



# Electrochemical separation and reuse of EDTA after extraction of Cu contaminated soil

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## ABSTRACT

Recycling chelant is a precondition for cost-effective EDTA-based soil washing remediation technologies. Soil contaminated with  $290 \text{ mg kg}^{-1}$  Cu was extracted with  $40 \text{ mmol EDTA per kg of soil}$ . The spent washing solution (containing  $73 \pm 1 \text{ mg L}^{-1}$  of Cu and  $8.4 \pm 0.0 \text{ g L}^{-1}$  of EDTA) was treated in a single-compartment electrolytic cell using a sacrificial Al anode, at current density  $96 \text{ mA cm}^{-2}$  and pH 6, 10 and pH left unregulated. Electrochemical treatment at pH 10 efficiently separated metal from chelant; 99% of Cu was removed from the solution, mostly by electro-deposition on the stainless steel cathode, while almost all the EDTA was preserved in the solution. The Cu in the EDTA complex was presumably replaced by Al electro-corroded from the anode after electro-reduction of the EDTA at the cathode. After trans-complexation, the EDTA in the treated washing solution retained from 82 to 69% of the Cu extraction potential. Reusing the washing solution in several soil extraction and EDTA recycling steps reduced the Cu soil concentration to  $70 \text{ mg kg}^{-1}$ , while a single use of EDTA solution removed less than half of the Cu from the soil.

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## 1. Introduction

Contamination with Cu is a major problem of viticulture soils and coffee plantations, in which Bordeaux broth ( $\text{CuSO}_4$  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 with chelants has potential as an effective and soil-friendly remediation option for metal contaminated soils. Chelants form coordinate chemical bonds with metals (complexes) and facilitate their solubilization from the soil into the washing solution. In the remediation of Cu contaminated soils, the efficiency of chelant ethylenediamine tetraacetic acid (EDTA) has been widely demonstrated [2,3]. However, EDTA-assisted washing of Cu contaminated soil is still in the development phase. The main obstacle to commercialization is treatment of the spent washing solution containing metallic EDTA complexes before safe wastewater disposal [4].

Several treatment approaches has been proposed. Di Palma et al. [3] evaporated the soil washing solution volume by 75% and then recycled the EDTA by substituting Cu in the EDTA complex with

$\text{Fe}^{3+}$  in acidic conditions, followed by precipitation of the released Cu and  $\text{Fe}^{3+}$  from the EDTA complex as hydroxides at high pH using NaOH, thus liberating EDTA. Lee and Marshal [5] used zero-valent bimetallic mixtures ( $\text{Mg}^0\text{-Pd}^0$ ,  $\text{Mg}^0\text{-Ag}^0$ ) to precipitate Cu and liberating and recycling the EDTA in alkaline pH. Hong et al. [6] separated Cu from EDTA with  $\text{Na}_2\text{S}$ , resulting in almost complete recovery of the metal through precipitation in the form of insoluble metal sulfides. Although these soil washing solution treatment methods have been demonstrated on a laboratory-scale, they are currently still not practical and commercially available.

Recently, electrochemical methods have been gaining importance in the treatment of different wastewaters. They are characterized by the compact size of the equipment, simplicity of operation, and low capital and operating costs [7]. To remove EDTA and Cu from waste soil washing solution, we introduced an electro-oxidation process with a boron-doped diamond anode (BDDA). BDDA has an extreme oxygen overvoltage ( $>3 \text{ V}$ ) before  $\text{O}_2$  forms and enables effective production of hydroxyl radicals ( $\cdot\text{OH}$ ) directly from the electrolysed water. The soil washing solution was electrochemically treated to oxidize EDTA with  $\cdot\text{OH}$ , while Cu was removed by electro-participation on a cathode and as insoluble hydroxide [8]. This method, however, does not recycle the EDTA. In an attempt to recover and recycle the EDTA, Juang and Wang [9] used a two chamber electrolytic cell with an iridium-oxide coated titanium anode and stainless steel cathode, separated by a cation-selective membrane to prevent oxidation of EDTA at the anode [10]. The Cu was reduced and deposited onto the cathode. This method,

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however, is prone to operational problems such as membrane fouling and degradation [3].

