sites is quite staggering, new and innovative physical, chemical, and biological methods are being developed for restoration and long-term management of the contaminated sites (1, 2).

To remediate these sites, both the metals and radionuclides must be removed. Various soil-washing techniques have been developed including physical methods, such as wet screening, attrition scrubbing, and chemical treatments with various organic and inorganic acids, bases, salts, and chelating agents. For example, nitric acid, hydrochloric acid, phosphoric acid, sulfuric acid, sodium hydroxide, sodium carbonate, ammonium carbonate, oxalic acid, citric acid, ethylenediaminetetraacetic acid (EDTA), and diethylenetriaminepentaacetic acid (DTPA) have been used to extract radionuclides and toxic metals. However, many of the inorganic chemicals used are corrosive, irreparably damaging the soil, while the synthetic organic chelating agents employed in decontamination persist in the environment causing the radionuclides to migrate from the disposal sites (3–5). Furthermore, chemical extraction methods generate secondary waste streams that create hazardous waste disposal problems.

Among the several organic compounds used in extracting metals, citric acid is the most preferred because it is a natural multidentate organic complexing agent, environmentally friendly, and readily biodegradable, and its efficiency in removing metals is relatively consistent. Citric acid forms different types of complexes with transition metals and actinides, which may involve the formation of bidentate, tridentate, dimeric, or polymeric complex species (6, 7). Citric acid was used to extract plutonium from soils (8); decontaminate the components of nuclear reactors (9); and remove metals and radionuclides from contaminated soils, wastes, and incinerator ash (10, 11). In this paper, we discuss the removal and recovery of uranium and toxic metals from contaminated soils and wastes by citric acid, followed by biodegradation to precipitate the toxic metals, and photodegradation to recover uranium.

Materials and Methods

Contaminated Soil and Sludge Samples. Soils contaminated with uranium from uranium processing facilities at Fernald, OH, were provided by FERMCO, and from the Ashtabula, OH, RMI project by Parsons Environmental Services, Inc. The sludge sample was obtained from a uranium process wastestream in the West End Treatment Facility at the U.S. Department of Energy's, Y-12 Plant, Oak Ridge, TN. Several million gallons of the sludge is stored awaiting disposal.

Analyses of Soil and Sludge Samples. The soil samples were air-dried in a HEPA-filtered hood and then sieved (<2.0 mm). The soil and the sludge samples were dried at 60 °C to constant weight, and 1 g of the sample was digested by sequential 5 mL additions of hot concentrated nitric, perchloric, and hydrofluoric acids in a platinum crucible and analyzed for metals by inductively coupled plasma–atomic emission spectroscopy (Varian Liberty ICP–AES spectrometer). The mineralogical association of uranium in the sludge and the predominant forms of uranium in the Fernald soil have been reported elsewhere (12–15). The oxidation states of uranium in the RMI soil and sludge were determined at the National Synchrotron Light Source (NSLS) by X-ray absorption near-edge structure (XANES) analysis at Brookhaven National Laboratory (BNL).

Citric Acid Extraction of Uranium and Metals. To determine the optimum concentration of citric acid required to extract uranium from sludge, 10 g of the sample in duplicates was extracted with 100 mL of either (i) deionized water, (ii) 0.2 M citric acid, (iii) 0.4 M citric acid, or (iv) 0.6 M citric acid using a wrist action shaker. Citric acid was added as free acid. At periodic intervals (1, 5, 24, 48, and 72

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TABLE 1. Extraction of Uranium and Other Metals by Citric Acid from Sludge and Contaminated Soils^a

metal	Y-12 Oak Ridge sludge		RMI soil		Fernald soil ^b	
	total ($\mu\text{g gdw}^{-1}$)	extracted (%)	total ($\mu\text{g gdw}^{-1}$)	extracted (%)	total ($\mu\text{g gdw}^{-1}$)	extracted (%)
Al	30500 \pm 500	59	6610 \pm 1760	nd	37000	3
Ba	427 \pm 25	24	nd	—	380	32
Ca	364000 \pm 6000	43	22700 \pm 400	72	42000	99
Cd	66 \pm 6	9	nd	—	nd	—
Co	0.7 \pm 0.3	75	nd	—	nd	—
Cr	342 \pm 10	75	3.2 \pm 2.3	nd	35	9
Cu	329 \pm 18	1	336 \pm 12	69	85	12
Fe	4700 \pm 100	—	13900 \pm 800	nd	28000	3
Mg	7510 \pm 100	90	2800 \pm 310	59	18000	52
Mn	234 \pm 3	83	334 \pm 19	60	730	66
Ni	1120 \pm 10	80	nd	—	nd	—
Pb	224 \pm 27	49	nd	—	nd	—
Sr	125 \pm 5	59	nd	—	140	65
Th	3.1 \pm 0.1	94	—	—	—	—
Ti	922 \pm 95	28	2300 \pm 60	17	3600	5
U	2410 \pm 100	87	732 \pm 94	85	449	99
Zn	839 \pm 7	60	169 \pm 13	51	82	16

