



EDTA leaching of Cu contaminated soil using electrochemical treatment of the washing solution

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ARTICLE INFO

Article history:

Received 28 July 2008

Received in revised form 6 October 2008

Accepted 6 October 2008

Available online 14 October 2008

Keywords:

Cu

Soil remediation

EDTA

Electrochemical advanced oxidation methods

ABSTRACT

The feasibility of a two-phase method for remediation of Cu ($364 \pm 2 \text{ mg kg}^{-1}$) contaminated vineyard soil was evaluated. In the first phase we used ethylenediamine tetraacetate (EDTA) for Cu leaching, while in the second phase we used an electrochemical advanced oxidation process (EAOP) for the treatment and reuse of the washing solution for soil rinsing (removal of soil-retained, chelant-mobilized Cu complexes) in a closed loop. In the EAOP, a boron-doped diamond anode was used for the generation of hydroxyl radicals and oxidative decomposition of EDTA-metal complexes at a constant current density (40 mA cm^{-2}). The released Cu was removed from the solution mostly as an electro-deposit on the cathode. Two consecutive additions of 10 mmol kg^{-1} EDTA removed 26% of Cu from the soil, mostly from carbonate and oxide soil fractions (58% and 40% Cu reduction). The soil Cu oral availability (*in vitro* Physiologically Based Extraction Test) was reduced after remediation by 42% and 51% in the simulated stomach and intestinal phases. The discharge solution was clear, almost colorless, with pH 8.4 and 0.5 mg L^{-1} Cu and 0.07 mM EDTA. The novel method enables soil Cu availability stripping using small volumes of process waters, and no wastewater generation or other emissions into the environment.

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1. Introduction

Contamination with Cu is a major problem of viticulture soils and coffee plantations in which Bordeaux broth (CuSO_4 and lime solution) or other Cu based fungicides (e.g., Cu oxychloride) have been applied for decades and are still in use. A high Cu concentration in soils causes low plant biomass, delay in flowering and fruiting, and low seed set [1].

Soil washing or leaching with chelants could be a viable remediation option, although it has been studied predominantly for Pb and much less for Cu contaminated soils [2]. Chelants form coordinate chemical bonds with metals (complexes) and facilitate their solubilization from the soil into the washing solution. Ethylenediamine tetraacetate (EDTA) has been the chelant most often used for soil washing/leaching, since it forms strong complexes with most polluting heavy metals [3] and is relatively inexpensive compared to other chelants (in Europe, it costs about 1.3 € kg^{-1} for the technical-grade chemical from a major European manufacturer). For remediation of Cu contaminated soil, the [S,S] isomer of ethylenediamine disuccinate ([S,S]-EDDS) has been reported to be

superior to EDTA [4], although the current high price of [S,S] EDDS (approximately 4 € kg^{-1} according to a European manufacturer) limits its use in soil remediation.

The toxic wastewaters laden with EDTA and heavy metals that are generated during soil washing/leaching cannot be treated using conventional methods such as filtration, flocculation and participation [5]. We recently proposed a combination of ozone and UV [6], an advanced oxidation process (AOP), for cleaning these wastewaters. AOP generated hydroxyl radicals ($\bullet\text{OH}$) for the oxidative decomposition of EDTA-metal complexes ($\bullet\text{OH}$ radicals are the most powerful oxidant in aqueous solutions). The released metals were then removed from the washing solution by absorption on zeolite material. However, EDTA leaching of Cu contaminated soil produced a washing solution with an intensive green color [7]. The coloration probably blocked UV light and made ozone-UV based AOP efficient only when we treated the soil with low (2.5 mM kg^{-1}) EDTA concentrations [7]. Another practical problem was removal of the released Cu, which consumed a significant quantity of expensive absorbent [7,8] and which later needs to be deposited.

A boron-doped diamond anode (BDDA) [9] has recently been developed, enabling effective $\bullet\text{OH}$ production using an electrochemical advanced oxidation process (EAOP). In EAOP, the anode material is the most important parameter, since molecular oxygen is mainly produced during water electrolysis if the oxygen overvoltage is not sufficiently high. BDDA, however, has an extreme oxygen overvoltage ($>3 \text{ V}$) before O_2 forms [10,11]. This electrochemical

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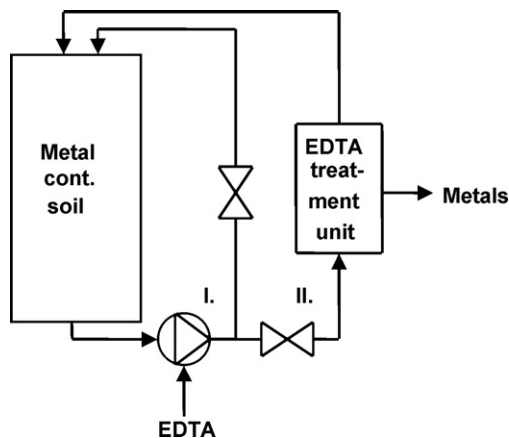


Fig. 1. Conceptual presentation of the two-phase method for remediation of heavy metal contaminated soils: (I) leaching of heavy metals from soil with chelants and (II) treatment and removal of heavy metals/chelants from the washing solution and soil rinsing.

window allows the production of $\bullet\text{OH}$ directly from the electrolysed water, according to Eq. (1).