In the current study, a sacrificial Al anode and conventional single chamber electrolytic cell were used for electrochemical treatment of spent washing solution obtained after EDTA extraction of Cu contaminated soil. The effect of the pH of the washing solution on the course of the electrochemical treatment was investigated for the separation of metal from the chelant, removal of Cu from the washing solution and recovery of EDTA in its active form for further reuse in soil extraction. This is the first report on using this type of simple electrochemical system for efficient EDTA recycling.

## 2. Materials and methods

### 2.1. Soil properties

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. Cu contaminated soil was collected from the 0 to 45 cm surface layer of a vineyard ( $x=40,370$  m and  $y=400570$  m, Gauss–Kruger coordinate system).

For standard pedological analysis, the pH in soils was measured in a 1/2.5 (w/v) ratio of soil and 0.01 M  $\text{CaCl}_2$  water solution suspension. Soil samples were analyzed for organic matter by modified Walkley–Black titrations [11], cation exchange capacity (CEC) by the ammonium acetate method [12] and soil texture by the pipette method [13].

### 2.2. Soil washing

To obtain the washing solution for the electrochemical treatment, we placed 0.5 kg of air-dried soil and 875 mL of aqueous solution of 40 mmol EDTA (disodium salt) per kg of soil (23 mM EDTA), pH 4.6, in 1.5 L flasks. The concentration of EDTA was selected based on a preliminary investigation. Soil was extracted on a rotating shaker (3040 GFL, Germany) for 24 h at 16 RPM and separated from the washing solution by centrifugation at  $2880 \times g$  for 7 min. Fine particles were removed from the solution by filtration (filter paper density was  $80 \text{ g m}^{-2}$ ).

To extract the soil with recycled EDTA solution, we placed 0.5 kg of air-dried soil and 875 mL of recycled EDTA solution in 15 L flasks. Soil was extracted on a rotating shaker, the washing solution separated and filtrated as described above.

### 2.3. Electrochemical treatment of the soil washing solution

The electrolytic cell consisted of an Al anode placed between two stainless steel cathodes (distance = 10 mm), the overall anode surface was  $63 \text{ cm}^2$  and the surface area ratio between the cathodes and anode 1:1. The electrodes were placed in 500 mL of magnetically stirred soil washing solution in a 1-L flask. Current density was kept at  $96 \text{ mA cm}^{-2}$ , and the cell voltage measured with a DC power supply (Elektronik Invent, Ljubljana, Slovenia). The electrode cell was cooled using a cooling mantle and tap water to keep the temperature of the treated washing solution below  $35^\circ\text{C}$ . The contact time of the electrochemical treatment was calculated as the ratio of the electrode cell volume to the volume of washing solution and multiplied by the operation time (initially 30 min of operation time equaled 3.8 min of contact time). During the process, the pH of the washing solution was left unregulated or regulated to pH 6 and 10 by drop-wise addition of 5 M NaOH and HCl. Samples (20 mL) of washing solution were collected periodically and the pH and EC measured immediately. Samples were subsequently

centrifuged at  $2880 \times g$  for 10 min and the supernatant stored in the cold for further analysis of metals and EDTA. The pellet was suspended in 200 mL of deionized water, acidified with 37% HCl to pH 1.5. The resulting solution was almost clear, with some finely suspended precipitate (probably EDTA, which is weakly soluble in acidic media) and was stored in the cold for further metal and EDTA determination. At the end of the electrochemical treatment, the cathodes were etched with 30 mL of 65%  $\text{HNO}_3$  to dissolve and later measure the concentration of electrodeposited metals. The Al anode was weighed before and after treatment of the washing solution to determine the amount of electro-corroded Al.

During electrolysis, the surface of the Al anode was passivised by an oxide/hydroxide layer, which increased the potential between the electrodes [14]. In order to break down this passive layer and reduce the power consumption, we applied small amounts of  $\text{Cl}^-$  (as NaCl) when the voltage increased above 8 V [7].

To prepare the recycled EDTA solution for soil extractions, the washing solution was electrochemically treated at pH 10 for 24 min (contact time), the recycled EDTA solution separated from the Al hydroxide precipitate by centrifugation at  $2880 \times g$  for 30 min and pH of the solution adjusted to 4.6 (pH of the fresh EDTA solution).