^a nd, none detected; —, not determined. Sludge and RMI soil were extracted with 0.4 M citric acid. ^b Fernald soil extracted with 0.3 M citric acid was provided by C. W. Francis, Oak Ridge National Laboratory.

h), 10-mL aliquots were removed, centrifuged for 10 min at 7000g, filtered through a 0.22- μm Millex filter (Millipore Corp., MA), and analyzed for uranium. The weight of the solids before and after citric acid extraction was determined by drying at 60 °C until a constant weight was obtained. The dried solids were digested as described above. The citric acid extract and digested solids were analyzed for metals by ICP-AES. The efficiency of extracting uranium and other metals was determined by analyzing the metals in the extract and in the remaining solids. One hundred fifty milliliters of 0.4 M citric acid was added to 15 g of the air-dried RMI soil sample (–2.0 mm), in duplicate, and extracted on wrist action shaker in the dark for 24 h. The sample was centrifuged at 9000g for 20 min, and the extract was filtered through a 0.45- μm filter and analyzed for pH and metals. The citric acid extract of the Fernald soil was provided by C. W. Francis (ORNL). It was obtained by extracting 400 g of air-dried soil with 4 L of 0.3 M citric acid. The extract was stored at 4 °C and shipped to BNL. Upon receipt the extract was filtered through a 0.45- μm filter and analyzed for uranium and metals by ICP-AES.

Biodegradation of Citric Acid Extract. We used *Pseudomonas fluorescens* (ATCC 55241), isolated from a low-level radioactive waste disposal site at West Valley, NY, to biodegrade the citric acid extracts. This bacterium degraded several metal–citrate complexes but not uranyl citrate (16). The extract was diluted 4-fold with deionized water, NH_4Cl (0.1%) was added, and the pH was adjusted to 6.5 with NaOH. One hundred fifty milliliters of the diluted extract, in triplicate, was inoculated with 4 mL of an 18-h old culture (OD, 0.3 at 600 nm) of *P. fluorescens* and incubated on a shaker at 24 °C. The bacterial inoculum was grown in modified Simmons citrate medium containing citric acid, 2 g; NH_4Cl , 1 g; KH_2PO_4 , 1 g; K_2HPO_4 , 1 g; NaCl, 4 g; MgSO_4 , 0.2 g; and deionized water, 1000 mL; pH 6.5. All samples were prepared under low light to minimize any photochemical reactions. Periodically, a 5-mL aliquot was removed, filtered through a 0.22- μm filter, and analyzed for pH, for citric acid by HPLC, and for uranium and metals by ICP-AES. After biodegradation of the citric acid, the extract was centrifuged at 7000g to separate the supernatant and the solids. The solids, consisting of bacterial biomass and precipitated metals, were dried, and after weighing them, they were digested in a mixture of hot nitric and perchloric acid in a microdigestion rack (Thomas Scientific, NJ) and analyzed for metals.

Photodegradation of Citric Acid Extract. The supernatant recovered after biodegradation of the citric acid extract was filtered through a 0.22- μm filter. The pH of the filtered supernatant was adjusted to 3.5 with HCl and then exposed to high output fluorescent growth lights placed ~20 cm above the sample in an incubator at 26 ± 1 °C (17). The lamps displayed a broad spectrum in the visible region from 400 to 700 nm, and the total intensity at the sample was 0.27 mEinstein $\text{m}^{-2} \text{s}^{-1}$. The maximum absorption of the uranyl citrate complex was at 435 nm, and the light intensity at this wavelength was 0.04 mEinstein $\text{m}^{-2} \text{s}^{-1}$. Control samples were incubated in the dark. Periodically, 2-mL samples were withdrawn, filtered through a 0.22- μm filter, and analyzed for uranium and citric acid. The precipitate from the photodegradation of the extract was recovered by centrifugation and characterized by X-ray absorption spectroscopy.