EAOP is more robust, technically simpler and cheaper than most AOP [10]. In the current study, we tested BDDA EAOP for treating the washing solution as part of a two-phase soil leaching method, recently proposed by Finzgar and Lestan [12]. In the first (leaching) phase, the soil is leached with EDTA washing solution to mobilize contaminating metals. In the second phase, the washing solution is treated and metals and EDTA are removed. The clean solution is then used to rinse the soil in a closed loop to remove EDTA and metallic complexes which are retained in the soil after the leaching phase (Fig. 1).

This is the first study of the use of BDDA EAOP in remediation of Cu contaminated soils. Before the bench-scale remediation experiments, we optimized the leaching parameters and the washing solution BDDA EAOP treatment conditions. In order to evaluate remediation efficiency, the percentage of Cu removed from the soil as well as chemical (sequential extractions) and oral availability [13] of residual Cu in the soil after remediation were determined.

2. Materials and methods

2.1. Soil samples and analysis

The sub-Mediterranean region in Slovenia has a long tradition of intensive grapevine growing, with frequent use of copper-based fungicides. The reason for their frequent use lies in the high air humidity and temperature typical of the period of vine growth [14]. Cu contaminated soil (eutric cambisol) was collected from the 0–45 cm surface layer of a vineyard ($x = 040370$ m and $y = 400570$ m, Gauss–Kruger coordinate system).

For pedological analysis the soil pH was measured in a 1/2 (w/v) ratio of soil and 0.01 CaCl_2 water solution suspension. Soil samples were analyzed for organic matter by Walkley–Black titrations, cation exchange capacity (CEC) by the ammonium acetate method and soil texture by the pipette method [15] (Table 1).

2.2. Small scale leaching experiments

Soil (150 g) was placed in perforated 250 mL polypropylene flasks with a 0.5 mm plastic mesh at the bottom to retain the soil. Soil was leached in triplicate with a 100 mL washing solution con-

Table 1

Selected properties of contaminated soil, Cu, Ca and Fe concentrations, and Cu fractionation before and after remediation. Where indicated standard deviation from mean value ($n=3$) was calculated. Means followed by the same letters are not significantly different, according to the Duncan test ($P < 0.05$).

Soil properties	Before remediation	After remediation
pH (CaCl_2)	7.3	7.4
Organic matter (%)	6.7	–
CEC ($\text{mmol C}^+ 100 \text{ g}^{-1}$)	29.3	26.6
Sand (%)	12.2	15.1
Silt (%)	50.2	50.2
Clay (%)	37.6	34.7
Texture	Silty clay loam	
Total Cu (mg kg^{-1})	^a 364 ± 2	^b 270 ± 16
Total Ca (mg kg^{-1})	^a 31919 ± 2206	^a 33844 ± 5116
Total Fe (mg kg^{-1})	^a 321652 ± 608	^b 30251 ± 1038
Cu fractionation (mg kg^{-1})		
In soil solution	^a 1.7 ± 0.2	^b 3.3 ± 0.1
Exchangeable	^a 2.8 ± 0.1	^b 2.0 ± 0.1
Bound to carbonate	^a 38 ± 1	^b 16 ± 0
Bound to Fe and Mn oxides	^a 99 ± 4	^b 59 ± 0
Bound to organic matter	^a 109 ± 6	^b 78 ± 1
Residual fractionation	^a 114 ± 3	^b 99 ± 4
Recovery (%)	100 ± 1	^b 95 ± 2

taining EDTA (disodium salt). The washing solution leached from the soil was collected and re-applied on top of the soil with a peristaltic pump (flow rate 2 mL min^{-1}).

In experiments in which the effect of EDTA–soil contact (reaction) time on Cu removal was studied, the washing solution (10 mmol kg^{-1} EDTA) circulated through the soil for 240 h, and concentrations of Cu in the washing solution were periodically measured.

In multi-dose leaching experiments, the EDTA washing solution ($5\text{--}15 \text{ mmol kg}^{-1}$) was circulated through the soil for 24 h (leaching phase). After the leaching phase, the soil was rinsed with 2 L of tap water (rinsing phase) to remove all measurable mobile Cu species. We checked this by measuring the Cu concentrations in the rinsing solutions (data not shown). We then added a new dose of EDTA. At the end, the washing and rinsing solutions were combined. The volume and Cu concentration in the combined solution was measured and used to calculate the percentage of Cu removed from the soil.

2.3. Electrolytic cell

The electrolytic cell consisted of a BDD anode (Diachem, Condias GmbH, Itzehoe, Germany) and two stainless steel cathodes with an electrode distance of 4.5 mm. The BDDA had a Ti base coated with a conductive polycrystalline diamond layer (the conductivity of the electrode was regulated by the addition of boron). The overall BDD anode surface was 100 cm^2 . The surface area ratio between the cathodes and anode was 1:2. Current densities were adjusted (from 15 to 40 mA cm^{-2}) and cell voltage measured with a DC power supply (Elektronik Invent, Ljubljana, Slovenia). It was ensured that the flow of soil washing solution was only through the space between the anode and cathodes. The electrode cell was cooled using a cooling mantle and tap water to keep the temperature of the treated washing solution below 35°C .