### 2.4. Treatment of the soil washing solution with dosing Al salt

A weight of 2.4 g of  $\text{AlCl}_3$  was dosed in 100 mL of the soil washing solution and gently stirred for 22.7 min, which corresponds to the total contact time of the electrochemical treatment. The amount of chemically dosed Al was the same as the molar amount of Al electro-corroded from the anode. During the coagulation treatment with Al dosing, the pH of the washing solution was kept at pH 10, using 5 M NaOH. The precipitate was removed from the treated solution by centrifugation at  $2880 \times g$  for 30 min, and the concentrations of Cu and EDTA in the supernatant measured. The pH of the chemically treated washing solution was then adjusted to 4.6 (pH of the fresh EDTA solution) and the solution reused for Cu extraction from soil.

### 2.5. EDTA determination

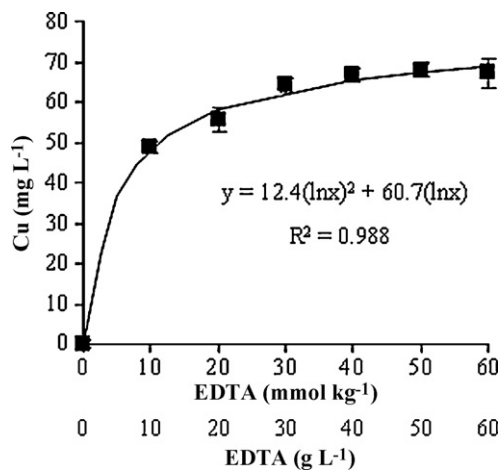
The concentration of EDTA was determined spectrophotometrically according to the procedure of Hamano et al. [15].

### 2.6. Metal determination

Air-dried soil samples (1 g) were ground in an agate mill, digested in *aqua regia* (28 mL), diluted with deionized water to 100 mL, and Cu, Al, Fe and Ca analyzed by flame (acetylene/air) AAS with a deuterium background correction (Varian, AA240FS). Metals in solution were determined by AAS directly. A standard reference material used in inter-laboratory comparisons (Wepal 2004.3/4, Wageningen University, Wageningen, Netherlands) was used in the digestion and analysis as part of the QA/QC protocol. The limits of quantification were 0.03, 0.01, 0.3 and  $0.06 \text{ mg L}^{-1}$  for Cu, Ca, Al and Fe, respectively. Reagent blank and analytical duplicates were also used where appropriate to ensure accuracy and precision in the analysis.

### 2.7. Statistics

The Duncan multiple range test was used to determine the statistical significance ( $P < 0.05$ ) among different treatments. Multiple regression analysis was performed to detect correlations between the EDTA concentration and Cu soil removal. The computer program Statgraphics 4.0 for Windows was used.



**Fig. 1.** The concentration of Cu in the washing solution after extraction of soil with different concentrations of EDTA. Experimental data were fitted with a regression model, which correlates Cu removal ( $y$ ) and EDTA concentrations ( $x$ ). Error bars represent standard deviation from the mean value ( $n=3$ ).

### 3. Results and discussion

#### 3.1. Soil washing with fresh EDTA solution

The following pedological properties of the soil used in the experiment were assessed: pH 7.2, organic matter 5.8%, CEC 39.4 mg 100 g<sup>-1</sup> of soil, sand 14.7%, silt 50.2%, clay 35.1%. The soil texture was sandy loam. The soil contained 290 mg kg<sup>-1</sup> Cu, 17.6 g kg<sup>-1</sup> Fe and 31.5 g kg<sup>-1</sup> Ca.

The results of optimization of the EDTA concentration indicated that Cu removal from soil increased with EDTA concentration (Fig. 1). We chose to use 40 mmol EDTA per kg<sup>-1</sup> of soil (23 mM EDTA) in further experiments, which removed 44 ± 1% of Cu (and 0.04% Fe and 9.6% Ca) from the soil. At higher EDTA concentrations, the Cu removal efficiency started to decrease considerably, as previously reported [8]. The molar ratio between Cu in the soil and EDTA in the chosen washing solution was 1: 8.8. It is known that even strong chelants, such as EDTA, cannot remove Cu and other toxic metals from soil entirely, even if they are applied in high molar ratios relative to the metals in soil [16].