Speciation of U by XANES and EXAFS. The speciation of uranium in the sludge and RMI soil was determined by XANES. Oxidation state determination by XANES is based on the observation that the position of the absorption edge of the target atom moves to higher energy with an increase in valence as a result of higher ionization energy. The dried sludge was mounted on Mylar foil using a mixture of acetone and DUCO cement (duPont de Nemours Co.) and placed in a He-flushed sample chamber. Measurements were made at the M_V absorption edge with a double crystal Si(111) monochromator using an electron yield detector at the NSLS as previously described (18). Data points in the absorption peak region were collected with a resolution of 0.1 eV and 3 s integration. The RMI sample was dried in a vacuum, placed in a heat-sealed polypropylene bag (0.2 mil), and analyzed on beamline X-18B with a Si(111) channel-cut crystal at the uranium L_{III} absorption edge at the NSLS using a fluorescence detector (19). Data points were collected with a resolution of 0.2 eV and an integration time of 2 s. Multiple scans (up to 12) were collected and averaged. The oxidation state of uranium in the samples was determined after background subtraction, normalization, and fitting using a least-squares program. The absorption edge positions of uraninite (UO_2) were calibrated to 3545 eV for the M_V and 17165 eV for the L_{III} absorption edge, respectively. The oxidation state of U in the sludge sample was obtained by comparison with the shift in peak position (maximum) of the uranium trioxide ($\gamma\text{-UO}_3$) standard. The oxidation state of U in the RMI soil was determined after obtaining the first

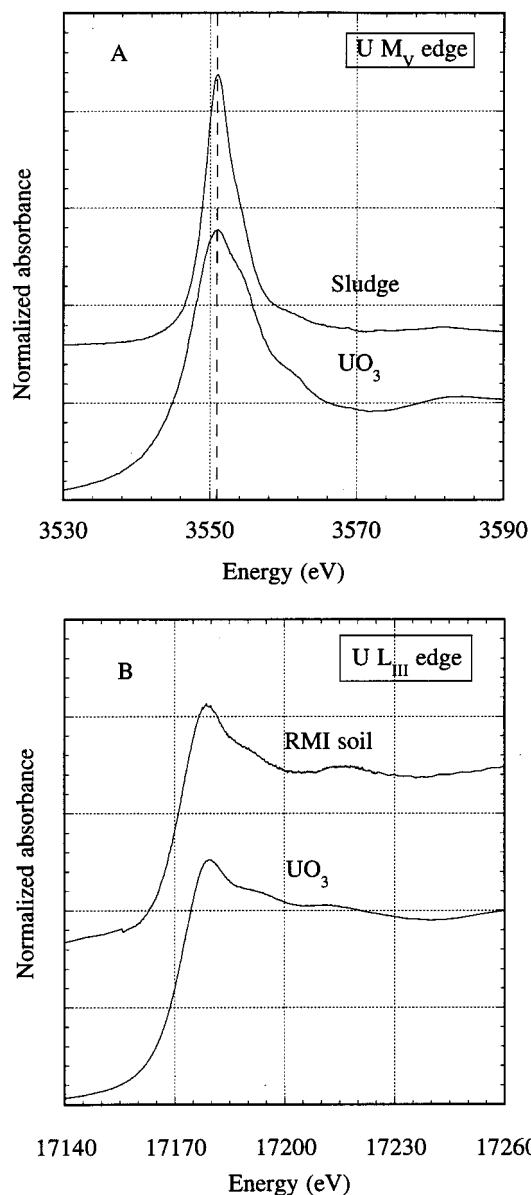


FIGURE 1. Comparison of XANES spectra at (A) M_V absorption edge for sludge at 3551.1 eV, and (B) U L_{III} absorption edge for RMI soil at 17172 eV with uranium trioxide (γ -UO₃).

derivative of the L_{III} absorption edge and comparing with the uranium trioxide standard.

Extended X-ray absorption fine structure (EXAFS) of the uranium precipitate recovered after photodegradation of the citric acid extract gave information on the nearest neighbor and the chemical bonding of the uranium (20). A multistep data analysis of the k^3 -weighted EXAFS spectra in the k range of 3.0–13.6 Å⁻¹ included Fourier transformation of the normalized spectra. The peak position and amplitude of the coordination shells of the sample were compared with standards for uranium trioxide, uranyl hydroxide, and UO₃·2H₂O. Uranyl hydroxide was prepared by adjusting the pH of a solution of uranyl nitrate to 7, decanting the supernate after centrifugation, washing three times with deionized water, and drying the solid at 60 °C overnight.