2.4. BDDA EAOP treatment of the EDTA soil washing solution

To obtain the washing solution, we placed 4.5 kg of air-dried soil in 15 cm diameter soil columns (three replicates) and leached the soil with a 4800 mL aqueous solution of 10 mmol kg^{-1} EDTA (disodium salt) for 48 h. Approximately 2500 mL of the washing solution per column was collected.

To test the feasibility of using BDDA EAOP for treatment of the soil washing solution, we circulated 500 mL of soil washing solution from a 1-L Erlenmeyer flask through the electrode cell (peristaltic pump, flow rate 90 mL min⁻¹). Current densities used were 15, 25 and 40 mA cm⁻². Samples (30 mL) of washing solution were collected at intervals from 10 to 60 min of contact time in the electrode cell. Contact time was calculated as the ratio of the electrode cell volume to the volume of washing solution and multiplied by the operation time (initially 44 min of operation time equaled 10 min of contact time). Samples were filtrated (filter paper grade 391, 84 g m⁻²), the pH and EC measured, and stored in the cold for further analysis of Cu and EDTA concentrations.

The cathodes were rinsed with 10 mL 37% HNO₃ to dissolve deposited Cu and the concentration of Cu was analyzed (AAS) to determine the percentage of Cu that had been removed from the washing solution by electrodeposition. The percentage of Cu removed from the washing solution by filtration was then calculated.

2.5. Two-phase remediation of Cu contaminated soil

A two-phase soil remediation method (Fig. 1) with two EDTA additions was simulated in a bench (laboratory) scale experiment. Air-dried soil (4.5 kg) was sieved (5 mm mesh) and placed in a 15 cm diameter column 26 cm high. Plastic mesh (0.2 mm) at the bottom of the column retained the soil. The soil was leached with a washing solution containing 10.0 mmol kg⁻¹ EDTA in 3 L unbuffered tap water (this volume was 145% of the soil water holding capacity). The washing solution was circulated in the first (leaching) phase (peristaltic pump, flow rate 15 mL min⁻¹) solely through the soil (pathway I, Fig. 1) for 48 h. In the second (rinsing) phase, the washing solution circulated through the soil, electrode cell (current density 40 mA cm⁻²) and three filters (pathway II, Fig. 1). High efficiency particulate air (HEPA) filter for cooker-hoods available from a local home appliances store was used as filtering material. Thirty millilitres samples of washing solution were collected from the column outlet after each 10 min of contact time in the electrode cell (10 min of contact time equaled 4 h and 42 min of operation time) and pH, EC and Cu and EDTA concentrations were determined. When the concentration of Cu in the treated washing fell below 5 mg L⁻¹, a fresh 10 mmol kg⁻¹ EDTA was added to the washing solution. Approximately 25% of the total initial water was added to the system after each EDTA addition, to compensate for water lost during the process (sampling, evaporation, electrolysis). After the second EDTA addition, the rinsing phase was prolonged to obtain a discharge solution with sufficiently low heavy metal and EDTA concentrations. The soil column was dismantled and samples were taken from different soil layers (profile) for further determination of residual Cu.

2.6. Cu oral bioavailability

Cu oral bioavailability before and after soil remediation was determined using a Physiologically Based Extraction Test (PBET), designed around pediatric gastrointestinal tract parameters for a child 2–3 years old [13]. The PBET included two phases. Firstly, 0.5 g of sieved soil sample (250 μm) was digested in a reaction flask for 2 h at a constant temperature (37 °C) in simulated gastric fluid (50 mL) prepared by adjusting 1 L of deionized water to pH 2.50 ± 0.05 with diluted HCl and adding 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. The pH of the reaction mixture was measured every 10 min and adjusted with HCl as necessary to keep it at a value of 2.50 ± 0.05. Samples (5 mL each) were collected after 2 h, centrifuged at 2500 × g min⁻¹ for 25 min. The liquid frac-

tion was decanted for further analysis. The 5 mL sample volume was replaced with gastric solution to maintain a constant volume in the reaction flask. After 2 h, the reaction was titrated to pH 7 with saturated NaHCO₃ solution. When the reaction vessel reached equilibrium at pH 7, 175 mg of bile salts (porcine, Sigma) and 50 mg of pancreatin (porcine, Sigma) were added, thus simulating small intestine conditions. After 2 h, the reaction solutions were centrifuged at 2500 × g min⁻¹ for 25 min. The liquid fraction was decanted and analyzed as the small intestine fraction. During both phases, a constant moistened argon flow (1 L min⁻¹) at 37 °C was conducted through the reaction mixture in order to simulate peristalsis. Three PBET extractions were performed for each sample.

2.7. Six-step sequential extraction

A sequential extraction procedure [16] was used to determine the fractionation of Cu in non-remediated and remediated soil into six fractions: soluble in soil solution, exchangeable from soil colloids, bound to carbonates, bound to Fe and Mn oxides, bound to organic matter and the residual fraction soluble in *aqua regia*. Three determinations of Cu concentration were made for each fractionation sequence. The final fractional recovery of Cu was calculated after summing the recoveries of all six steps of sequential extractions.

2.8. EDTA determination

Samples of washing and soil rinsing solution were filtrated (filter paper grade 391, 84 g m⁻²) and EDTA determined spectrophotometrically according to the procedure of Hamano et al. [17].

