Pilot-scale washing of metal contaminated garden soil using EDTA

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ABSTRACT

Ten batches (75 kg each) of garden soil with >50% of silt and clay and average 1935 mg kg^{-1} Pb, 800 mg kg^{-1} Zn, 10 mg kg^{-1} Cd and 120 mg kg^{-1} As were remediated in a pilot-scale chemical extraction plant. Washing with 60 mmol ethylenediaminetetraacetic acid (EDTA) per kg of soil on average removed 79, 38, 70, and 80% of Pb, Zn, Cd and As, respectively, and significantly reduced the leachability, phyto-accessibility and oral-availability of residual toxic metals, as assessed using deionised water, toxicity characteristic leaching procedure (TCLP), diethylenetriamine pentaacetic acid extraction (DTPA) and physiologically based extraction test (PBET) tests. The used soil washing solution was treated before discharge using an electrochemical advanced oxidation process with graphite anode: EDTA was removed by degradation and toxic metals were electro-precipitated onto a stainless steel cathode. The novelty of the remediation technique is separation of the soil from the washing solution and soil rinsing (removal of mobilized contaminants) carried out in the same process step. Another novelty is the reuse of the soil rinsing solution from the previous batch for cleansing the soil sand, soil rinsing and for preparation of the washing solution in subsequent batches. The cost of energy and material expenses and disposal of waste products amounted to approximately 75€ton^{-1} of soil.

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1. Introduction

Soil contamination with potentially toxic metals and metalloids (PTMs) is ubiquitous in the world and is a serious health and environmental problem. There are more than 1.8 million contaminated sites in western central and south-eastern Europe, of which 240,000 are in need of remedial treatment. In almost 40% of these sites, PTMs are the most important contaminants [1]. In the United States, PTMs are present in 77% of the Superfund sites (National Priority List), in 72% of the Department of Defence Sites and in 55% of the Department of Energy sites [2].

The full-scale remediation of PTM contaminated sites has traditionally involved soil excavation followed by immobilization of PTMs by additives, such as cement, phosphates and clays, prior to disposal of the treated material in a permitted landfill. Since excavation-mobilisation-disposal is no longer considered to be a viable solution [3], soil washing remains one of the few remedial options to remove PTMs permanently from soils. Soil washing involves either:

- physical separation processes, in which PTM contaminated fines are segregated from the relatively uncontaminated bulk;
- chemical extraction, in which the contaminants are selectively dissolved;
- a combination of both physical and chemical processes [4].

Physical separation processes are effective and commercialized for sandy soils in which clay, silt and organic matter content (particles less than 0.063 mm) is less than 30–35% of the soil [4]. As such, they are not applicable for gardens soils, which usually have a higher content of fines. Chemical extraction processes, on the other hand, are not constrained by soil texture. They are a two-stage process that involves soil extraction, usually with acids and chelating agents and recovery of the dissolved PTMs from the used washing solution. Extraction with acids changes the soil matrix, while chelating agents largely preserve soil properties as a plant substrate. Many different chelating agents (mostly aminopolycarboxylic acids) have been tested for soil washing. Di-sodium salt of ethylenediamine tetraacetate (EDTA) has been the most frequently used because of its efficiency, availability and relatively low cost [5]. Nevertheless, washing soils with EDTA still poses significant problems:

- Washing soils rich with clay and other fines is difficult.
- Various PTMs, both cationic (e.g., Pb) and anionic (e.g., As), coexist in most contaminated soils. A single washing reagent makes it difficult efficiently to remove all of them simultaneously [6].

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- Large volumes of waste solutions are generated, which must be treated before disposal. In addition to highly contaminated waste soil washing solution obtained after PTM extraction, additional volumes of waste rinsing solution, with lower EDTA and PTM concentration, are also generated (rinsing soil is necessary completely to remove EDTA mobilized PTM species which remain in the soil after extraction).
- The practical means of combining soil extraction and soil rinsing in a simple process scheme is another unsolved problem.

Dermont et al. [3] recently reviewed field and pilot-scale applications of physical/chemical soil washing technologies. Only two reported technologies, BioGenesis' Sediment Decontamination Technology [7], and NFL's CACITOX process [8], use chelating agents as auxiliary active compounds in their washing solutions. Both technologies are a combination of physical separation and downstream chemical processes for the treatment of contaminated sediments. To the best of our knowledge, there are no reports in the scientific literature on full or pilot-scale chemical extraction of PTMs from fines-rich contaminated soils using EDTA.

In this pilot-scale experiment, we used EDTA for extraction of Pb, Zn, Cd and As from contaminated garden soil. The EDTA was degraded on a graphite anode using an electrochemical advanced oxidation process (EAOP) and the PTMs were electro-precipitated onto a stainless-steel cathode before discharge of the cleansed waste soil washing solution. The main novelty of the tested technology is the separation of the soil solid phase from the washing solution and subsequent soil rinsing in a chamber filter press in a single process. The remediation efficiency and materials and energy costs were evaluated. The mobility, phyto- and oral availability of PTMs remaining in the soil after chemical extraction were also measured.

2. Experimental

2.1. Soil samples and analysis

Soil was collected from the 0 to 30 cm surface layer of a vegetable garden in the Meza Valley, Slovenia. The Meza Valley has been exposed to more than 300 years of active lead mining and smelting. Soils in the valley, including 6600 ha of agricultural land, are polluted, primarily with Pb but also with Zn, Cd and As. The excavated soil was transported to a temporary storage location at the pilot-scale soil remediation plant at the Biotechnical Faculty, University of Ljubljana campus.

