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Leaching of Pb Contaminated Soil using Ozone/UV Treatment of EDTA Extractants

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Abstract: One of the main problems of EDTA based soil-washing technologies for remediation of heavy metals contaminated soils is the separation of EDTA-heavy metals complexes from the waste extractant. In our study an advanced oxidation process using ozone and UV was used for the decomposition of EDTA-Pb complexes in soil extractants obtained during leaching of Pb contaminated soil. Released Pb was removed by absorption. Twenty consecutive soil treatments with 2.5 mmol kg^{-1} EDTA removed 58.4% of Pb and greatly reduced the Pb mobility and oral-availability. The waste extractant was colorless, with slightly basic pH and with low Pb and EDTA concentrations.

Keywords: Advanced oxidation, Pb, EDTA, ozone/UV, soil remediation

INTRODUCTION

Heavy metals contamination of soils is one of the world's most prevalent public health problems, especially through heavy metal intake in concentrations regarded as non-toxic over extended periods. Current remediation activities have involved excavation and removal of the contaminated soil, immobilization of heavy metals in the soil by mixing or injecting agents such as cement, lime and different phosphates, electrokinetic mobilization and removal of heavy metals from the soil by precipitation on the electrodes,

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phytoextraction of heavy metals by plants, and soil washing. In practice, acid washing and chelator washing of heavy metals contaminated soils are the two most prevalent methods. These can be done in a reactor (extraction of soil slurry) or as soil heap leaching. A number of chelators have been tested. Ethylenediamine tetraacetate (EDTA) was in most cases the most effective (1).

Soil washing involves the separation of contaminants from soil solids by solubilizing them in a washing solution. The main problem of current EDTA based soil washing technologies is the separation of chelator-heavy metals complexes from the waste extractant. EDTA and its complexes are toxic (2) and poorly chemo- and biodegradable (3) and must therefore be removed before the extractant can be safely discharged.

To treat decontamination wastewaters from the nuclear industry and other aqueous effluents contaminated with EDTA, the chemical destruction of EDTA and its complexes using advanced oxidation processes (AOP) has been proposed (4–6). AOP involves the use of ozone, H_2O_2, ultrasonic waves, UV irradiation, Fenton's reagent (Fe^{2+} and H_2O_2), alone or in combination, to generate free hydroxyl radicals; these are powerful, effective, non-specific oxidizing agents. In our recent paper (7) we examined the feasibility of using ozone, ozone/sonification, and ozone/UV to destruct EDTA Pb and Zn complexes in soil extractants. Of the AOPs tested only the use of ozone/UV was effective.

The aim of this study is to assess the feasibility of novel soil leaching technology for remediation of soil heavily contaminated with Pb, using ozone/UV irradiation for degradation of EDTA complexes and removal of Pb from soil extractant by absorption. The method involves the reuse of treated extractant in a closed process loop. Previously, this method was evaluated for soils with low Cu ($<350\ \mathrm{mg\ kg^{-1}}$) and medium Pb and Zn ($<1300\ \mathrm{mg\ kg^{-1}}$) contamination (8, 9).

METHODS

Soil

A loam-sandy loam soil containing $4529 \pm 143\ \mathrm{mg\ Pb\ kg^{-1}}$ of soil was collected from the 0–30 cm surface layer at an industrial site of a former Pb smelter in the Mežica Valley in Slovenia. The Mežica Valley has been exposed to more than three hundred years of active lead mining and smelting.

The Effect of EDTA Contact Time on Pb Removal Efficiency

Soil (150 g—small-scale experiment) was placed in perforated 250 ml polypropylene flasks with 0.5 mm plastic mesh at the bottom to retain the soil. The soil was leached in triplicates with 180 ml of $2.5\ \mathrm{mmol\ kg^{-1}}$

EDTA disodium salt (un-buffered). Extractant was circulated through the soil for 72 h using a peristaltic pump (flow rate 1.2–1.5 ml min^{-1}), periodically sampled and the pH and Pb concentration measured.