2.9. Heavy metal determination

Air-dried samples of non-leached and leached soil (1 g) were ground in an agate mill, digested in *aqua regia* (28 mL), diluted with deionized water up to 100 mL, and Cu, Fe and Ca analyzed by flame (acetylene/air) AAS with a deuterium background correction (Varian, AA240FS). Cu in washing, rinsing and PBET solutions was determined by AAS directly. A standard reference material used in inter-laboratory comparisons (Wepal 2004.2.2) was used in the digestion and analysis as part of the QA/QC protocol. The recovery percentage for Cu was 100 ± 3. Reagent blank and analytical duplicates were also used where appropriate to ensure accuracy and precision in the analysis.

2.10. Statistics

The Duncan multiple range test was used to determine the statistical significance ($P < 0.05$) between different treatments, using the computer program Statgraphics 4.0 for Windows.

3. Results and discussion

3.1. Optimization of soil leaching conditions

We used small scale experiments (150 g of soil) to optimize the EDTA contact time, concentration and dosage (single dose vs. multi-dosage). As shown in Fig. 2, the efficiency of EDTA removal of Cu increased with the contact time up to 48 h and thereafter remained almost constant. For practical reasons, we allowed a 24 h reaction time in other small-scale experiments and a 48 h reaction time in further experiments. The efficiency of Cu extraction increased with EDTA concentration (Fig. 3). In accordance with previous observations [17] the percentage of Cu removal did not follow the increase

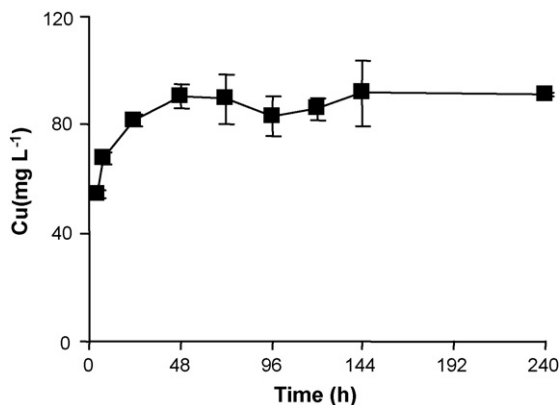


Fig. 2. The concentration of Cu in the washing solution after soil leaching (small-scale experiment) with 10 mmol kg^{-1} EDTA using different contact times. Error bars represent standard deviation from the mean value ($n=3$).

in EDTA concentration. Cu and other heavy metals are present in soil in various chemical forms and bound to different soil fractions. They are usually not entirely accessible to chelants. Consequently, only part of the total soil heavy metals content is typically removed by soil washing, especially from soils rich in organic matter or clay. Nowack et al. [18] compiled data from 28 publications to evaluate the efficiency of chelants to remove Pb, Zn, Cd and Cu from contaminated soil. They reported that, except in some isolated cases for Pb, complete heavy metal solubilization and removal did not occur, even at high chelant-to-metal ratios. Finzgar and Lestan [19] reported that multiple-dosages of EDTA were substantially more effective for leaching Pb from contaminated soils than using one large single dose. Similarly, two dosages of 5 mmol kg^{-1} EDTA and three dosages of 5 mmol kg^{-1} more Cu than a single 15 mmol kg^{-1} EDTA addition (Fig. 3). However, although differences were statistically significant ($P<0.05$) they were practically quite small. We arbitrarily chose to use 10 mmol kg^{-1} EDTA in further experiments. In the soil remediation study, this amount was added in two consecutive dosages.

When EDTA was added in several consecutive (multiple) dosages the labile, more easily extractable Cu species were probably removed from the soil first. This explains why later EDTA dosages were less effective (Fig. 3).

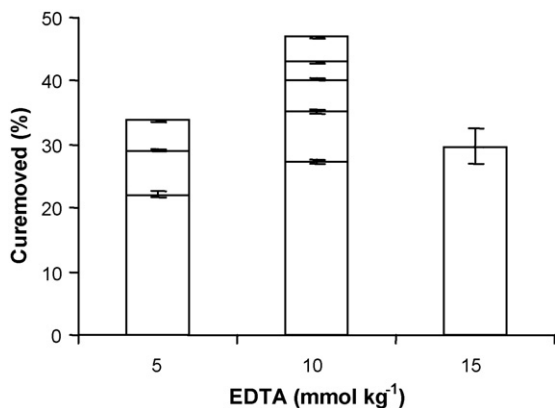


Fig. 3. The amount of Cu removed from the initial total Cu content after multi-dose soil leaching using different EDTA concentrations (small-scale experiment). Error bars represent standard deviation from the mean value ($n=3$).

