

RECLAMATION WITH RECOVERY OF RADIONUCLIDES AND TOXIC METALS FROM CONTAMINATED MATERIALS, SOILS, AND WASTES

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ABSTRACT

A process has been developed at Brookhaven National Laboratory (BNL) for the removal of metals and radionuclides from contaminated materials, soils, and waste sites. In this process, citric acid, a naturally occurring organic complexing agent, is used to extract metals such as Ba, Cd, Cr, Ni, Zn, and radionuclides Co, Sr, Th, and U from solid wastes by formation of water soluble, metal-citrate complexes. Citric acid forms different types of complexes with the transition metals and actinides, and may involve formation of a bidentate, tridentate, binuclear, or polynuclear complex species. The extract containing radionuclide/metal complex is then subjected to microbiological degradation followed by photochemical degradation under aerobic conditions. Several metal citrate complexes are biodegraded and the metals are recovered in a concentrated form with the bacterial biomass. Uranium forms binuclear complex with citric acid and is not biodegraded. The supernatant containing uranium citrate complex is separated and upon exposure to light, undergoes rapid degradation resulting in the formation of an insoluble, stable polymeric form of uranium. Uranium is recovered as a precipitate (polyuranate) in a concentrated form for recycling or for appropriate disposal. This treatment process, unlike others which use caustic reagents, does not create additional hazardous wastes for disposal and causes little damage to soil which can then be returned to normal use.

INTRODUCTION

The presence of radionuclides and toxic metals such as As, Be, Cd, Cr, Hg, Mn, Ni, and Zn in wastes, soils, and materials, at many Department of Energy (DOE) and other facilities is a major environmental concern. For decontamination of the waste material, both metal and radionuclide contaminants must be removed from the contaminated site so that the site can be returned to a useful condition. It would be desirable and beneficial to the environment to provide a comprehensive method for the removal of toxic metals and radionuclides from contaminated sites with reclamation of the soil.

Previous large-scale methods devised to deal with the problems of contaminated materials and soils have utilized caustic reagents such as hot sulfuric or hydrochloric acids, and oxidizing agents such as sodium hypochlorite, to extract the metals. While these methods can remove contaminants, they also cause irreparable damage to the soil, generating secondary waste streams which create additional hazardous waste disposal problems. For example, various soil washing methods were discussed at the DOE Soil Washing Workshop [1]. Madic et al. [2] used bidentate phosphamides enhanced by nitric acid to extract metal ions such as lanthanides, U(IV), Am(III) and Pu(IV). Kim et al. [3] immobilized radioactive Sr-90 by coprecipitation with Ca-, Al-, and Fe-phosphate in contaminated soils. Raghavan et al. [4] described three generic types of extractive treatments for cleaning excavated soils: water washing, augmented with a basic or surfactant agent to remove organics, and with acidic or chelating agents to remove organics and heavy metals, organic-solvent washing to remove hydrophobic organics and polychlorinated biphenyls; and air or stream stripping to remove volatile organics. Kochen and Navatil [5] removed americium and plutonium from contaminated soil by wet-screening, attrition scrubbing, wet-screening additives, and fixation by conversion to glass.

Other methods of metal removal from materials have also been reported. For example, U.S. Patent No. 4,973,201 describes a method for solubilizing precipitated alkaline earth-metal-sulfate scale in contaminated earth by contacting the earth with a polyaminocarboxylic acid chelating agent (EDTA, DTPA) and an oxalate ion synergist, and leaching the solubilized precipitate from the earth with water. To dispose of the dissolved sulfates, the leachate is either treated by chemical methods or returned to subterranean formation. Radioactive contaminated components of nuclear reactors have been decontaminated using citric acid (U.S. Patent Nos. 4,839,1000; 4,729,855; 4,460,500; 4,587,043; 4,537,666; 3,664,870 and 3,103,909). In these patents, metal recovery methods involve ion exchange columns, porous DC electrodes, or combusting the organics. Nishita et al. [6] used inorganic and organic compounds including citric acid to extract Pu from contaminated soils in order to correlate with Pu uptake by plants. Photochemical oxidation of uranium(IV) citrate by tungsten filament lamp, and the formation of an insoluble, stable polymeric form of uranium upon exposure of uranium citrate to light, has been reported [7,8].