Uranium Concentration and its Removal from Soil Extract. To determine the effect of uranium concentration in the soil extract on the extent of its removal after biodegradation followed by photodegradation, we used the citric acid extract of Fernald soil containing 0.03 mM U. This extract was spiked with 1:1 uranyl citrate to obtain samples

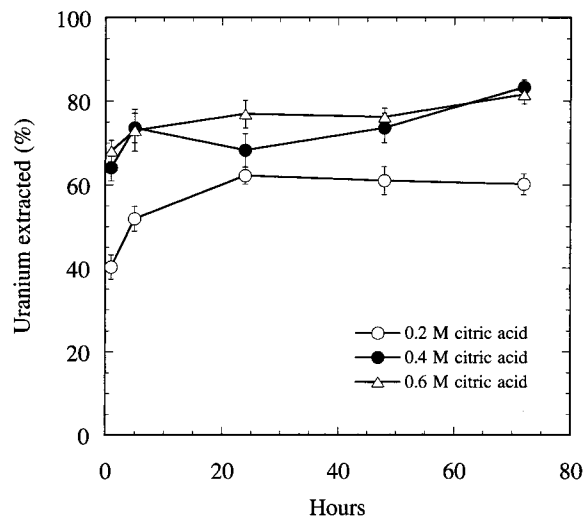


FIGURE 2. Extraction of uranium from Y-12 sludge by citric acid. Error bars are ± 1 SEM.

with a final concentration of 0.13, 0.24, and 0.45 mM U. The extract was then subjected first to biodegradation then to photodegradation, as described earlier.

Citric Acid Analysis. Citric acid was determined by high-pressure liquid chromatography (HPLC) with a Bio-Rad HPX-87H column using a UV-vis detector at 210 nm. The samples were filtered through a 0.22- μ m Millex filter before analysis. The detection limit was 20 μ M.

Results

Chemical Characterization. The sludge contained predominantly calcium carbonate (91%) resulting from waste treatment and a small amount of organic carbon (1.2%); the pH was alkaline (pH 9.2). Table 1 gives the concentrations of metals in the sludge; the major elements were Al, Fe, Mg and toxic metals Cd, Cr, Co, Cu, Pb, Mn, Ni, and Zn. Uranium and Th concentrations were 2410 and 3.1 μ g gdw⁻¹ (g dry wt), respectively. The mineralogical association of U in the sludge determined by the sequential selective-extraction procedure showed that one-half of the total uranium (1200 μ g) was associated with the carbonate fraction (12). The association of uranium with other fractions was as follows: exchangeable, 400 μ g; iron-manganese oxide, 216 μ g; organic, 516 μ g; and inert, 80 μ g gdw⁻¹. Comparison of the M_V peak position of the XANES spectra for the sludge (3551.1 eV) with uranium trioxide (U⁶⁺) showed identical maxima, confirming that U was in the hexavalent state (Figure 1A).

The Fernald soil consisted primarily of quartz, clays, dolomite, and calcite (13–15); its total organic matter content was 15% and the pH 8.1. It contained 449 μ g gdw⁻¹ uranium and the toxic metals Ba, Cr, Cu, Mn, and Zn (Table 1). X-ray absorption and microprobe analyses of the soil samples showed that ~75–95% of the uranium was in the hexavalent oxidation state (13, 14). The presence of uranyl phosphate (*m*-autunite), uranium oxide (uraninite), and uranium metaphosphate [U(PO₃)₄] phases were identified by electron beam analysis (15). The RMI soil sample contained 11% total organic matter, 732 μ g gdw⁻¹ uranium and the toxic metals Cr, Cu, Mn, and Zn (Table 1). The soil pH was 7.3. Comparison of the U L_{III} absorption edge position of the XANES spectra for the RMI soil at 17172 eV with uranium trioxide confirmed that the U was in the hexavalent state (Figure 1B). Other features of the U L_{III} spectra included two peaks in the near-edge region at 15 and 40 eV above the absorption edge. These peaks result from multiple scattering resonances from the axial oxygens and are observed when hexavalent uranium is present.