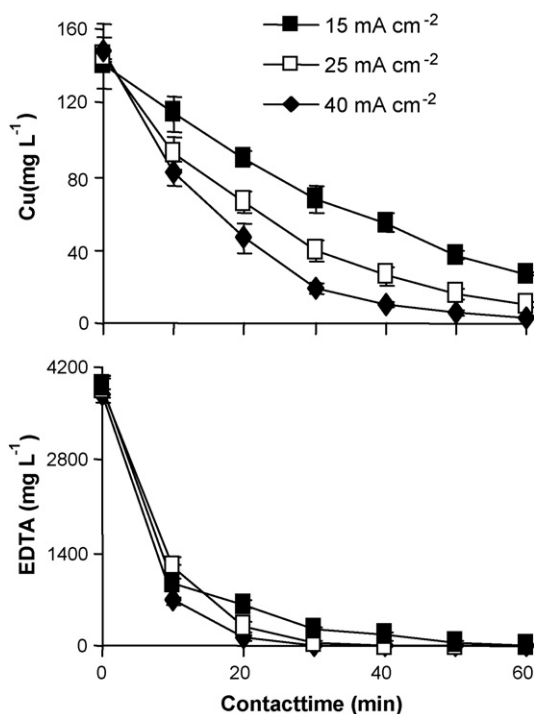


Fig. 4. Effect of current density on Cu and EDTA removal from the washing solution using BDDA EAOP. Error bars represent standard deviation from the mean value ($n=3$).

3.2. Feasibility of BDDA EAOP for treatment of EDTA-Cu soil washing solution

The concentration of Cu in the soil washing solution before treatment in the electrolytic cell was $145 \pm 4 \text{ mg L}^{-1}$. The initial EDTA concentration was $3851 \pm 67 \text{ mg L}^{-1}$ ($10.4 \pm 0.2 \text{ mM}$) and the pH of the washing solution was 8.0 ± 0.1 . Fig. 4 shows that the BDDA EAOP treatment efficiently removed Cu and EDTA from the washing solution. After 60 min contact time, 98%, 93% and 81% of Cu was removed using 40, 25 and 15 mA cm^{-2} , respectively, and EDTA was completely removed at all current densities. The voltage slightly decreased during the treatment (from 2.9 ± 0.1 to $2.0 \pm 0.3 \text{ V}$, from 2.8 ± 0.1 to $2.1 \pm 0.1 \text{ V}$, and from 2.8 ± 0.1 to $2.2 \pm 0.2 \text{ V}$ for current densities 15, 25 and 40 mA cm^{-2} , respectively). The pH of the washing solution slightly increased during the treatment from 8.0 ± 0.1 up to 8.7 ± 0.0 in the treatment with 40 mA cm^{-2} . The initial electrolyte concentration and thus electric conductivity in the soil washing solution was high, $2810 \pm 90 \mu\text{S cm}^{-1}$, but slightly decreased during the treatment regardless of the current density applied (down to $2020 \pm 240 \mu\text{S cm}^{-1}$).

As shown in Fig. 4, the dynamics of EDTA degradation was similar for all treatments, while Cu removal was faster at higher current densities. A possible reason is the degradation pathway of EDTA electrolytic oxidation. Yamaguchi et al. [20] reported that EDTA was oxidized through sequential removal of the acetate groups. The products of partial degradation could therefore still exhibit chelating activity and prevent Cu precipitation from the solution. These products would be more abundant and long-lived in treatments with lower current densities.

Literature on using BDDA EAOP to treat process or wastewaters containing EDTA is scarce. Kraft et al. [10] successfully treated industrial wastewater with an approximately four times higher EDTA concentration than in our washing solution, using a current density as low as 7.5 mA cm^{-2} . Their results, however, are difficult

to compare to ours since the efficiency of EDTA degradation by EAOP probably depends on many parameters: the geometry of the electrolytic cell and electrode materials, the nature of EDTA (non-complexed or complexed with different metals), concentration of reactants, presence of electrolytes, pH and T .

After EDTA electrolysis, Cu was removed from the washing solution as an electrodeposit on the cathode or by filtration. Approximately 70% of Cu was removed by electrodeposition, regardless of the current density applied. The remaining Cu was precipitated from the treated washing solution and was easily removed by filtration. The Cu probably precipitated as metal hydroxide, formed close to cathode where a higher pH is expected due to the formation of OH^- during water electrolysis [21]. Another possible mechanism is the anodic oxidation of metals by hydroxyl radicals [22].

3.3. Remediation of Cu contaminated soil

In a laboratory scale simulation of a two-phase leaching method (Fig. 1), the concentrations of Cu in the washing solution (measured immediately after the first, leaching phase) was lower after the second dose of 10 mmol kg^{-1} EDTA, as expected (Fig. 5). During the second (rinsing) phase, the washing solution was treated by BDDA EAOP to remove EDTA and Cu and was then re-used for soil rinsing in a closed process loop, as shown in Fig. 1.

A constant current density of 40 mA cm^{-2} was applied in the electrolytic cell. The voltage increased from an initial 11–15 V towards the end of remediation, as electric conductivity in the soil washing solution decreased from an initial $2790\text{--}1990 \mu\text{S cm}^{-1}$. Removal of Cu and EDTA from the soil washing solution with BDDA EAOP was faster (and the treatment more efficient) at higher Cu/EDTA concentrations (Fig. 5), as also observed in small-scale experiments (Fig. 4). This could be partly attributed to the observed decrease of electric conductivity and could presumably be amended by the addition of electrolyte, since higher electrolytic efficiency can be expected in solutions with a higher conductivity [23].

The electrodeposited Cu was removed from the cathode by etching with nitric acid. The suspended Cu and other metallic precipitates were removed from the washing solution by filtration during the second phases of the remediation process. The discharge solution lost its initial intensive green color and was clear, almost colorless and slightly basic (pH 8.4). The concentrations of Cu (0.47 mg L^{-1}) and EDTA (0.07 mM) could presumably be reduced even further by prolonging the last second phase of the remediation process.