For standard pedological analysis, the pH in the soil was measured in a 1/2.5 (w/v) ratio of soil and 0.01 M $CaCl_2$ water solution suspension. Soil samples were analyzed for organic matter by modified Walkley–Black titrations [9], cation exchange capacity (CEC) by the ammonium acetate method [10] and soil texture by the pipette method [11].

2.2. Electrolytic cell

The electrolytic tank cell (V = 10 L) contained six graphite anodes and eight stainless steel cathodes (distance = 10 mm) arranged in mono-polar mode. The overall anode surface area was 2523 cm^2; the anode:cathode surface area ratio was 1:1. Used soil washing solution gravitationally flowed into the electrolytic cell (flow rate 6 L min^{-1}) from the mixing reactor (total working V = 200 L) and was pumped back into the reactor in a closed loop. The current density on the electrodes was kept at 91 mA cm^{-2} using a DC power supply (Envit d.o.o., Slovenia). The voltage between the electrodes ranged from 8.1 to 11.6 V, with an average voltage of 8.4 V. During the electrochemical process, the temperature of the treated

washing solution in the electolytic cell increased from an initial 15 °C up to 69 °C. During the process, the pH of the washing solution was left unregulated. To keep the voltage near 8 V and reduce the power consumption, we applied up to 730 mL of NaCl (saturated solution) as electrolyte when the voltage increased over the set value.

The contact time of electrochemical treatment was calculated by multiplying the operation time with the ratio of the electrode cell volume and the volume of washing solution (30 min of operation time equalled 3.56 min of contact time). Samples (20 mL) of washing solution were collected periodically, centrifuged at 2113 × g for 3 min and the Pb, Zn and As concentrations measured. The rest of the supernatant was stored in the cold for further analysis. The electrochemical treatment was terminated when the concentration of Pb decreased below 5 mg L^{-1} and the treated waste solution was discharged.

At the end of the electrochemical treatment, the cathodes were etched with 220 mL of 65% HNO$_3$ and rinsed with 1780 mL of water to dissolve and later measure the concentration of electro-deposited PTMs. The graphite anodes were weighed before and after treatment of 10 soil batches to determine the amount of electro-corroded material.

2.3. EDTA determination

The concentration of EDTA was determined spectrophotometrically according to the procedure of Hamano et al. [12]. The method involves the reaction of EDTA in washing solution with Fe^{3+} under acidic conditions to produce Fe-EDTA chelate (trans-complexation), followed by the removal of excess of Fe^{3+} by chelate extraction in the aqueous phase, using chloroform and N-benzoyl-N-phenylhydroxylamine and the formation of a chromophore with 4,7-diphenyl-1,10-phenanthroline-disulfonic acid. Using a spectrophotometer, absorbance was measured at 535 nm against a blank solution with the 4,7-diphenyl-1,10-phenanthroline-disulfonic acid replaced with an equal volume of distilled water. The limit of EDTA quantification was 20 mg L^{-1}.

2.4. Deionised water extraction test

The soil samples were air-dried, ground and sieved through a 2 mm mesh again. One hundred mL of deionised water was applied to each soil sample (10 g) and agitated for 24 h at room temperature [13]. Elutriates were filtered through a Whatman no. 4 filter. Concentrations of Pb, Zn, Cd and As were determined using flame atomic absorption spectrometry (FAAS).

2.5. Toxicity characteristic leaching procedure

The toxicity characteristic leaching procedure (TCLP) was applied as defined by the US Environmental Protection Agency [14]. The soil sample specimens were crushed and ground to reduce the particle size to less than 2.0 mm and agitated in 20 mL of 0.0992 M acetic acid and 0.0643 M NaOH extraction solution (1:20 ratio) with a pH of 4.93 ± 0.05 for 18 h at 300 rpm. The leachate was filtered through a 0.45-μm membrane filter to remove suspended solids and stored in the cold for determination of Pb, Zn, Cd and As present in the leachate, using FAAS.

2.6. PTM phyto- and oral-accessibility

PTM accessibility for plants was assessed with the diethylenetriamine pentaacetic acid (DTPA) test [15]. The DTPA extraction solution was prepared by mixing 0.005 M DTPA, 0.01 M $CaCl_2$, and 0.1 M (triethanolamine) TEA and the solution adjusted to pH 7.30 ± 0.05. Soil samples (5 g) were sieved through a 2 mm mesh,

10 mL of DTPA solution was poured over and the mixture shaken for 2 h on a horizontal shaker at about 120 cycles min^{-1}. The samples were filtered through Whatman no. 4 filter paper and analyzed for Pb, Zn, Cd and As content.

The physiologically based extraction test (PBET) for oral-accessibility assessment involves simulations of human gastric and intestinal digestion [16]. The 0.5 g sample was sieved through a 250 μm mesh and digested in a reaction flask for 2 h at constant temperature (37 °C) in simulated gastric fluid (50 mL). The extraction fluid was prepared by mixing 1.25 g of pepsin (porcine, Sigma), 0.50 g of citrate, 0.50 g of malate, 420 μL of lactic acid and 500 μL of acetic acid with pH 2.50 ± 0.05. The pH of the reaction mixture was measured and adjusted if necessary every 5 min with the addition of 12 M HCl. After 2 h, 5 mL samples were collected and centrifuged at 1500 × g for 25 min; the supernatant was stored at 5 °C. The 5 mL volume samples were replaced with gastric solution to maintain a constant volume in the reaction flask. The solution was furthered titrated to pH 7 by the addition of NaHCO$_3$ solution; to simulate small intestine conditions, 175 mg of bile salts (porcine, Sigma) and 50 mg of pancreatin (porcine, Sigma) were added. After 2 h digestion at constant temperature (37 °C), the reaction solutions were collected, centrifuged at 1500 × g for 25 min, stored at 5 °C and analyzed for Pb, Zn, Cd and As content. During both phases, a constant moistened argon flow of 1 L min^{-1} at 37 °C was conducted through the reaction mixture in order to simulate peristaltic movement.