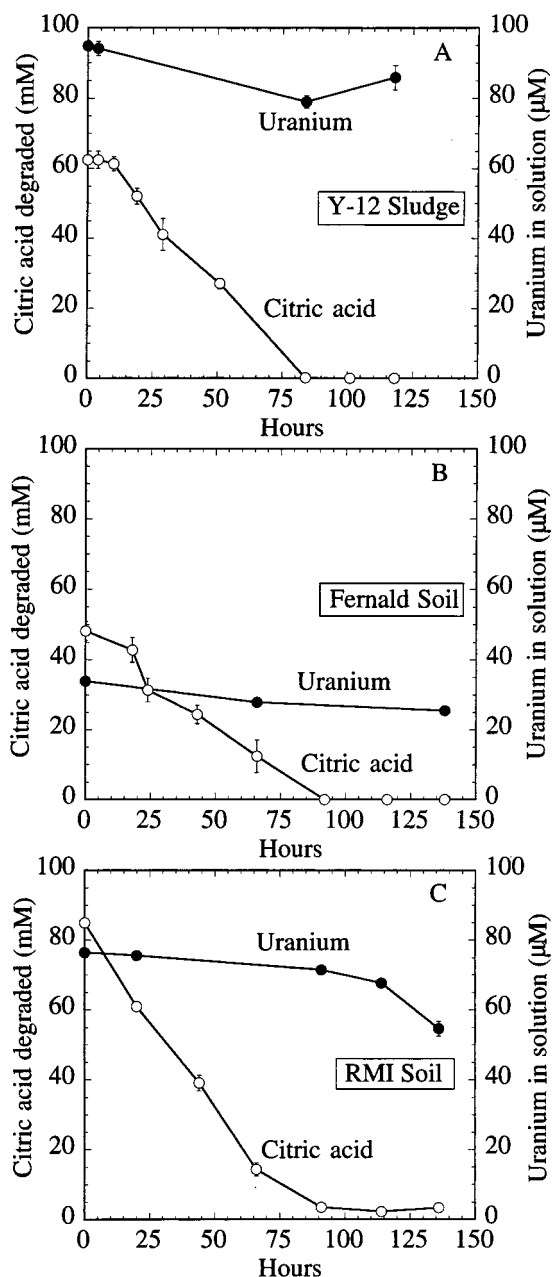


FIGURE 3. Biodegradation of citric acid extracts of (A) Y-12 sludge, (B) Fernald soil, and (C) RMI soil.

Extraction of Uranium and Toxic Metals. The efficiency of various concentrations of citric acid in extracting uranium from the sludge is shown in Figure 2. With 0.2 M citric acid, 60% of the uranium was extracted in 24 h, whereas with 0.4 M citric acid, 80% of the U was extracted. There was only slight increase in the removal of uranium with 0.6 M citric acid. Table 1 shows the efficiency of citric acid in extracting uranium and several other metals from the sludge and soils. Uranium was removed from the RMI and Fernald soils with an efficiency of 85% and 99%, respectively. In addition, significant amounts of Al, Ca, Co, Cr, Mg, Mn, Ni, Pb, Sr, Th, and Zn from the sludge; Ca, Cu, Mg, Mn, and Zn from the RMI soil; and Ca, Mg, Mn, and Sr from Fernald soil were extracted.

Biodegradation of Citric Acid Extract. Diluted (4×) citric acid extracts of Y-12 sludge, Fernald, and RMI soil samples were biodegraded by *P. fluorescens* at the rate of 0.83, 0.63, and 1.01 mmol h⁻¹, respectively (Figure 3A–C). The pH of the extracts increased from 6.5 to ~8.5 due to the degradation