Many of the chelating agents used in decontamination have been shown to undergo little degradation by microorganisms [9-11]. Biodegradation of these metal chelates should result in the precipitation of released ions as water-insoluble hydroxides, oxides, or salts, thereby retarding the migration of metals. Recently, we reported that the type of complex formed between the metal and citric acid plays an important role in determining its biodegradability [12]. The presence of free hydroxyl groups of citric acid is the key determinant in effecting biodegradation of the metal complex. For example, Ca, Fe(III), and Ni formed mononuclear bidentate complexes and were readily biodegraded; whereas, Cd, Cu, Fe(II), and Pb formed mononuclear tridentate complexes, and U formed a binuclear complex involving the hydroxyl group of the citrate, and were not biodegraded. The lack of degradation of tridentate and binuclear complexes was not due to toxicity, but probably limited by the transport and/or metabolism of the complex by the bacteria.

Various isolated concepts involving biodegradation, photodegradation, or chemical pretreatment have been reported in the literature. The problem of providing a thorough decontamination of the waste site as of yet has not been solved. In this paper, we present a total method for reclaiming radionuclide or toxic metal-contaminated materials, soils, sediments, and wastes with recovery of the contaminating metals to reduce toxic waste and with restoration of the soil [13].

TREATMENT PROCESS

The method for decontaminating radionuclides and other toxic metal-contaminated materials, soils, sediments, sludges and wastes, involves treating the contaminated material with citric acid and extracting the metals and radionuclides as citrate complexes. The solution is then treated with a *Pseudomonas fluorescens* ATCC No. 55241 and subjected to photolysis to degrade the complex and recover the radionuclides and metals through precipitation and biosorption reactions (Figure 1). The treated material is returned to its original use.

Extraction of Radionuclides and Metals

A sludge sample containing uranium and several toxic metals was obtained from a uranium processing facility. Ten grams of sludge was extracted with 100 ml of 0.40 M citric acid, for five hours in the dark using a wrist action shaker. The dry weight of the sludge before and after citric acid extraction was determined by drying at 60°C until a constant weight was obtained. The solids were digested in a mixture of hot nitric, perchloric and hydrofluoric acids in platinum crucibles. The citric acid extract and digested solids were analyzed for metals by ICP-MS. Table 1 shows extraction efficiency of various metals from sludge by citric acid. In this sample, metals Ag, As, Au, B, Bi, Cu, Gd, Hg, Li, Mo, Pb, and V were poorly extracted by citric acid treatment. Lack of extraction of these metals is probably due to the nature of mineralogical association with stable mineral phases in this particular waste [14]. For example, Cu was predominantly associated with the organic fraction and a small amount with the iron oxide and inert fractions and was not extracted by citric acid treatment.

Biodegradation of Metal Citrate Extract

Duplicate samples of undiluted (as is) and diluted (1 to 4) citric acid extract from the sludge were amended with nutrients consisting of 0.1% of NH_4Cl , K_2HPO_4 , and KH_2PO_4 . The pH was adjusted to 6.5 with NaOH and then the extracts (100 ml) were inoculated with 4 ml of 18-hour old culture of *Pseudomonas fluorescens* ATCC 55241. The samples were incubated on a shaker at 24°C. The bacterial inoculum was grown in medium containing citric acid, 2g; NH_4Cl , 1g; KH_2PO_4 , 1g; K_2HPO_4 , 1g; NaCl, 4g; MgSO_4 , 0.2g; distilled water, 1000 ml; and pH 6.5. All sample preparations were performed under low light to minimize any photochemical reactions. Periodically, 5 ml aliquots were removed, filtered through a 0.22 μm filter, and analyzed for (i) pH, (ii) citric acid biodegradation by HPLC using uv and refractive index detectors, and (iii) soluble uranium. At the end of the incubation period (after 118 hours for the diluted sample and after 322 hours for the undiluted sample) the supernatant and the solids consisting of bacterial biomass and any precipitated metals were separated from solution by centrifugation. The dry weight of the solids was determined and digested in a mixture of hot nitric and perchloric acids. The supernate and the digested solids were analyzed for uranium and other metals by ICP-MS (Table 2). The bacteria degraded citrate at a rate of 0.5-0.7 mM per day (Figure 2). The rate of degradation was much higher in the diluted extract than the undiluted sample. There was little change in concentration of uranium in samples subjected to biodegradation, indicating that the uranium citrate complex was not biodegraded (Figure 2). This is consistent with the previous results that uranium and certain metal complexes of citric acid are resistant to biodegradation [12]. About 9% of the total uranium was present in the bacterial biomass. Increased levels of cobalt, nickel, zinc, and zirconium, in the biomass digest, indicated that their citrate complexes were readily biodegraded.