2.7. PTMs determination

Air-dried soil samples (1 g) were ground in an agate mill, digested in aqua regia (28 mL), diluted with deionized water up to 100 mL, and Pb, Zn and Cd analyzed by flame (acetylene/air) AAS with a deuterium background correction (Varian, AA240FS). The metals in the solution were determined by FASS directly. A standard reference material used in inter-laboratory comparisons (Wepal 2004.3/4, Wageningen University, Wageningen, The Netherlands) was used in the digestion and analysis as part of the QA/QC protocol. The limits of quantification (LQ) were 0.1, 0.01 and 0.02 mg L^{-1} for Pb, Zn and Cd, respectively. Reagent blank and analytical duplicates were also used where appropriate to ensure accuracy and precision in the analysis.

During the remediation process, we assessed metal and Cl concentration in process (soil washing and rinsing) solutions directly, using portable X-ray fluorescence spectrophotometer (XRF, Delta DS-4000, Olympus Innov-x, USA). The following factors relate XRF to ASS measurements: Pb (mg L^{-1})$_{XRF}$ × 0.779, Zn$_{XRF}$ × 0.789, As$_{XRF}$ × 0.5, Cl$_{XRF}$ × 1.477 and Fe$_{XRF}$ × 0.878. High regression coefficients (R^2): 0.998 for Pb, 0.996 for Zn, 0.990 for As, 0.982 for Cl and 0.997 for Fe, respectively, indicate a comparable accuracy of AAS and XRF measurements, although XRF had a higher LQ of all PTMs. XRF was not used to measure Cd, since the LQ of this element (10 mg L^{-1}) was above or close to the actual concentration in the samples.

3. Pilot-scale soil extraction process

Ten batches of soil were treated using a pilot-scale chemical extraction plant. Batches were from the same contaminated garden but excavated from different parts of the garden and from different depths. The following are the average pedological properties of the soils: pH 7.0 ± 0.05, organic matter 5.4 ± 0.3%, CEC 18.9 ± 0.6 mg 100 g^{-1} of soil, sand 45.4 ± 1.3%, silt 49.5 ± 1.3%, clay 5.1 ± 0.5%. Since the soil contained >50% of fines, the soil texture was sandy loam. The scheme of the EDTA-based pilot-scale soil extraction process is shown in Fig. 1, in which the balance and flow of process water is also indicated.

3.1. Soil extraction and sand separation

The excavated garden soil contained almost no gravel or objects larger than 3 cm. Seventy-five kg batches of soil (air-dry weight, av. 8.4 ± 0.2% humidity) were extracted in a concrete mixer (max. capacity 350 L) with 75 L of soil washing solution. For the initial batch, 60 mmol EDTA (disodium salt) per kg of soil (60 mM EDTA) was dissolved in tap water. For the extraction of subsequent soil batches, washing solution was prepared by dissolving EDTA in rinsing solution recycled from the previous batch, obtained downstream of the process, as indicated in Fig. 1. The elemental composition and properties of the washing solutions (minimum and maximum values) are given in Table 1. The final volume of soil suspension in the mixer was 95 L. Soil was extracted for 2 h. After extraction, sand and other larger objects were physically separated using wet screening through a 2 mm sieve. In an average batch, 33.5% of initial bulk soil weight was separated as sand. Sand from the initial batch was washed (cleansed) on the sieve with 45 L of tap water. Sand from subsequent batches was washed with 20 L of rinsing solution (recycled from the previous batch) and then with 25 L of tap water. The solution/suspension from sand-washing/rinsing (Section 3.2) was combined with the suspension of soil fines (which was separated from the sand on the sieve). The total volume of combined suspension was 140 L.

### 3.2. Soil–liquid separation combined with soil rinsing

The 140 L of combined suspension was pumped (using a membrane pressure pump) into a chamber filter press (Lotos Ltd., Slovenia) with the following working capacity: 12 plates (50 cm × 50 cm), working V = 21.3 L, working P = 190–260 bar, filter cloth MKI-3290 with 22 dm^3/dm^2 min air permeability (Ecofil Ltd., Slovenia). In the press, the soil solid fraction (fines) was first separated from the waste soil washing solution (Fig. 1). The soil in the filter press was then rinsed until all the EDTA mobilized PTMs had been removed completely from the soil (concentration in the waste soil rinsing solution below LQ, as determined using on line XRF measurements). A volume of 1.5–2 L of tap water was needed for rinsing 1 kg of soil (Fig. 2). For rinsing soil from the initial batch, we therefore used 140 L of tap water. For rinsing soil from subsequent batches, 25 L of rinsing solution (recycled from the previous batch) followed by 115 L of tap water was used.

The products of the soil–liquid separation process were (av. batch): 113 L of used soil washing solution, 120 L of soil rinsing solution and 75 kg of cleansed soil. The composition and properties of the used washing solutions and soil rinsing solutions are given in Table 1. The cleansed soil was mixed with cleansed sand, air-dried overnight and hand-crushed to prepare remediated soil as a final product (av. humidity 24.7 ± 0.9%).