After soil extraction and before treatment in the electrolytic cell, the concentration of Cu in the spent soil washing solution was 73 ± 1 mg L<sup>-1</sup>. Concentrations of Fe and Ca, the two major soil metals which also form strong complexes with EDTA and could therefore interfere with Cu removal from the soil, were 7 ± 1 and 968 ± 3 mg L<sup>-1</sup>, respectively. The complex formation stability constant ( $\log K_s$ ) of Fe<sup>3+</sup> with EDTA is 25.1 (at 25 °C and ionic strength  $\mu = 0.1$ ) and is higher than the  $\log K_s$  of Cu–EDTA (18.8 at 25 °C and  $\mu = 0.1$ ). The  $\log K_s$  for Fe<sup>2+</sup> and Ca<sup>2+</sup> are 14.3 and 10.6, respectively, significantly lower than the  $K_s$  of Cu–EDTA [17]. The relatively low concentration of Fe in the washing solution could be the consequence of the low solubility of Fe soil minerals and prevalence of reduced over oxidized Fe. The high concentration of Ca was presumably the consequence of the dissolution of soil carbonates after soil extraction with EDTA [18]. The EDTA concentration was 8.4 ± 0.0 g L<sup>-1</sup> (39.0 ± 0.5 mM) and the pH of the washing solution 7.1. The difference between the initial EDTA concentration and the concentration after soil washing (1.6%) presumably occurred due to the partial absorption of EDTA into soil solid phases [19].

#### 3.2. Electrochemical treatment of soil washing solution

After soil extraction, the spent soil washing solution was treated in an electrolytic cell, in which Al ions were generated from the

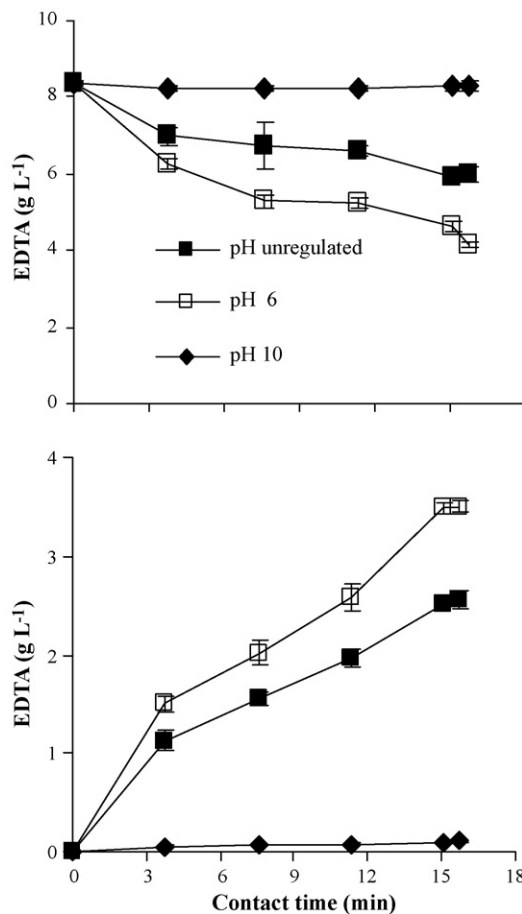
sacrificial Al anode, Eq. (1):