Photodegradation of Uranium Citrate Extract

The supernate from the biodegradation treatment containing primarily uranium citrate complex was exposed to light to degrade the complex and recover uranium (Figure 3). The pH of the supernate was adjusted to 3.5 with HCl and the sample exposed to seven 60 watt, high output fluorescent growth lights. Periodically 2 ml samples were withdrawn, filtered through a 0.22 μm filter and analyzed for uranium, citric acid, and photodegradation products. At the end of the experiment (after 157-hours of exposure to light) the solutions were filtered through a 0.22 μm Millipore filter and analyzed for citric acid degradation products by HPLC, and for metals by ICP-MS. The uranium precipitated out of solution as a polymer soon after it was exposed to light (Figure 3). After 50 hours, ~ 85% of the uranium was removed from solution. In Table II, the removal efficiency of various metals from the citric acid sludge extract first subjected to biodegradation, followed by photodegradation, is presented.

Weight Loss

The solids remaining after extraction with citric acid were washed with deionized water, transferred to weighing dishes, and dried in an oven overnight at 105°C to determine the weight loss due to citric acid extraction. The extraction of the wastes with citric acid resulted in significant reduction in weight. Almost half (47%) of the sludge showed loss in weight due to solubilization and removal of toxic and nontoxic bulk components in the waste.

SUMMARY

These results show that (i) uranium was extracted from the waste sample with >85% efficiency using 0.4 M citric acid; (ii) other metals such as chromium, cobalt, manganese, nickel, strontium, thorium, zinc, and zirconium were also extracted from the waste; (iii) the uncomplexed excess citrate and several metal citrate complexes (Co, Ni, Zn and, Zn) with the exception of binuclear complexes were readily biodegraded by the bacterium, *P. fluorescens* ATCC 55241 and were recovered with the bacterial biomass; and (iv) the uranium citrate complex was photodegraded, allowing the uranium to form a polymer which was recovered as a concentrated solid.

This process has significant potential for commercialization because (i) it can be applied to a variety of materials and waste forms, (ii) it does not generate secondary waste streams, (iii) it causes little damage to soil, and (iv) environmentally and economically important metals are removed in a concentrated form for recovery and recycling. The use of combined chemical, photochemical, and microbiological treatment processes of contaminated materials will be more efficient and result in considerable savings in clean-up and disposal costs.

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TABLE 1

Extraction Efficiency of Metals From Sludge by Citric Acid

Metal	Total Metal in sludge ($\mu\text{g}\cdot\text{gdw}^{-1}$)	% Metal Extracted
Ag	41 \pm 30	2.4
Al	30500 \pm 500	58.7
Au	1800 \pm 500	<1
Ba	427 \pm 25	24.4
Be	5.21 \pm 0.45	60.1
Cd	66 \pm 6	9.1
Co	10.7 \pm 0.3	74.8
Cr	342 \pm 10	74.6
Cu	329 \pm 18	1.2
Ga	28.8 \pm 0.6	25.7
Mg	7510 \pm 100	89.2
Mn	234 \pm 3	82.9
Ni	1120 \pm 10	80.0
Pb	224 \pm 27	<1
Pd	5.51 \pm 0.70	49.0
Sb	5.67 \pm 0.05	68.8
Sn	17.6 \pm 0.4	93.1
Sr	125 \pm 5	59.2
Th	3.08 \pm 0.10	94.2
Ti	922 \pm 95	28.4
U	2410 \pm 100	86.8
V	121 \pm 7	4.1
Zn	839 \pm 7	59.6
Zr	209 \pm 4	84.2

Sludge extracted for 5 hours with 0.4 M citric acid solution.

TABLE 2

Effects of Biodegradation Followed by Photodegradation
in the Treatment of Citric Acid Sludge Extract

Metal	Before Treatment ¹ (μM)	% Removal		Total
		After Biodegradation ²	After Photodegradation ³	
Al	7410	92	1	93
Ba	12.0	92	< 1	92
Be	3.22	>99	< 1	>99
Co	0.866	71	6	77
Cr	60.8	< 1	25	25
Ga	0.889	73	16	89
Mn	37.2	98	< 1	98
Ni	192	64	1	65
Pd	0.311	64	30	94
Sb	0.361	2	14	16
Sn	1.71	>99	< 1	>99
Sr	10.2	98	1	99
Th	0.112	96	3	>99
Ti	80.2	96	< 1	96
U	94.8	9	78	87
Zn	86.1	90	5	95
Zr	61.7	97	2	99

¹ Sludge was extracted for five hours with 0.4M citric acid.