The whole volume of used soil rinsing solution obtained here was reused for soil treatment in the subsequent batch, as described above: preparation of soil washing solution, sand-washing, initial phase of sol-rinsing (Fig. 1). The used soil washing solution was treated further as follows.

3.3. Electrochemical treatment of the used soil washing solution

According to the generally accepted mechanism of EAOP, water is first discharged at the anode active sites (M), producing adsorbed hydroxyl radicals M($\bullet$OH), which are involved in the mineralisation of organic pollutants (R), in our case EDTA complexes with PTMs, in aqueous solution:

$$R + (n/2)M(\bullet OH) \rightarrow (n/2)M + mineralisation\,products + (n/2)H^+$$
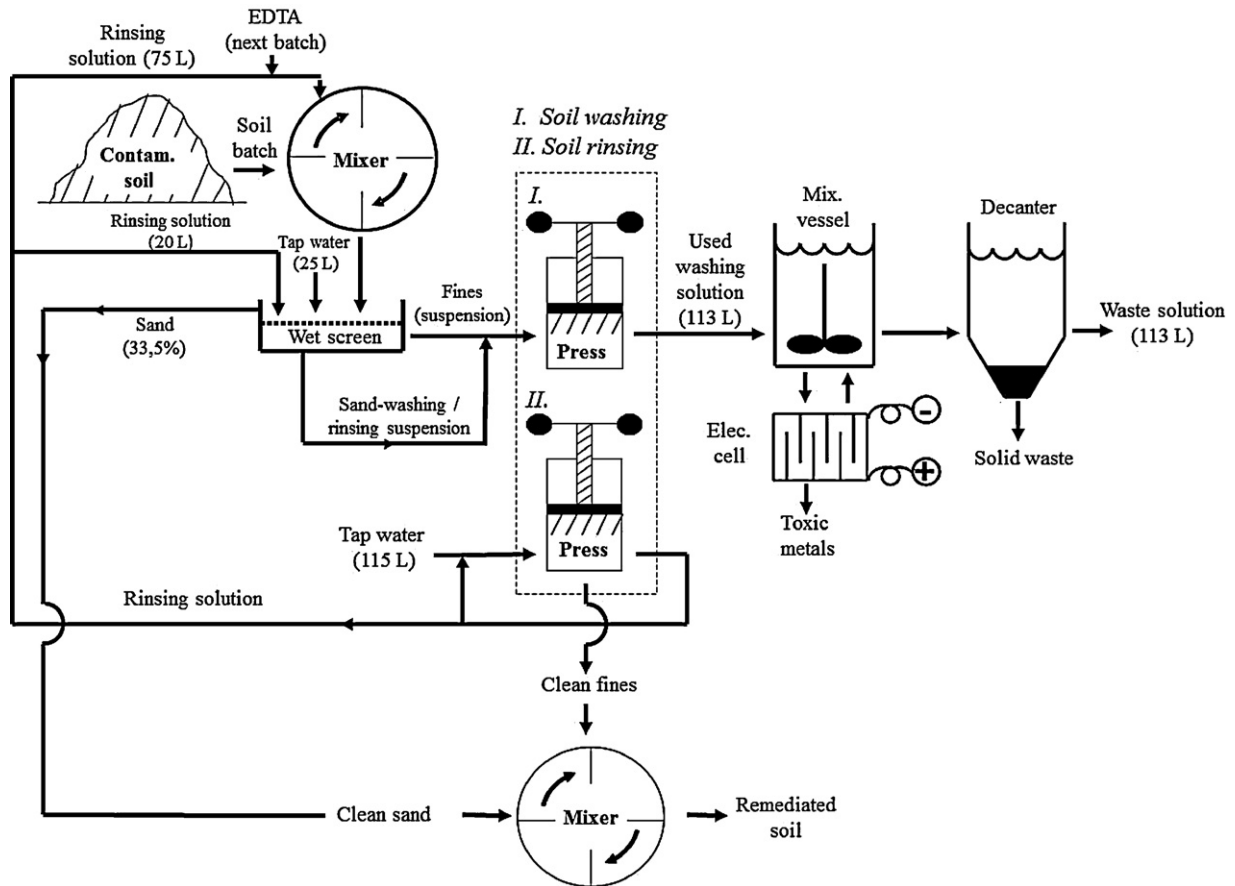$$+ (n/2)e^- \tag{1}$$
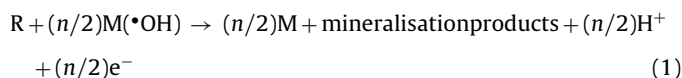
Fig. 1. Scheme of EDTA-based pilot-scale soil extraction process.