After leaching with $2 \times 10 \text{ mmol kg}^{-1}$ EDTA, 26% Cu was removed from the soil. Remediation did not considerably effects other measured soil properties (Table 1). Soil Cu was removed quite uniformly through the lower soil profile, but the concentration of Cu in the upper layer was significantly higher (Fig. 6). Heap leaching in soil columns was less effective ($P < 0.05$) than small-scale heap leaching simulation, in which 35% Cu was removed. A possible explanation for this discrepancy is less efficient filtration of Cu in a bench-scale compared to a small-scale experiment. It is likely that the part of the Cu precipitates in the washing solution that were small enough passed through the filtering system and re-contaminated the upper soil layer, as indicted in Fig. 6.

Another and the main reasons for relatively poor Cu removal was the specific Cu fractionation profile (Table 1), in which most of the Cu was bound to the residual fraction (31%) and soil organic matter (30%). Metals from these (last) fractions of sequential extractions are the least extractable and therefore also the least bio-available and toxic.

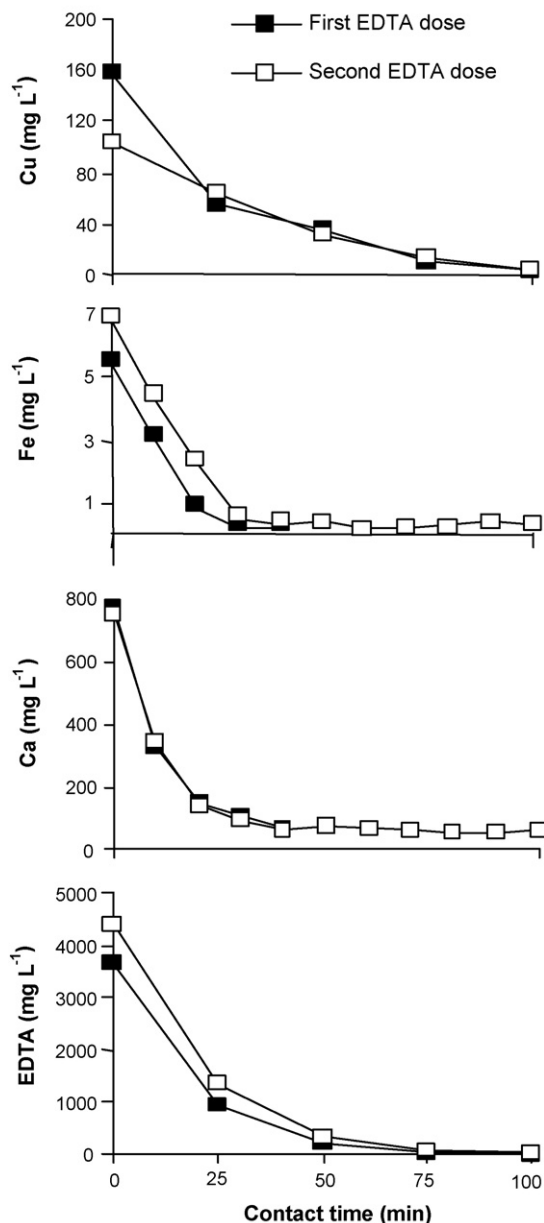


Fig. 5. Concentrations of Cu, Fe, Ca and EDTA in the washing solution during two-phase soil remediation using BDDA EAOP. Soil was remediated with two consecutive doses of 10 mmol kg^{-1} EDTA.

Common soil cations, particularly the most abundant Fe and Ca, may compete with heavy metals to form complexes with EDTA and thus reduce the Cu removal efficiency [3]. Competition in a metal-chelant system is controlled by dissolved metal concentrations, reaction kinetics and many soil parameters, particularly the pH of the soil solution [24]. Nevertheless, interference by Fe in Cu complexation with EDTA could be expected due to their high stability constant ($\log K_s$) for EDTA complexes formation. The $\log K_s$ for Fe^{3+} -EDTA is 25.1 (at 25°C and $\mu = 0.1$) and is considerably higher than the $\log K_s$ of Cu-EDTA formation (18.8 at 25°C and $\mu = 0.1$; [25]). The $\log K_s$ for Fe^{2+} -EDTA (14.3 at 25°C and $\mu = 0.1$) is somewhat lower. The total soil concentration of Fe and Ca in soil was much higher than that of Cu (Table 1). However, the competitiveness of Fe species for complexation with EDTA could be hindered by the low aqueous solubility of Fe bearing soil minerals in usual soil conditions [26], which explains low concentration of Fe in the washing