Multi-step vs. Single-dose Soil Leaching

Soil (150 g—small-scale experiment) was placed in 250 ml flasks as described above. The soil was treated in triplicates with 180 ml of 2.5 and 20 mmol kg^{-1} EDTA as 8-step and single-dose leaching, respectively. In each leaching step, the extractant was circulated through the soil for 24 h (contact time) using a peristaltic pump (flow rate 1.2–1.5 ml min^{-1}) and subsequently rinsed with 1.5 l of tap water (flow rate 1.2–1.5 ml min^{-1}) to remove all residual EDTA-Pb complexes. Extractant and rinsing solution were collected and analyzed for Pb. Pb soil removal was calculated from the Pb concentration in the solutions.

Advanced Oxidation of Metal-EDTA Complexes and Metal Recovery

Ozone was produced in an ozone generator (V-4, Crystal Air, Surrey, British Columbia) from pure commercial oxygen (flow rate 0.45 ml min^{-1}). An extractant treatment unit consisted of an ozone generator, ozonation flask (oxygen/ozone flow rate 0.15 ml min^{-1}), UV-light in a continuous flow housing, and absorption filter (Fig. 1). Peristaltic pumps were used to force the solution or extractant (flow rate 12 ml min^{-1}) through the unit. Metals, released after advanced oxidation of EDTA complexes, were removed from

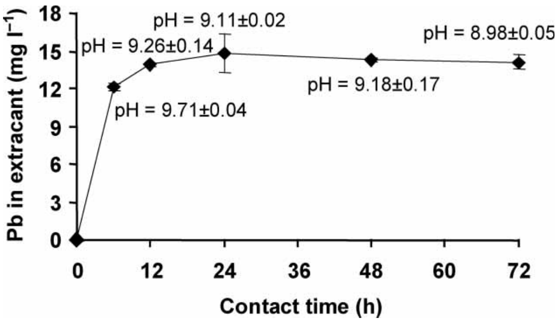

Figure 1. Concentration of Pb and pH of extractant after soil leaching (small-scale experiment) with 2.5 mmol kg^{-1} EDTA using different contact times. Error bars represent standard deviation from the mean value (n = 3).

soil extractants by passing them through the absorption filter with 50 g of commercial sorbent Slovakite (IPRES, Bratislava, Slovak Republic). Slovakite is a mixture of natural raw materials: dolomite, diatomite, smectite basaltic tuff, bentonite, alginite, and zeolite.

Soil Leaching

Soil leaching was simulated in triplicate in 15 cm diameter soil columns at room temperature. Air-dried soil (4.6 kg) was sieved through a 5-mm mesh sieve and placed in a column 27 cm high. Plastic mesh ($D = 0.2$ mm) at the bottom of the column retained the soil. The soil was treated with twenty consecutive EDTA additions with 2.5 mmol kg^{-1} EDTA in 2400 ml un-buffered tap water. In each leaching step the extractant (2400 ml) was first circulated solely through the soil column for 48 h using a peristaltic pump (flow rate 12 ml min^{-1}) to remove Pb. The extractant was then circulated in a closed loop through the soil column to remove soil residual EDTA-Pb complexes and through an extractant solution treatment unit as shown in Fig. 1. After 18 h Pb concentrations in the extractant decreased to less than 5% of initial concentrations. The extractants were supplemented with tap water to compensate for the water lost during the process (approx. 10%), and re-used as a medium for new 2.5 mol kg^{-1} EDTA soil addition. The sorbent (Slovakite) was discharged and replaced with fresh sorbent. After soil leaching was completed, samples were taken from different soil layers in the columns and from the bulk of the soil.

Metal Determination

The soil was ground in an agate mill, digested in *aqua regia*, and analyzed by AAS. Pb, Cu, Fe, and Ca extractants were determined by AAS directly.