where n is the number of electrons involved in the oxidation reaction of organics [17]. In our experiment, we added sodium chloride salt to the used washing solution to control the voltage (the operational range was 8.1–11.6 V) and power consumption and for generation of hypochlorite ions, which were an additional oxidizing agent for indirect EDTA electro-oxidation [18]. The reaction of anodic oxidation of chloride ions to form chlorine is given as:

$$2Cl^- \rightarrow Cl_2 + 2e^- \qquad (2)$$

The liberated chlorine forms hypochlorous acid:

$$Cl_2 + H_2O \rightarrow 2H^+ + Cl^- + HOCl \qquad (3)$$

and is further dissociated to give a hypochlorite ion, which acts as the main oxidizing agent:

$$HOCl \rightarrow H^+ + OCl^- \qquad (4)$$

Table 1 shows the minimum and maximum concentrations of PTMs and EDTA in the used soil washing solution. We treated the used washing solution in an electrolytic cell with graphite anodes and stainless steel cathodes. The pH of the solution was left unregulated during the electrochemical process to rise from an average initial 7.4 ± 0.3 to an average final 8.83. As shown in Fig. 3E, EAOP was effective in oxidative degradation and removal of EDTA and a very low chelant concentration, on average $6.5\,mg\,L^{-1}$, was measured in the final waste solution (Table 1). The electrochemical system also efficiently separated PTMs from the treated solution, mostly by electrodeposition (from 98.5% of Zn to 99.9% of Pb) on the stainless steel cathode.

The graphite anode removed Pb and Zn from the used washing solution slightly more effectively in the first batch (Fig. 3), presumably due to the anode surface damage observed in later batches and blocking of active surface of electrodes with flocks of corroded graphite. Nevertheless, PTMs were removed almost completely (Fig. 3, Table 1). The final concentrations of Cl, Na and Fe and the electro-conductivity of the waste solution obtained after electrochemical treatment are also shown in Table 1. The value of

Table 1
Concentration of PTMs, Fe, Na, Cl, EDTA, electroconductivity and pH of different process waters that occur in the soil remediation process. Minimum and maximum values are shown for 10 consecutive batches of soil remediation.

| Process waters	$Pb_{min, max}$ $[mg\,L^{-1}]$	$Zn_{min, max}$ $[mg\,L^{-1}]$	$Cd_{min, max}$ $[mg\,L^{-1}]$	$As_{min, max}$ $[mg\,L^{-1}]$	$Fe_{min, max}$ $[mg\,L^{-1}]$	$Na_{min, max}$ $[mg\,L^{-1}]$	$Cl_{min, max}$ $[mg\,L^{-1}]$	$EDTA_{min, max}$ $[mg\,L^{-1}]$	$Ec_{min, max}$ $[mS]$	$pH_{min, max}$
Washing solution	27, 61	4, 13	0.01, 0.014	0, 0	0, 24	0, 4	0, 0.6	22,266, 22,612	4.12, 9.21	4.39, 4.97
Used washing solution	548, 766	105, 164	3.2, 5.2	18, 47.5	438, 1000	1, 5	0, 0.5	9527, 10,043	4.63, 5.29	6.9, 7.8
Rinsing solution	28, 64	4, 12	0.01, 0.016	0, 0	8, 82	0, 0.6	0, 0.4	386, 786	0.98, 1.12	6.96, 7.81
Waste solution	2.9, 3.6	0, 6.1	0.02, 0.06	0, 0	0, 0	2215, 3422	626, 1654	4, 9	8.6, 10.9	8.6, 9.6
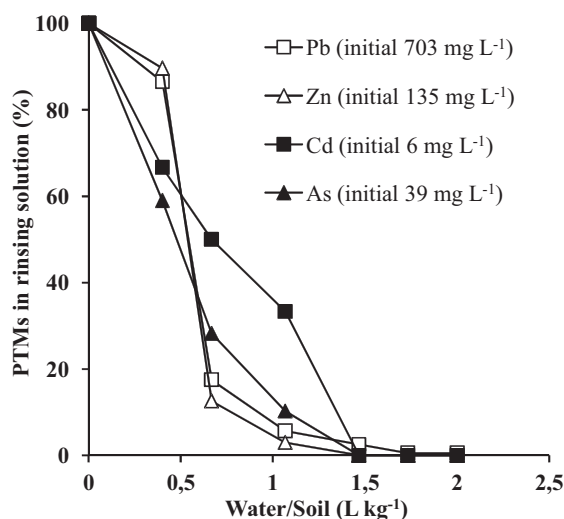
Fig. 2. Removal of mobile PTMs species from soil in the filter press by soil rinsing. The decrease of the PTM concentration in the rinsing solution (indicating more efficient removal of mobile PTMs species), expressed as a percentage of initial PTM concentration, by applying increasing specific volumes of tap water (relative to the soil weight), is shown.

the Cl concentration exceeds Slovenian legislation requirements for waste waters release into natural waters and public sewage system [19] by a factor of 1453. An additional waste-water facility (i.e., reverse osmosis) would therefore required in a commercial scale application of this technology. In our pilot-scale trial, the pH of the waste solution was adjusted to pH 7.1 with HCl and the solution was afterwards released into a drain.

The amount of graphite consumed from the anode after the treatment of all 10 soil batches was 14% of the initial graphite mass (see Section 5). The calculated specific consumption of graphite relative to the mass of removed Pb, Zn, Cd and As was $0.109\,g\,g^{-1}$. The electrochemical treatment also produced 3.7 kg of solid waste (separated from the waste solution as precipitate), with 16, 16 and $118,089\,mg\,kg^{-1}$ of Pb, Zn and Fe. Cd and As were not detected in the solid waste using XRF. The solid waste was collected and disposed of in an official industrial waste disposal facility. The total amount of EDTA, water and energy consumed for the treatment of all 10 soil batches was 16.75 kg, 2170 L and 503 kWh, respectively (Section 5).