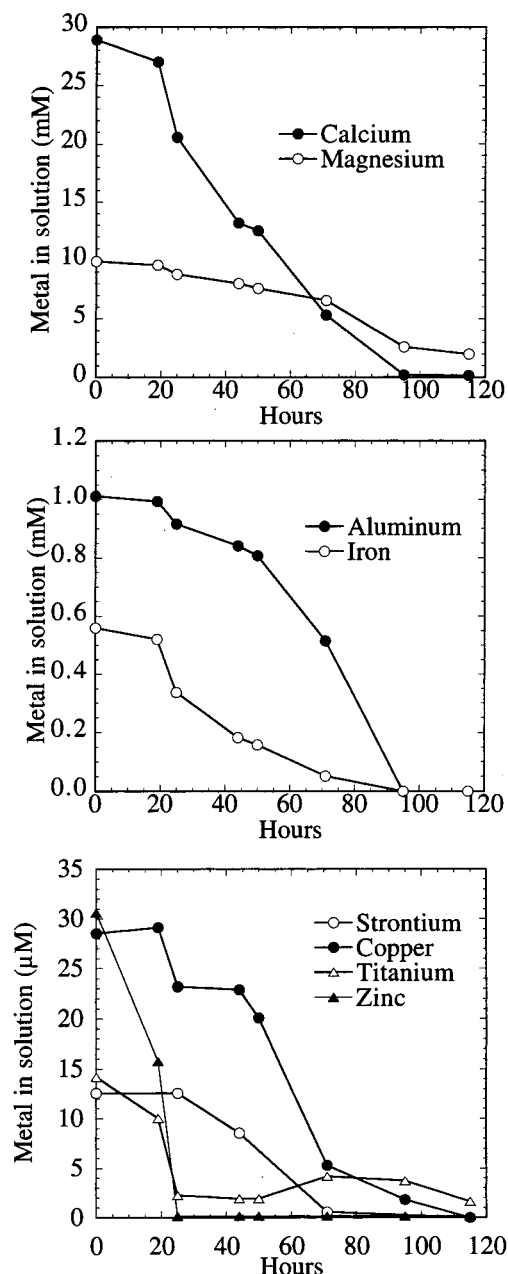


FIGURE 4. Removal of selected metals during biodegradation of citric acid extracts of soils.

of citric acid. The uranyl–citrate complex was recalcitrant and remained in solution. However, a slight decrease in concentration of soluble uranium was noticed in all extracts when most of the citrate was degraded and the culture had reached a stationary phase. In contrast, the concentration of other soluble metals in the extract generally decreased with time. Figure 4 shows the removal of selected soluble metals during biodegradation of the citric acid extracts of the soils; most were removed with >99% efficiency in 120 h. The following are the rates and extent of removal of selected metals from the extract (μmol h⁻¹, %): Al (10.5, >99), Ca (41.7, >99), Cu (0.46, >99), Fe (6.2, >99), Mg (9.1, 80), Sr (0.26, >99), Ti (0.11, 89), and Zn (2.6, >99). Analysis of the solids following biodegradation showed concentration and recovery of precipitated metals with the biomass.

Photodegradation of Extract. Exposure of the citric acid extracts containing uranium to light after biodegradation resulted in the precipitation of uranium, the rate and extent of which varied with the extract: Y-12 sludge (1.5 μmol h⁻¹,

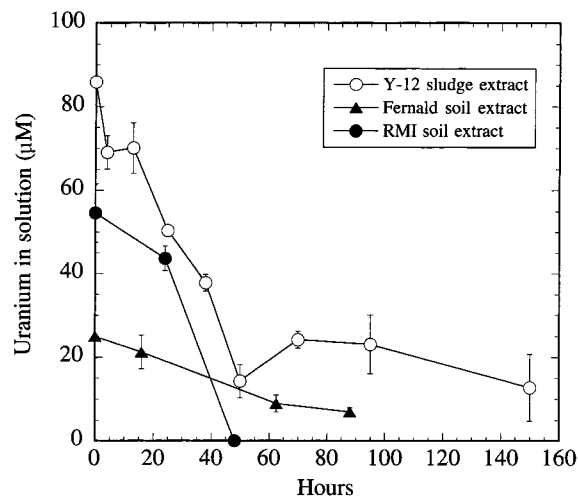


FIGURE 5. Photochemical precipitation of uranium from citric acid extracts of soils and sludge following biodegradation. Error bars are ± 1 SEM.

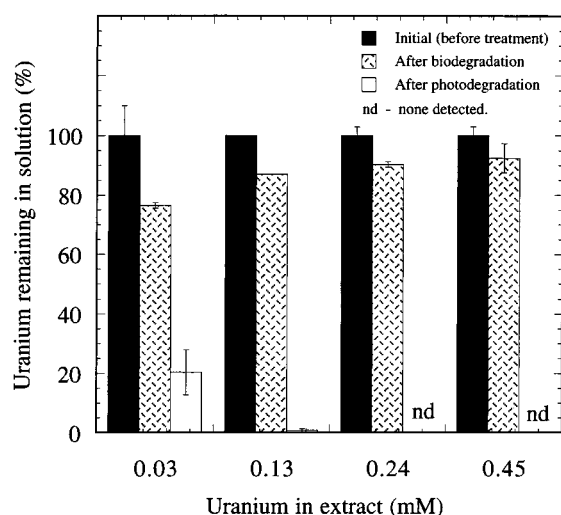


FIGURE 6. Effect of initial concentration of uranium on the extent of its removal from citric acid extract of Fernald soil.