Sequential Extraction

A sequential extraction procedure (10) was used to determine the fractionation of Pb and Zn in non-remediated and remediated soil and in earthworms casts, into six fractions: soluble in soil solution, exchangeable from soil colloids, bound to carbonates, bound to Fe and Mn oxides, and bound to organic matter and residual fraction soluble in *aqua regia*. Three determinations of Pb and Zn concentration were made for each fractionation sequence. The final fractional recovery of Pb and Zn was calculated after summing the recoveries of all the six steps of sequential extractions, against *aqua regia* Pb and Zn concentration.

Pb Mobility

The mobility of Pb in the soils before and after remediation was determined using TCLP analyses (11), conducted in triplicate. The procedure involved shaking a 10 g soil sample in 200 ml of 0.0992 M acetic acid and 0.0643 M NaOH with a pH of 4.93 ± 0.05, for 18 h on a rotary shaker at about 300 rpm.

Pb Oral Bio-availability

Pb bio-availability in non-remediated and remediated soil was determined as oral bio-availability in simulated stomach (pH 2.5) and intestinal (pH 7) phases of the human gastrointestinal tract using PBET (12).

EDTA Determination

EDTA in extractants was determined spectrophotometrically according to procedure of Hamano et al. (13).

RESULTS AND DISCUSSION

EDTA Contact Time and Efficiency of Multi-step Leaching

Small-scale experiments (150 g of soil) were used to provide process parameters for soil column experiment. In soil washing technologies the removal of heavy metals depends, among other factors, on the contact time allowed for the reaction to occur between the chelator and metals. As shown in Fig. 1, the concentration of Pb in extractant increased with contact time up to 24 h and thereafter remained constant. Therefore we allowed a 24 h contact time in further experiments. The extractant pH slightly decreased with the contact time (Fig. 1).

Eight-step leaching with 2.5 mmol kg^{-1} EDTA (total 20 mmol kg^{-1} EDTA) removed approximately 25% more Pb than single-dose leaching with 20 mmol kg^{-1} EDTA (Fig. 2). A multi-step leaching approach was therefore used in the further evaluation of the proposed remediation method.

EDTA Soil Leaching using AOP for the Extractant Treatment in a Closed Process Loop

The soil leaching process, simulated in our laboratory-scale experiment, is operationally simple. Heavy metal contaminated soil is excavated, screened, and mounded on a pad. Heavy metals are removed by passing a chelator

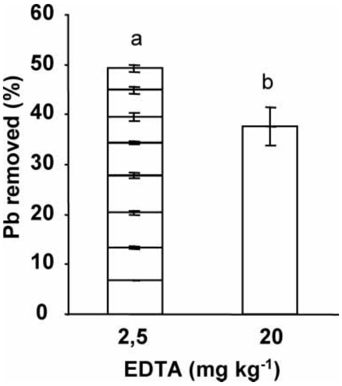

Figure 2. Pb removal after 8-step soil leaching with 2.5 mmol kg^{-1} EDTA and after single dose leaching with 20 mmol kg^{-1} EDTA (small-scale experiment). Error bars represent standard deviation from the mean value ($n = 3$). Letters denote significantly different treatments according to the t-test ($P < 0.05$).

solution through the soil using some type of liquid distribution system. The extractant is collected in a pregnant solution pit and processed to remove heavy metals. The proposed set up of the novel soil leaching method with ozone/UV treatment of extractant and reuse of treated extractant in a closed process loop is shown in Fig. 3. As expected, the concentrations of Pb in the extractant decreased with the time (Fig. 4), due to the degradation of heavy metal-EDTA complexes and recovery of the released metals in the ozone/UV extractant treatment unit. After 18 h, more than 95% of Pb was removed from the extractant (Fig. 4). The extractant was then used as a medium for the next addition of 2.5 mmol kg^{-1} EDTA. As expected, the initial concentration of Pb the extractant was lower after each of the consecutive EDTA additions (Fig. 4). The concentrations of Pb and residual EDTA in the final extractant obtained after the 20th leaching step were very low, 0.8 ± 1.1 mg l^{-1} and 35.7 ± 0.2 $\mu g\,l^{-1}$, respectively. The final extractant was colorless, with pH 8.39 ± 0.19. The concentrations of Fe (0.42 ± 0.39 mg l^{-1}) and Ca (86.0 ± 0.19 mg l^{-1}), the two metals readily chelated by EDTA (14), were also measured in the final extractant.