4. PTM removal from soil

An average soil used in the experiment contained $1935\pm93\,mg\,kg^{-1}$ Pb, $800\pm14\,mg\,kg^{-1}$ Zn, $10.2\pm0.2\,mg\,kg^{-1}$ Cd and $120.1\pm4.6\,mg\,kg^{-1}$ As. Soil was extracted for 2 h using a soil washing solution with 60 mM EDTA per kg of dry soil. This concentration of EDTA and extraction time was selected as optimal, based on laboratory-scale experiments (data not shown). The main differences between laboratory and pilot scale experiments was use of centrifuge for the separation of the soil solid phase from the washing solution and for the soil rinsing in laboratory, and use of chamber filter press for these operations in pilot-scale experiments. The molar ratio between the (average) concentration of PTMs in the soil and the EDTA applied was 1:2.6. It is known that even higher ratios cannot remove PTMs completely from the soil [20] and that only part of the EDTA in the washing solution is complexed with PTMs; the rest remains in differently protonated forms or complexed with major soil cations, such as Fe, Mn and Ca [21]. EDTA forms particularly stable complexes with soil Fe, with a stability constant of complex formation $(\log K_S) = 14.3$ and 25.0 (at 25 °C and ionic strength, $\mu = 0.1$) for Fe^{2+} and Fe^{3+},

Table 2
Initial concentrations of Pb, Zn, Cd, As (minimum and maximum values from 10 consecutive soil batches) in original soil and residual concentrations of PTMs in remediated soil are shown. Average percentages of removed PTMs are calculated.

Element	Initial$_{min, max}$ [$mg\,kg^{-1}$]	Residual$_{min, max}$ [$mg\,kg^{-1}$]	Removed$_{avrg}$ [%]
Pb	1659, 2133	320, 482	79
Zn	724, 869	378, 640	38
Cd	8, 14	2.1, 4.4	70
As	100, 149	16, 39	80

respectively [22]. Log K_S for Pb-EDTA, for example, is 18.0. Another possible reason for the required high EDTA:PTM molar ratio is the absorption of EDTA into solid soil phases. In our study, an average $48.4 \pm 1\%$ of initial EDTA was retained in the soil after extraction. EDTA and metal complexes that are formed during soil extraction are absorbed by soil minerals, especially crystalline iron oxides [20]. Noren et al. [23] suggested that EDTA is mainly absorbed by iron oxide through outer-sphere complexation. Outer sphere surface complexes are relatively weak and more susceptible to leaching on changes of environmental conditions [24]. The potential long-term risk of EDTA release and transport from the remediated soil therefore merits careful further investigation.

The washing solution efficiently extracted from 70 to 80% of Pb, Cd and As (Table 2), while (on average) less than 40% of Zn was removed. It has been reported previously that Zn is usually bound to non-labile soil fractions and is therefore difficult to remove, even under strong acidic, reducing or oxidising conditions [25]. The removal of As, which is an anionic semi-metal and does not form stable complexes with EDTA, was surprisingly efficient. Oxyanions of As are preferentially bound in soil to the surface of Al, Mg and especially Fe hydroxyoxides [26]. Partial dissolution of Fe by EDTA presumably released As species and enabled the observed washing-off.

4.1. Leachability, accessibility and availability of PTMs in remediated soil

As shown above, EDTA extraction cannot remove PTMs from soil entirely. Furthermore, extraction with EDTA can leave some highly mobile and bio-available PTM-EDTA species in the remediated soil if soil rinsing is not effective or sufficient. To assess the hazard of soil residual PTMs, we applied an array of extraction tests. PTM leachability from the soil matrix was determined in deionised water and in acidic TCLP solution elutriates. The DTPA test was originally designed to assess plant accessible Zn, Fe, Mn and Cu in near-neutral and calcareous soil [15] and later adopted to assess PTMs phyto-accessibility and ecotoxicity [27]. The physiologically based extraction test (PBET) was designed to assess the oral-availability of PTMs in the stomach and small intestine for a two to three year-old child; it estimates the amount of metals ready to be absorbed from the intestine into the blood system. Due to their mouthing behaviour (ingestion of soil particles), children are more exposed to soil pollutants than adults [28].