85%); FERMCO soil, ($0.26 \mu\text{mol h}^{-1}$, 72%); and RMI soil ($1.82 \mu\text{mol h}^{-1}$, 100%) (Figure 5). The pH of the samples increased slightly from 3.5 to 3.6 during the photodegradation.

Uranium Concentration and Its Removal from Soil Extract. The effect of the initial concentration of uranium in the Fernald soil extract on its removal during biodegradation and photodegradation is shown in Figure 6. Biodegradation of the citric acid extract resulted in the removal of less than 23% U from the unspiked extract containing 0.03 mM U and 13%, 7%, and 5% removal from samples containing 0.13, 0.24, and 0.45 mM uranium, respectively. These results showed that U removal from the extract during biodegradation decreased with an increase in U concentration and that the U in the extract had no effect on the growth of bacteria or on the extent of citrate degradation. The overall removal efficiency of U during photodegradation increased with an increase in U concentration in the extract from 80% to $\geq 99\%$.

Characterization of Precipitate from Photodegradation. Comparison of the U L_{III} absorption edge position and the structural features of the XANES region of the precipitate from photodegradation with the $\gamma\text{-UO}_3$ standard and $\text{UO}_2(\text{OH})_2$ confirmed that U is in the hexavalent state (data not shown). The EXAFS spectrum shows the radial distribution of atoms surrounding the uranium (Figure 7). The predominant features of this spectrum are the two coordination

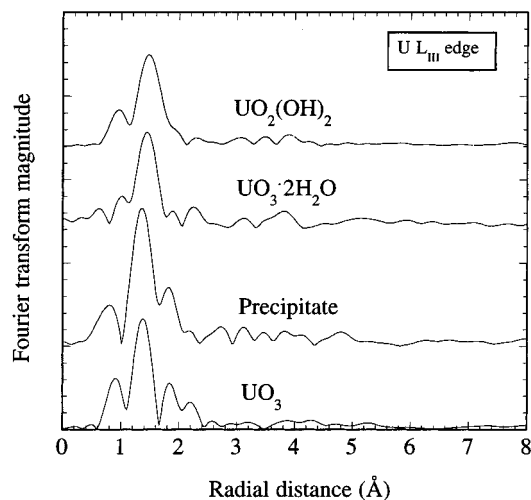


FIGURE 7. Comparison of EXAFS spectra of uranium precipitate recovered from photochemical degradation of RMI soil extract with $\gamma\text{-UO}_3$, synthetic schoepite ($\text{UO}_3 \cdot 2\text{H}_2\text{O}$), and uranyl hydroxide.

shells at approximately 1.4 and 1.8 Å distant from uranium representing the two axial ($-\text{yl}$) oxygens and equatorial oxygen atoms of the precipitate, respectively. Analysis of the amplitudes and position of the first (1.38 Å) and second shell (1.83 Å) oxygens of the precipitate and $\gamma\text{-UO}_3$ standard shows similar nearest-neighbor features, although there is a slight difference in the amplitude of the second shell peak. This difference is probably due to variations in the speciation of the uranium with oxygen in the sample (21, 22). The distances shown are lower than the actual distances due to EXAFS phase shifts, which differ for each neighboring atom ($\Delta R = 0.2\text{--}0.5$ Å). A log-amplitude ratio analysis of the first shell for the sample and standard shows the average coordination number for the precipitate is 0.2 atom greater than $\gamma\text{-UO}_3$, suggesting a more ordered $-\text{yl}$ oxygen arrangement in the sample.

Discussion

The extraction of uranium and the metals by citric acid was influenced by the form of the metal and its mineralogical association. Uranium associated with exchangeable and carbonate fractions was readily extracted by citric acid (12). Although citric acid is an effective chelating agent for removing metals and radionuclides, the ultimate disposal of the citric acid extract containing the metals is a concern. It was shown that biodegradation of metal-citrate complexes should result either in the bioprecipitation of released ions as water-insoluble hydroxides, oxides, carbonates, or salts or bio-sorption by the biomass. Biodegradation of metal-citrate complexes varied with the type of microorganism used and also the type of complex formed between the metal and citric acid played an important role in determining its biodegradability (16). For example, bidentate complexes of Fe(III) -, Ni -, and Zn -citrate were readily biodegraded, whereas complexes involving the hydroxyl group of citric acid, the tridentate Al -, Cd -, and Cu -citrate complexes, and the dimeric U-citrate complex were not. The recalcitrant tridentate Fe(II) -citrate complex, however, was readily biodegraded after oxidation and hydrolysis to the bidentate Fe(III) -citrate form, denoting a structure-function relationship in the metabolism of the complex (23). No relationship was observed between biodegradability and stability of the complexes. Lack of degradation was not due to their toxicity but was limited by the transport or metabolism of the complex by the bacterium. Cell-free extracts of *P. fluorescens* degraded U-citrate but not Cd - and Cu -citrate (24). The pH of the medium increased during degradation of the citric acid