² Samples analyzed 118 hours after inoculation with Pseudomonas fluorescens ATCC No. 55241 but before photodegradation.

³ Samples analyzed after biodegradation and 157 hours of exposure to light.

ND-none detected

Waste Site Reclamation With Recovery Of Radionuclides and Metals

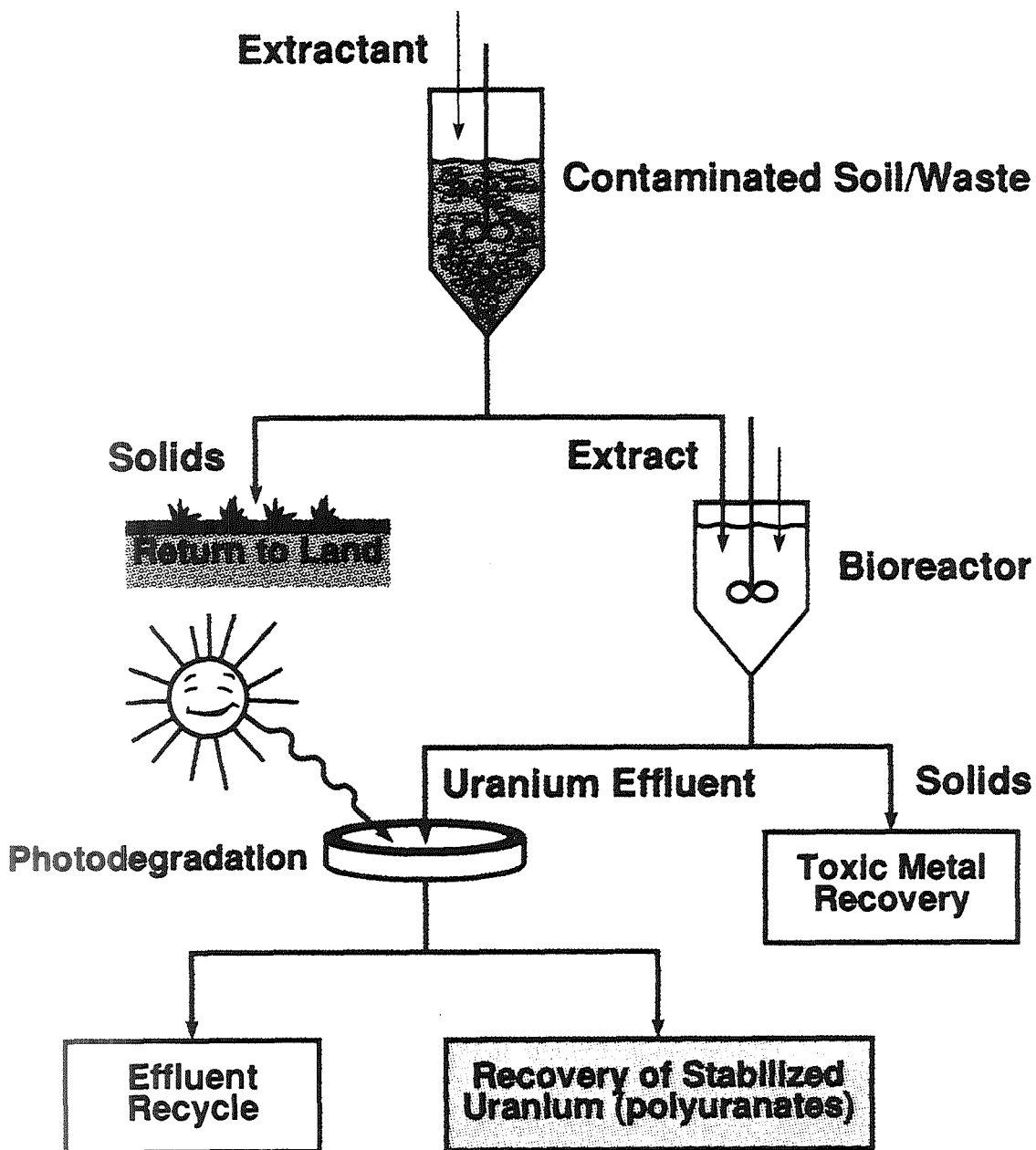


Figure 1. Schematic of the Treatment Process

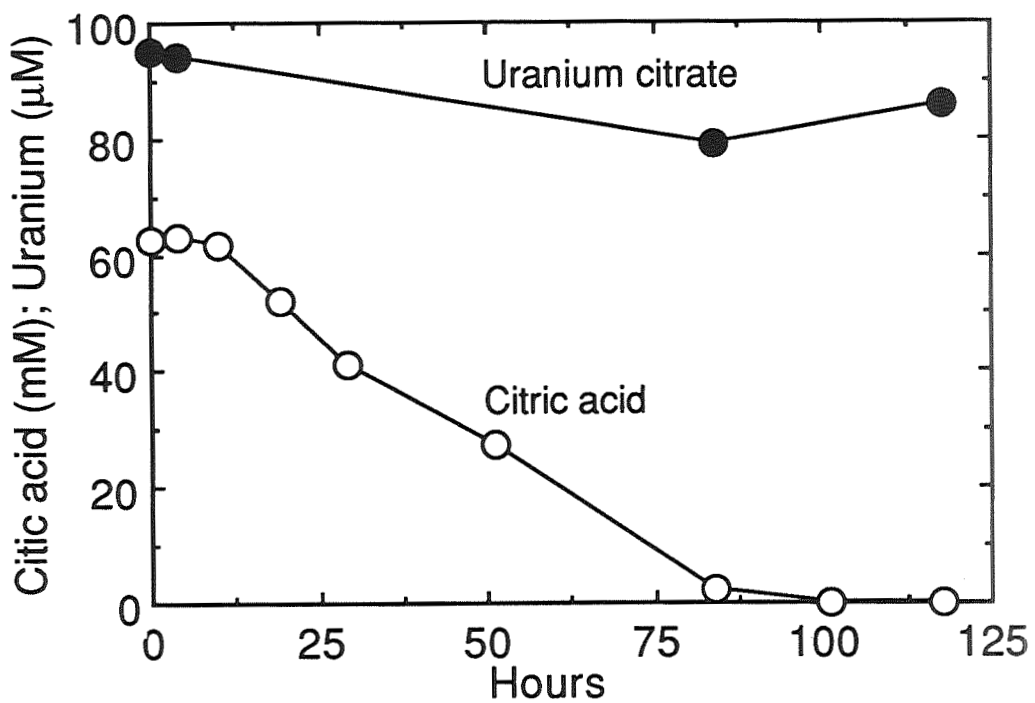


Figure 2. Biodegradation of citrate sludge extract

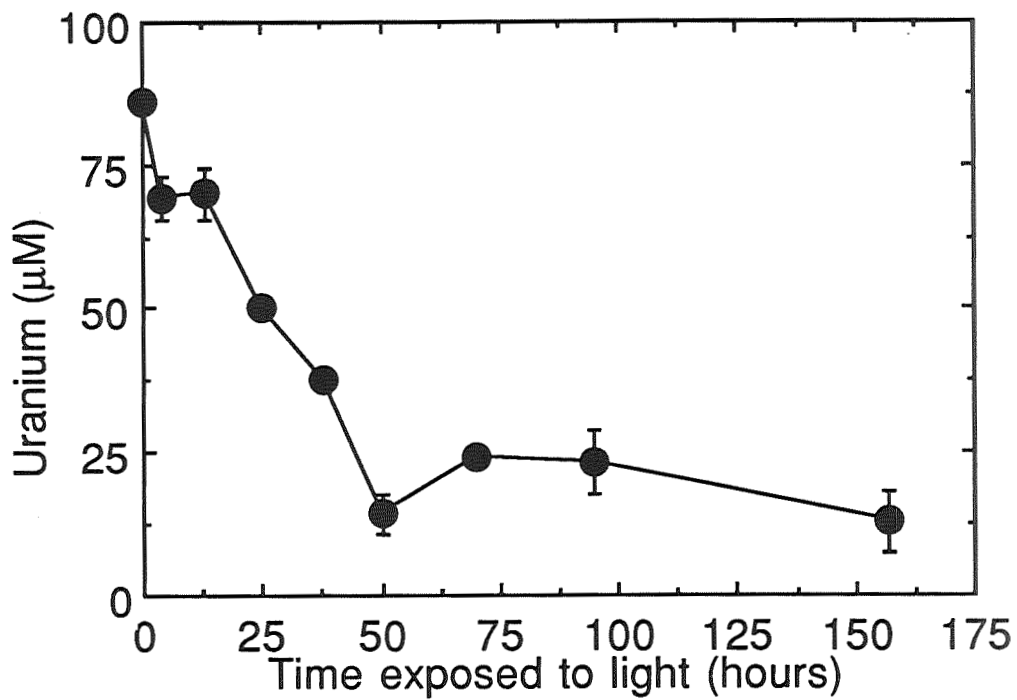


Figure 3. Photodegradation of uranium citrate sludge extract after biodegradation