Extraction tests, except for DTPA, removed only small amounts of PTMs from the original soil (Table 3). This indicates strong bondage of PTMs into the soil solid phases and their low leachability and oral-availability. For example, the concentrations of Pb, Cd and As in TCLP extracts were well below 5.0, 1.0 and $5.0\,mg\,L^{-1}$, respectively, specified as hazardous by the US Environmental Protection Agency. There is no TCLP regulatory standard for Zn, because Zn is not classified as hazardous waste [14]. The significant share of Pb, Zn and Cd removed by DTPA (up to 21.2% for Cd) indicates potential PTM uptake by plants as possibly the most important PTMs exposure route for human poisoning. The DTPA results were expected,
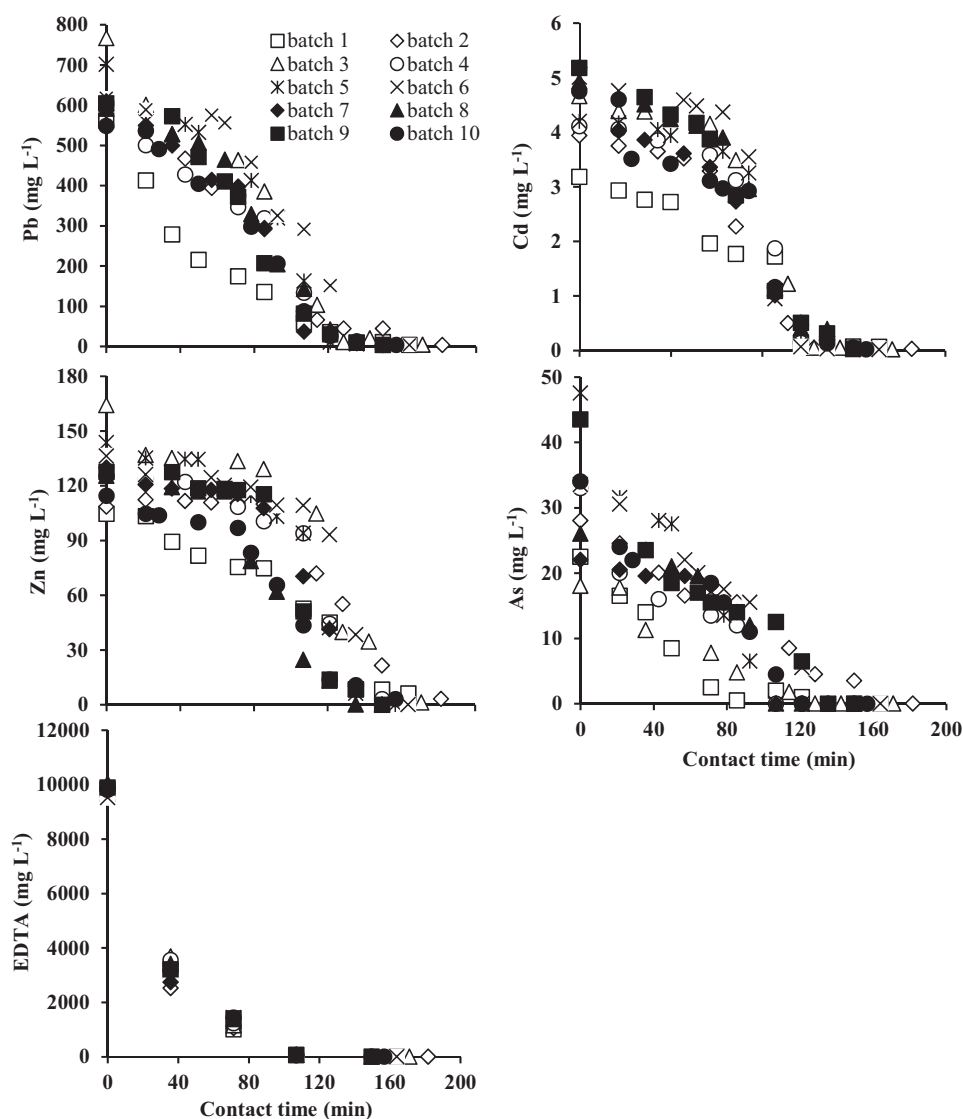
Fig. 3. Concentrations of Pb, Zn, Cd, As and EDTA in the used soil washing solution (10 consecutive batches) during electrochemical treatment using a graphite anode.

Table 3
Pb, Zn, Cd and As leachability and bio-accessibility/availability assessed using deionised water extraction, TCLP, DTPA and PBET tests. Minimum and maximum concentrations of PTMs in extracts from original and remediated soil (10 batches) are shown. The average share of leachable and bio-accessible/available PTMs in the original soil and the reduction of leachability and bio-accessibility/availability in remediated soil are calculated.

Availability test	Pb$_{min, max}$ [mg L^{-1}]	Share$_{avrg}$ [%]	Zn$_{min, max}$ [mg L^{-1}]	Share$_{avrg}$ [%]	Cd$_{min, max}$ [mg L^{-1}]	Share$_{avrg}$ [%]	As$_{min, max}$ [mg L^{-1}]	Share$_{avrg}$ [%]
Original soil								
H$_2$O	1.19, 2.57	0.104	1.21, 1.81	0.178	0.014, 0.03	0.226	0.077, 0.16	0.094
TCLP	1.24, 1.78	0.08	1.26, 1.43	0.17	0.055, 0.07	0.588	0.01, 0.025	0.016
DTPA	186, 236	11	47.2, 59.9	6.48	2.01, 2.39	21.2	0.03, 0.05	0.038
PBET (stomach)	1.52, 2.89	0.121	1.27, 2.29	0.253	0.04, 0.085	0.686	0.038, 0.05	0.033
PBET (intestine)	1.32, 3.21	0.131	0.84, 1.05	0.116	0.02, 0.04	0.294	0.05, 0.06	0.047

Availability test	Pb$_{min, max}$ [mg L^{-1}]	Reduction$_{avrg}$ [%]	Zn$_{min, max}$ [mg L^{-1}]	Reduction$_{avrg}$ [%]	Cd$_{min, max}$ [mg L^{-1}]	Reduction$_{avrg}$ [%]	As$_{min, max}$ [mg L^{-1}]	Reduction$_{avrg}$ [%]
Remediated soil								
H$_2$O	1.05, 1.63	36	0.59, 1.12	34	0.001, 0.01	70	0.003, 0.01	90
TCLP	0.91, 1.41	29	0.98, 1.34	18	0.02, 0.04	41	0.01, 0.02	35
DTPA	38, 47	79	8.9, 11.2	80	0.72, 0.79	64	0.01, 0.024	65
PBET (stomach)	0.77, 2.02	39	0.56, 0.81	68	0.01, 0.04	74	0.002, 0.01	87
PBET (intestine)	0.95, 1.49	54	0.41, 0.59	46	0.01, 0.02	56	0.02, 0.05	39

Table 4
Material and energy consumption of the soil remediation process for 10 soil batches and per ton of processed soil; solid and liquid waste generated and cost of their disposal.