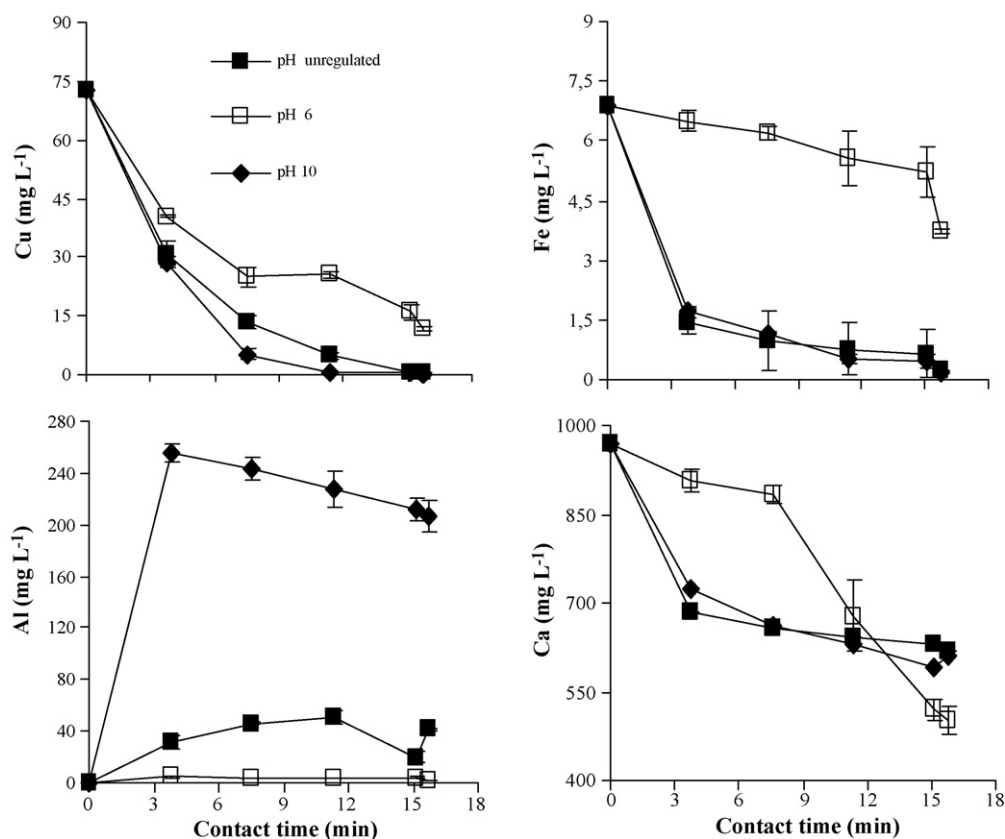
The hydrolysed Al ions form large networks of Al–O–Al–OH flocks, with a large surface area and considerable absorption (electro-coagulation) capacity [20].

To investigate the effect of pH on the electrochemical treatment process, the washing solution was left either unregulated or the pH was adjusted to 6 and 10. In the solution left unregulated, the pH of the treated washing solution increased over time from pH 7.1 to 9.0 since the electrochemical system generated enough OH<sup>-</sup> at the electrode to counteract the H<sup>+</sup> released by the formation of Al hydroxides [21]. The voltage between the electrodes was kept close to the initial 8 V, as described in Experimental section. The amount of Al consumed from the Al anode ranged from 2.4 ± 0.2 for solution treated at pH 10 to 2.7 ± 0.3 at pH 6. Although the difference in the amount of electro-corroded Al was not significant ( $p < 0.05$ ), it could be due to the higher efficiency of electrochemical systems with an Al anode at alkaline compared to neutral pH [22]. The electro-conductivity of the washing solution decreased from the initial 10.9 ± 1.0 to 2.1 ± 0.5 mS cm<sup>-1</sup> (treatment at pH 10), presumably due to the electro-coagulation of ionic species on the Al-hydroxide flocks or electro-deposition on the stainless steel cathode.

After treatment at pH 10, the EDTA remained almost entirely preserved in the washing solution (Fig. 2). On the other hand, approximately one third and one-half of the initial EDTA, respectively, was removed from the solution with pH left



**Fig. 2.** Concentration of EDTA in the washing solution and in the precipitate during electrochemical treatment at pH 6, 10 and pH left unregulated. Error bars represent standard deviation from the mean value ( $n=3$ ).



**Fig. 3.** Concentrations of Cu, Fe, Al and Ca in the washing solution during electrochemical treatment at pH 6, 8 and pH left unregulated. Error bars represent standard deviation from the mean value ( $n=3$ ).

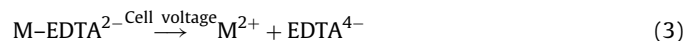
unregulated and solution treated at pH 6 (Fig. 2). This happened presumably by electro-coagulation of negatively charged EDTA complexes (i.e. Cu-EDTA<sup>2-</sup>) by various Al hydroxides, such as Al(OH)<sup>2+</sup>, Al(OH)<sub>2</sub><sup>+</sup>, Al<sub>2</sub>(OH)<sub>2</sub><sup>4+</sup>, Al<sub>6</sub>(OH)<sub>15</sub><sup>3+</sup>, Al<sub>7</sub>(OH)<sub>17</sub><sup>4+</sup>, Al<sub>8</sub>(OH)<sub>20</sub><sup>4+</sup>, Al<sub>13</sub>O<sub>4</sub>(OH)<sub>24</sub><sup>7+</sup>, Al<sub>13</sub>(OH)<sub>34</sub><sup>5+</sup> formed during the electrochemical process. These species have a long lasting positive charge before they finally transform into amorphous Al(OH)<sub>3</sub> [14]. Al(OH)<sub>3</sub> is a typical amphoteric metal hydroxide and in alkaline conditions forms negatively charged Al hydroxide, Eq. (2):



This negative charge of Al-hydroxide flocks also explains why negatively charged EDTA complexes were not removed but remained in the washing solution treated at pH 10 (Fig. 2).