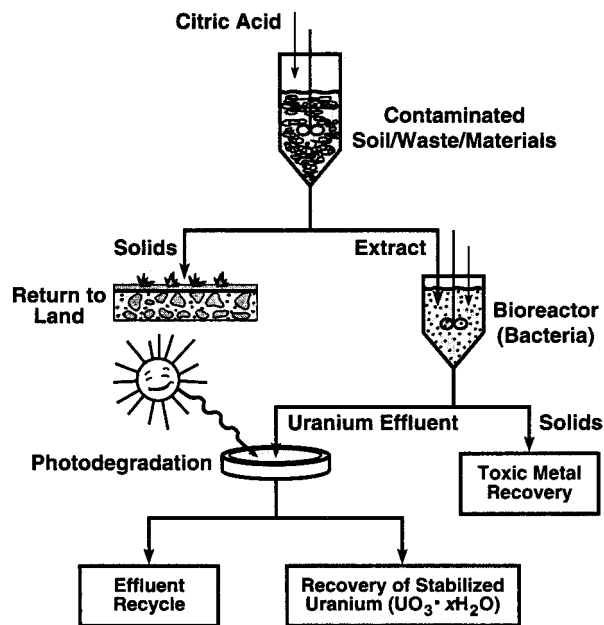


FIGURE 8. Process flow diagram for remediating soils and wastes contaminated with uranium and toxic metals.

extract causing dissociation of some metal-citrate complexes and their removal by precipitation as low solubility metal hydroxides, carbonates, phosphate, or coprecipitates of iron oxyhydroxide. For example, biodegradation of Al-, Ca-, Sr-, Pb-, or Ni-citrate by *P. fluorescens* in a culture medium containing excess citric acid caused the precipitation of Al as $(\text{Al}(\text{OH})_3)$ (manuscript in preparation), Ca as calcite (CaCO_3) (25), Sr as strontium carbonate (SrCO_3) (26), Pb as lead phosphate (27), and coprecipitation of Ni with iron (oxy)-hydroxide (28). An increase in bacterial biomass also may have contributed to removing the metals from solution due to their bioprecipitation and biosorption. Although the reasons for the slight decrease in uranium in solution during biodegradation of the citric acid extract are not fully understood, it may be attributed to slow dissociation of the complex (29) or degradation of the complex by enzymes released from the cells during the stationary growth phase (24).

There are distinct differences in the Fourier transform spectra of the precipitate from the soil extract and the product resulting from photodegradation of 1:1 U-citric acid. Specifically, the scattering from the equatorial oxygens of uranium is more pronounced in the soil extract precipitate, and the radial distances are identical to that of uranium trioxide. The photodegradation product of 1:1 U-citric acid (schoepite, $\text{UO}_3 \cdot 2\text{H}_2\text{O}$) (17) and uranyl hydroxide shows radial distribution functions at greater distances (1.45 and 1.93 Å), with less pronounced scattering. These differences indicate the absence of a hydroxide phase in the precipitate and may reflect the low pH (3.6) encountered during its formation as compared to pH 5.6 for schoepite (17). The effect of pH on the formation of uranium oxides in aqueous solution was found to determine the nature of the equatorial oxygen bonding to uranium (30). The results indicate that the precipitate is most probably uranium trioxide $\text{UO}_3 \cdot x\text{H}_2\text{O}$.

The concentration of U in the extract affected the rate and extent of U precipitation. At higher concentrations of U, it was completely removed from solution. Although the mechanism of action is not known, the increasingly efficient removal of U during photodegradation may result from an increased reaction rate with increasing U concentration as well as from an increase in the number of nucleation sites.

These results demonstrate the potential for removing uranium and toxic metals from wastes, contaminated soils,

and materials in a process involving extraction with the complexing agent citric acid, biodegradation of the extract to recover the toxic metals, and followed by photochemical degradation of the extract to recover uranium as $\text{UO}_3 \cdot x\text{H}_2\text{O}$ (Figure 8). Thus, the mixed wastes containing toxic metals and uranium can be separated and recovered in a concentrated form as hazardous and radioactive waste fractions for recycling or for disposal.

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