Consumables	Total consumption/generation	Consumption/generation per tone of soil	Cost	Costs per tone of soil
Energy				
Apparatus	23.6 kWh	31.5 kWh	0.0545€kWh^{-1}	1.72€
Electrolysis	503 kWh	671 kWh	0.0545€kWh^{-1}	36.6€
Materials				
Graphite	97.5 g	130 g	1.8€kg^{-1} [a]	0.234€
EDTA	16.75 kg	22.3 kg	1.5€kg^{-1} [a]	33.5€
Water	2170 L	2893 L	0.5347€m^{-3}	1.55€
Wastes				
Toxic solid waste	3.7 kg	4.9 kg	0.2€kg^{-1}	0.98€
Waste water	1120 L	1493 L	/	/

[a] Internet source (http://www.alibaba.com) average price of 5 sellers.

since DTPA is achelating agent like EDTA, albeit with lower $\log K_s$ for cationic PTMs [22].

Although the leachability and oral-availability of PTMs in the original soil assessed using deionised water, TCLP and PBET were already quite low, they were reduced even further in remediated soil (Table 3). This indicates that the soil rinsing part of the remediation process (Fig. 1) was effective, leaving very little mobile PTM-EDTA species in the remediated soil. Potential PTM plant-availability was the most reduced in the remediated soil: 79, 80 and 64% for Pb, Zn and Cd, respectively. DTPA extraction of PTMs was otherwise significant in the original soil. The main reason for the observed reduction was soil extraction with EDTA, which is a more powerful chelating agent than DTPA, and had previously removed most of the chelant-available PTMs from soil.

5. Cost

An evaluation of total costs associated with soil remediation includes capital investment in the equipment, personnel, material costs and profit. This would require simulation of the operation of full-scale facility of given capacity. We do not have sufficient input data to make such a simulation. However, the material and energy costs of our pilot-scale experiment can be calculated accurately. Table 4 presents data on electric energy consumption for all apparatus used in the process (Fig. 1): pumps, compressor, filter press, mixing reactors for soil and solutions, and separately for the DC power supply for electrolysis. Data on quantity and the acquisition and disposal costs of the materials used and produced during the remediation process are also shown in Table 4. During the process, a toxic solid sludge was formed. The sludge can be deposited after treatment, i.e., after solidification and stabilisation using bitumen or other thermoplastic materials. The disposal cost of solid hazardous waste treatment, transportation and disposal was assessed as approximately 200€ton^{-1} [29]. The cost of other chemicals and materials was obtained from an internet source (http://www.alibaba.com), the expenses for consumed electricity and water were based on the cost specified by local providers.

The total estimated cost of energy and material expenses for the treatment of 1 ton of contaminated soil amounts to approximately 75€ton^{-1} of remediated soil. This cost does not include the additional expense of the required polishing of waste solution before disposal (Section 3.3). Nevertheless, the cost seems favourable compared to the current cost of soil washing, which can be as much as 350€ton^{-1} [30].

The cost of electrolysis and EDTA represents almost 93.5% of the total cost (Table 4). The use of new anodic materials, such as boron-doped diamond (BDD) with an extreme oxygen overpotential of 1.3 V [31] would significantly improve the efficiency and economy of the electrochemical part of the remediation process. The reason for this is the activity of hydroxyl radicals (•OH), which is strongly

linked to their interaction with the anode material; the weaker the interaction, the lower is the electrochemical activity towards oxygen evolution (higher O_2 overpotential). Currently, BDD anodes are still rather difficult to produce on a pilot-plant scale and are expensive.

EDTA is a chemically stable molecule and requires a significant energy input for its complete degradation. Even partial EDTA recycling, rather than chelant destruction, would therefore improve the economics of soil washing, both through chelant recovery and through savings of energy for the treatment of the used soil washing solution. However, although several approaches to EDTA recycling have been proposed [32–34], none has been commercialised or tested on a pilot-scale.

6. Conclusions

The results of our pilot-scale study indicate that chemical soil washing with EDTA is feasible. The proposed method efficiently removed Pb, Zn, Cd (cationic metals) and As (anionic semi-metal) from contaminated soil and has the following advantages over traditional physical separation processes:

- The proposed remediation process can be used for soils rich with fines, such as garden soil, which is a valuable natural resource.
- The proposed remediation process efficiently removes the more toxic, easily bio-available (accessible) part of the PTMs from the soil.
- The soil fines are cleansed and soil thus preserved as a plant substrate.
- The method enables treatment of multi-metal contaminated soil.
- The amount of waste material is reduced compared to physical separation methods.
- The proposed novelties are soil-liquid separation combined with soil rinsing in the chamber filter press and partial recycling of process waters.
- The material costs, electricity and consumables, seem to be within the frame of currently available technologies.
- XRF enables accurate on-line measurements of the concentration of PTMs and other elements in the process liquids and thus offers the possibility of process control and future automatisation.

The following problems were identified:

- Additional treatment of waste-water is needed to fulfill legislative requirements for disposal.
- EDTA consumption.
- EDTA absorption into the soil poses the future risk of EDTA release and transport from the remediated soil.

Suggested solutions, which will be tested in future pilot-scale studies, include EDTA recycling and the use of a more effective electrochemical waste-water treatment system. The problem of EDTA soil absorption, which presumably relates to the pH of the washing solution, will be addressed in a separate study.

Acknowledgment

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2012.02.022.

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