While the EDTA remained almost completely preserved in the washing solution, electrochemical treatment at pH 10 efficiently removed Cu (Fig. 3). This can be explained by the replacement of Cu from the complex with EDTA, removal of liberated Cu from the solution and formation of Al-EDTA complex (trans-complexation). EDTA is a hexaprotic system. The degree of EDTA protonation and

complexation with metals depends on the pH of the washing solution and the nature and concentration of the metal ions present. Although Al-EDTA has a lower log  $K_s$  than Cu-EDTA (16.3 and 18.8, respectively [20]), Al ions formed in abundant concentrations during electro-corrosion of the Al anode. Furthermore, the stability of Al-EDTA complex has been reported to be higher in a solution with pH 9 than in solutions with pH 7 and 4 [22], while the stability of Cu-EDTA complex slightly decreases in solutions with pH > 9 [23]. Cu (and possibly other metals, M) could be released from the EDTA complex after the reduction reaction at the cathode [9], Eq. (3):



The higher concentration of Al (presumably as Al-EDTA) in the washing solution treated at pH 10 compared to solutions treated at lower pH (Fig. 3) supports the trans-complexation hypothesis. To verify whether reduction of the EDTA complex on the cathode (Eq. (3)) is a necessary condition for trans-complexation, we compared the electrochemical process and direct dosing of Al into the spent washing solution at pH 10. The same amount of Al (as AlCl<sub>3</sub>) was dosed as the amount of electro-corroded Al. When the treated solution was reused for soil extraction, only 4 ± 1% of Cu was removed. Simple dosing of Al obviously does not lead to EDTA recovery in an active form. Chemical Al dosing did, however, remove 52 ± 1% of Cu and 24 ± 31% of EDTA from the washing solution. This was expected, since coagulation of pollutants by dosing Al salts is a commonly used process [21].

After trans-complexation, metals liberated from the EDTA complex could be removed from the solution by direct electro-deposition on the cathode, Eq. (4):



**Table 1**

Balance of Cu after electrochemical treatment of the soil washing solution at various pH. Standard deviation from the mean value ( $n=3$ ) was calculated; letters (a, b, c) denote statistically different values within each category according to the Duncan test ( $p < 0.05$ ).

Treated washing solution	Cu balance (%)			$\Sigma$
	In solution	Precipitated	Electrodeposited	
pH unregulated	0.6 ± 0.1 <sup>a</sup>	8 ± 1 <sup>c</sup>	91 ± 1 <sup>b</sup>	100 ± 3
pH 6	16 ± 1 <sup>c</sup>	10 ± 1 <sup>b</sup>	73 ± 1 <sup>a</sup>	99 ± 3
pH 10	0.3 ± 0.1 <sup>b</sup>	5 ± 1 <sup>a</sup>	94 ± 1 <sup>c</sup>	99 ± 3



**Table 2**  
Cu removal with fresh and electrochemically treated EDTA solutions from original and continuously extracted soil during four consecutive steps of soil extraction and washing solution treatment. The loss of EDTA after soil extraction, after electrochemical treatment of the solution and the EDTA extraction potential were calculated.

Soil extraction/Solution treatment	Cu removed (%)	Initial EDTA conc. (g L <sup>-1</sup> )	EDTA conc. after extraction (g L <sup>-1</sup> )	EDTA conc. after treatment (g L <sup>-1</sup> )	Lost EDTA - extraction (%)	Lost EDTA - treatment (%)	EDTA extraction potential (%)
Fresh soil							
1. Ext./treat.	44	8.5	8.4	8.2	1.6	1.6	100
2. Ext./treat.	32	8.2	7.2	6.1	13	15	82
3. Ext./treat.	26	6.1	5.7	5.4	6	6	69
4. Ext./treat.	25	5.4	5.1	/	5	/	69
Continuously extracted soil							
1. Ext./treat.	44	8.5	8.4	8.2	1.6	1.6	/
2. Ext./treat.	19	8.2	7.1	6.3	13	11	/
3. Ext./treat.	8	6.3	5.6	5.3	6	6	/
4. Ext./treat.	5	5.3	5.0	/	5	/	/
Total Cu extracted	76						

precipitation as insoluble hydroxides, or absorption and co-precipitation on Al-hydroxide flocks, Eq. (5):