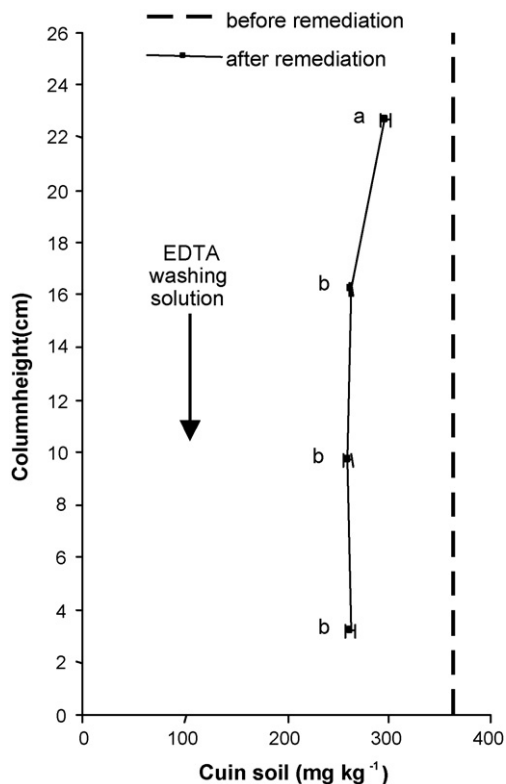


Fig. 6. Cu concentration through the soil profile in the soil column before (dotted line) and after (solid line) leaching with two doses of 10 mmol kg^{-1} EDTA. Error bars represent standard deviation from the mean value ($n=3$). Means followed by the same letters are not significantly different, according to the Duncan test ($P<0.05$).

solution (Fig. 5). Ca forms less stable complexes with EDTA ($\log K_s$ 10.6 at 25°C and $\mu = 0.1$; [25]) than Cu and the high concentration of Ca in the washing solution (measured immediately after leaching phase, Fig. 5) was partly due to the high background concentration of Ca in the tap water (85.5 mg L^{-1}). Fe and Ca concentration in the washing solution decreased during EAOP treatment (Fig. 5). The difference in concentration of both cations in the soil before and after remediation was small (Table 1) and for Ca not statistically significant ($P<0.05$).

While the percentage of total metal removal is an important remediation criterion it is even more important that heavy metals left in the soil after remediation are as non-mobile and non-bioavailable (non-toxic) as possible [27]. Although the concentration of Cu in the soil solution and exchangeable from soil colloids slightly increased after remediation (Table 1), these two soil fractions comprise only a small share of the total soil Cu (1.1% in original and 2.1% in remediated soil). Most of the Cu was removed from the carbonate fraction (58% reduction) and the fraction of soil oxides (40% reduction). Cu was removed from these two fractions by acid extraction (carbonate) and by reductive dissolution (oxides). Since such conditions also occur in the human gastrointestinal tract, metals bound to carbonates and oxides could potentially be orally available to humans after soil ingestion.

Ingestion of soil and dust particles is an important form of exposure to soil pollutants, especially with children, due to their mouthing behavior [28]. We used the PBET model for oral bioavailability, which was designed to simulate both stomach and intestinal phases of the human gastrointestinal tract [13]. The results of the PBET test confirmed the results of sequential extractions. Soil remediation reduced the concentration of Cu available

in the stomach phase by 41.9% and from the intestinal phase by 51% (Table 1). The Cu concentration in the intestinal phase is preferable as a measure of potential metal oral bioavailability, because metal absorption takes place in the small intestine [29,30].

4. Conclusions

The following conclusions can be drawn from our study:

- BDDA EAOP is a viable method for the treatment of soil washing solutions containing EDTA complexes with Cu. The final solution was almost free of Cu and EDTA and safe for discharge.
- BDDA EAOP is also viable as part of a two-phase (soil leaching, soil rinsing) soil remediation method. After BDDA EAOP treatment, Cu was easily removed from the washing solution as electro-deposits on a cathode or by filtration of insoluble metallic precipitate.
- Soil leaching with EDTA ($2 \times 10 \text{ mmol kg}^{-1}$) removed only a minor part of total Cu from the soil, mostly due to fractionation of Cu into non-labile soil fractions, whereby Cu was not easily accessible to the chelant. This is a soil-specific phenomenon, however.
- Regardless of the small total Cu reduction, a significant part of the potentially bio-available Cu was stripped from the soil by remediation.
- In further studies, we will focus on further process optimization and cost-efficiency evaluation of the proposed remediation method.

Acknowledgments

This work was supported by the Slovenian Ministry for Education, Science and Sport, grant J4-6134-0481-04/4.03.