In total, 58.4% of initial soil Pb was removed with soil leaching using AOP (Table 1). As shown in Figure 5, Pb was removed quite uniformly throughout the soil profile. However, it is the bio-accessible and bio-available and not the total heavy metal concentration in soil that poses an environmental and health threat. The bio-accessibility and bio-availability of heavy metals are highly dependent on the heavy metal soil fractionation (15). The results of sequential extractions indicated that before and after remediation, most of the Pb in the soil resides in the organic soil fraction (Table 1). Soil leaching removed Pb from all soil fractions. Proportionally, however, more Pb was removed from the beginning soil fractions of the sequential

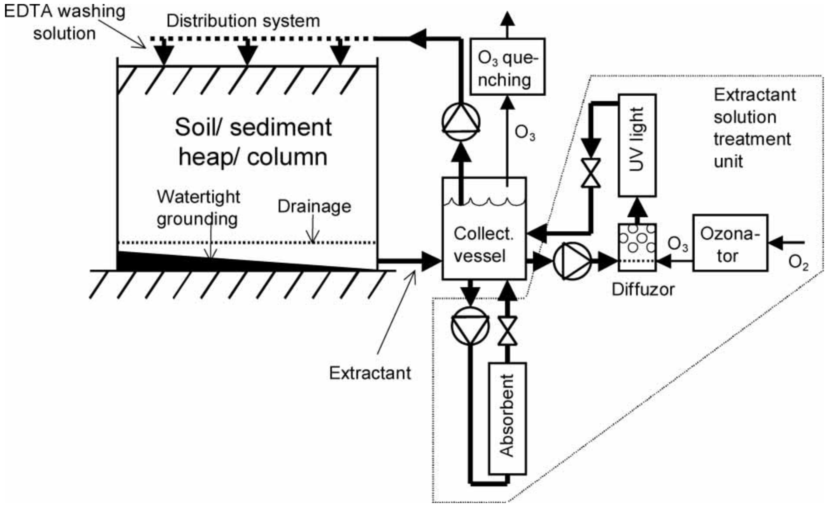

Figure 3. Flowsheet of the novel EDTA soil leaching method with ozone/UV treatment and reuse of extractant in a closed process loop.

extractions scheme, indicating significantly reduced bio-accessibility and bio-availability of the Pb residual in the soil after remediation (15).

Mobility and transport of heavy metals in soils is a potential threat for groundwater contamination and thus for human health. The TCLP test (11) was used to access Pb mobility. As shown in Table 1 the TCLP extractable Pb after was reduced for more than 6-times after soil remediation.

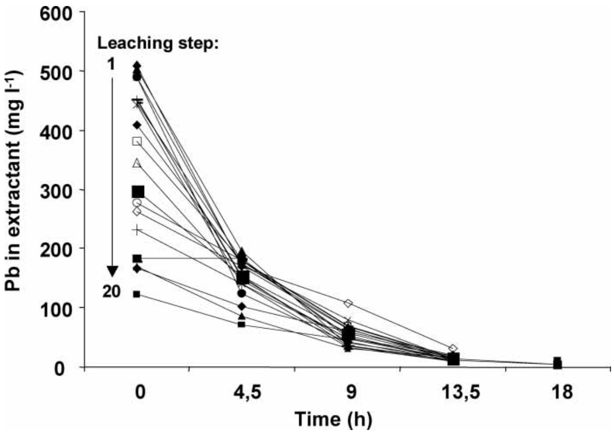

Figure 4. Concentration of Pb in extractants during 20-step soil leaching of Pb contaminated soils with 2.5 mmol kg^{-1} EDTA (soil column simulation). The mean values of three replicates are shown.

Table 1. Concentration of Pb, fractionation of Pb, Pb mobility (assessed using TCLP), and Pb oral-availability in the stomach and intestinal phases (PBET), before and after soil remediation. Results are presented as means of three replicates ± s.d

	Before remediation	After remediation
Total soil Pb (mg kg^{-1})	^{a}4529 ± 143	^{b}1885 ± 42
Pb soil fractionation (mg kg^{-1})		
In soil solution	^{a}2.44 ± 0.10	^{b}0.01 ± 0.01
Exchangeable	^{a}10.07 ± 0.25	^{b}0.32 ± 0.13
Bound to carbonate	^{a}1150.72 ± 47.88	^{b}160.16 ± 12.08
Bound to Fe and Mn oxides	^{a}19.69 ± 1.7	^{b}3.25 ± 0.50
Bound to organic matter	^{a}3062.87 ± 174.92	^{b}1333.66 ± 95.96
Residual fraction	^{a}462.76 ± 53.07	^{b}250.27 ± 13.21
Recovery (%)	104.0	92.8
TCLP		
Mobile Pb (mg l^{-1})	^{a}1.66 ± 0.06	^{b}0.27 ± 0.05
PBET		
Pb in stomach phase (mg kg^{-1})	^{a}1411.1 ± 268.6	^{b}451.6 ± 184.0
Pb in intestinal phase (mg kg^{-1})	^{a}66.4 ± 35.2	^{b}21.3 ± 10.9

The superscript letters (*a*, *b*) denote statistically different results before and after remediation (t-test, $P < 0.05$).

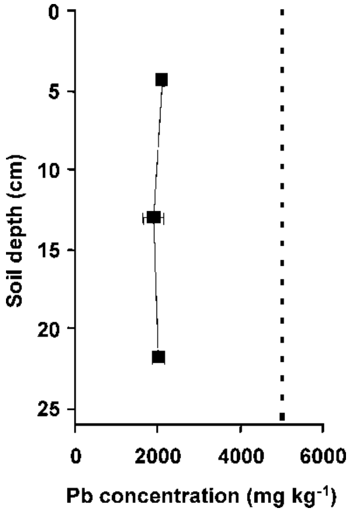

Figure 5. Pb concentration through the soil profile in soil column before (dotted line) and after (solid line) 20-step soil leaching with 2.5 mmol kg^{-1} EDTA. Error bars represent standard deviation from the mean value (n = 3).

Incidential ingestion is one of the major pathways of exposure to Pb in soils. Oral bio-availability of Pb was determined in vitro using Ruby's PBET test (12). The PBET model was designed to simulate the human gastrointestinal tract. As shown in Table 1, soil leaching with EDTA and using AOP significantly reduced concentrations of residual soil Pb orally available in the stomach and intestinal phase.

CONCLUSION

The results of our laboratory scale study indicated that the use of ozone/UV and the absorption of released metals is viable for treatment of EDTA soil extractants, obtained during the leaching of soils contaminated with Pb. Treated extractants were successfully reused for rinsing the soil after EDTA extraction, and as a medium for the chelator in soil treatment with consecutive EDTA additions. The ozone/UV treatment of the extractant could therefore also reduce the requirements for process water. The final extractant was almost free of heavy metals and safe for discharge. The use of ozone/UV treatment of EDTA soil extractant could lead to environmentally safe, efficient, new soil heap leaching technology. However, much more work with different soils, heavy metals, sorbents, and operational conditions is needed to fully evaluate its feasibility.

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