References

- [1] L.A. Brun, J. Maillat, P. Hisinger, M. Pepin, Evaluation of copper availability to plants in copper-contaminated vineyard soils, *Environ. Pollut.* 111 (2001) 293–302.
- [2] J.W. Huang, J.J. Chen, W.R. Berti, S.D. Cunningham, Phytoremediation of lead-contaminated soils: role of synthetic chelates in lead phytoextraction, *Environ. Sci. Technol.* 31 (1997) 800–805.
- [3] C. Kim, Y. Lee, S.K. Ong, Factors affecting EDTA extraction of lead from lead-contaminated soils, *Chemosphere* 51 (2003) 845–853.
- [4] S. Tandy, K. Bossart, R. Mueller, J. Ritschel, L. Hauser, R. Schulin, B. Nowack, Extraction of heavy metals from soils using biodegradable chelating agents, *Environ. Sci. Technol.* 38 (2004) 937–944.
- [5] D. Jiraroj, F. Unob, A. Hagege, Degradation of Pb-EDTA complex by H_2O_2 /UV process, *Water Res.* 40 (2006) 107–112.
- [6] D. Lestan, N. Finzgar, Leaching of Pb contaminated soil using ozone/UV treatment of EDTA extractants, *Separ. Sci. Technol.* 42 (2007) 1575–1584.
- [7] M. Udovic, D. Lestan, EDTA leaching of Cu contaminated soils using ozone/UV for treatment and reuse of washing solution in a closed loop, *Water Air Soil Pollut. B181* (2007) 319–327.
- [8] N. Finzgar, A. Zumer, D. Lestan, Heap leaching of Cu contaminated soil with [S,S]-EDDS in a closed process loop, *J. Hazard. Mater.* 135 (2006) 418–422.
- [9] I. Troster, I. Schafer, M. Fryda, Recent development in production and application of DiaChem® electrodes for wastewater treatment, *New Diam. Front. Carbon Technol.* 12 (2002) 89–97.
- [10] A. Kraft, M. Stadelmann, M. Blaschke, Anodic oxidation with doped diamond electrodes: a new advanced oxidation process, *J. Hazard. Mater.* B103 (2003) 247–261.
- [11] R.T.S. Oliveira, G.R. Salazar-Banda, M.C. Santos, M.L. Calegario, D.W. Miwa, S.A.S. Machado, L.A. Avaca, Electrochemical oxidation of benzene on boron-doped diamond electrodes, *Chemosphere* 66 (2007) 2152–2158.
- [12] N. Finzgar, D. Lestan, Heap leaching of Pb and Zn contaminated soil using ozone/UV treatment of EDTA extractants, *Chemosphere* 63 (2006) 1736–1743.
- [13] A. Turner, K.H. Ip, Bioaccessibility of metals in dust from the indoor environment: application of a physiologically based extraction test, *Environ. Sci. Technol.* 41 (2007) 7851–7856.
- [14] D. Rusjan, M. Strlič, D. Pucko, Z. Korošec-Koruza, Copper accumulation regarding the soil characteristics in Sub-Mediterranean vineyards of Slovenia, *Geoderma* 141 (2007) 111–118.
- [15] Y.P. Kalra, D.G. Maynard, *Methods Manual for Forest Soil and Plant Analysis*, first ed., Canadian Forest Service, Northern Forestry Centre, Edmonton, 1991.

- [16] D. Lestan, H. Grcman, M. Zupan, N. Bacac, Relationship of soil properties to fractionation of Pb and Zn in soil and their uptake into *Plantago lanceolata*, *Soil Sediment Contam.* 12 (2003) 507–522.
- [17] T. Hamano, Y. Mitsuhashi, N. Kojima, N. Aoki, Sensitive spectrophotometric method for the determination of ethylenediaminetetraacetic acid in foods, *Analyst* 118 (1993) 909–912.
- [18] B. Nowack, R. Schulin, B.H. Robinson, Critical assessment of chelant-enhanced metal phytoextraction, *Environ. Sci. Technol.* 40 (2006) 5225–5232.
- [19] N. Finzgar, D. Lestan, Multi-step leaching of Pb and Zn contaminated soils with EDTA, *Chemosphere* 66 (2007) 824–832.
- [20] Y. Yamaguchi, Y. Yamanaka, M. Miyamoto, A. Fujishima, K. Honda, Hybrid electrochemical treatment for persistent metal complexes at conductive diamond electrodes and clarification of its reaction route, *J. Electrochem. Soc.* 153 (2006) 1123–1132.
- [21] D.-M. Zhou, C.-F. Deng, L. Cang, A.N. Alshwabkeh, Electrokinetic remediation of a Cu-Zn contaminated red soil by controlling the voltage and conditioning catholyte pH, *Chemosphere* 61 (2005) 519–527.
- [22] S. Chitra, K. Paramasivan, P.K. Sinha, K.B. Lal, Ultrasonic treatment of liquid waste containing EDTA, *J. Clean. Prod.* 12 (2004) 429–435.
- [23] R.-S. Juang, S.-W. Wang, Metal recovery and EDTA recycling from simulated washing effluents of metal-contaminated soils, *Water Res.* 34 (2000) 3795–3803.
- [24] B. Nowack, Environmental chemistry of aminopolycarboxylate chelating agents, *Environ. Sci. Technol.* 36 (2002) 4009–4016.
- [25] A.E. Martell, R.M. Smith, NIST Critically Selected Stability Constants of Metal Complexes Version 7.0, NIST, Gaithersburg, 2003.
- [26] P. Vandevivere, F. Hammes, W. Verstraete, T. Feijtel, D. Schowanek, Metal decontamination of soil, sediment, and sewage sludge by means of transition metal chelant [S,S]-EDDS, *J. Environ. Eng.* 127 (2001) 802–811.
- [27] J. Kumpiene, A. Lagerkvist, C. Maurice, Stabilization of Pb- and Cu-contaminated soil using coal fly ash and peat, *Environ. Pollut.* 145 (2007) 365–373.
- [28] S. Davis, D.K. Mirick, Soil ingestion in children and adults in the same family, *J. Expo. Sci. Environ. Epid.* 16 (2006) 63–75.
- [29] M.V. Ruby, A. Davis, R. Schoof, S. Eberle, C.M. Sellstone, Estimation of lead and arsenic bioavailability using a physiologically based extraction test, *Environ. Sci. Technol.* 30 (1996) 422–430.
- [30] D.C. Adriano, Trace Elements in Terrestrial Environments; Biogeochemistry Bioavailability and Risks of Metals, second ed., Springer-Verlag, New York, 2001.