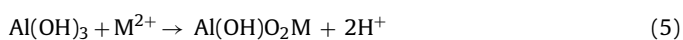


Table 1 indicates that the majority of Cu was removed from the spent washing solution by electro-deposition on the cathode. A small amount of Cu, up to 10% (treatment at pH 6), was precipitated. Cu removal from the solution treated at pH 10 was faster and more efficient than from other two solutions, resulting in a fairly low final Cu concentration of  $0.3 \pm 0.1 \text{ mg L}^{-1}$  (Fig. 3, Table 1). Removal of Fe from solutions with pH 10 and with pH unregulated (but predominantly alkaline) was more efficient than from the solution with pH 6 (Fig. 3), presumably due to the formation of insoluble Fe hydroxides under alkaline conditions.

Johnson et al. [10] reported that using a Pt anode oxidized EDTA into various compounds, including CO<sub>2</sub>, formaldehyde and ethylenediamine. Juang and Wang [9] concluded that, due anodic oxidation, the recovery of Cu and EDTA was not possible in a conventional electrolytic cell. They introduced a two-chamber electrolytic cell separated by a cation-selective membrane to prevent EDTA contact with electrodes. We demonstrated, however, that using an Al anode at pH 10 enables efficient Cu and EDTA separation in a conventional, simple, single-compartment electrolytic cell, without significant EDTA degradation. Al is presumably oxidized at the anode (Eq. (1)) preferentially to EDTA oxidation, due to the high Al reactivity (electro-positivity).

### 3.3. Reuse of the treated EDTA soil washing solution

Since we used a high molar ratio of EDTA against soil Cu, as is usual practice in soil washing [16], only part of the EDTA in the washing solution was complexed to Cu; some EDTA was presumably left in the original form or in various stages of protonation. The spent non-treated washing solution was therefore expected to retain some extraction potential and indeed we found that it removed  $15 \pm 2\%$  of Cu from contaminated soil.

Table 2 shows the efficiency of the recycled EDTA (at pH 10) for Cu extraction from the original (always new) soil and from continuously extracted (always the same) soil through several soil extraction and washing solution treatment (ext./treat.) steps, followed by pH adjustment to 4.6 (pH of the fresh EDTA solution). First, fresh EDTA solution was used (1st ext./treat. step), followed by the reuse of electrochemically recycled EDTA in 2nd, 3rd and 4th ext./treat. steps.

The efficiency of the reused washing solution for Cu removal from original soils decreased by 43% from the 1st to the 4th ext./treat. step. This could partly be explained by the absorption of EDTA into the soil during extraction (up to 8.2%, Table 2) and EDTA

lost during the solution treatment phase (up to 15%, Table 2). This loss consisted of EDTA precipitation (electro-coagulation), anodic oxidation [10] and degradation by chlorine (Cl<sub>2</sub>) and hypochlorite (HOCl), which are strong oxidants generated anodically following additions of NaCl into the electrolytic chamber to break down the anodic passive film [7]. In addition to the material lost, recycled EDTA lost up to 31% of inherent Cu extraction potential (Table 2). This decrease was calculated by comparing the measured Cu removal data (Table 2) with data calculated from a regression model that correlates Cu removal and EDTA concentration in freshly prepared washing solutions (Fig. 1). The Cu extraction efficiency of Al-EDTA (formed during electrochemical treatment) is presumably lower compared to the Na<sub>2</sub>-EDTA in the fresh washing solution.

As shown in Table 2, considerably less Cu was removed from continuously extracted soil with each ext./treat. step. This was expected, since Cu from labile soil fractions was first removed, leaving behind metal in chemically stable species and bound to non-labile soil fractions. Nevertheless, recycling EDTA washing solution enabled the reduction of Cu soil content from an initial  $290\text{--}70 \text{ mg kg}^{-1}$ , significantly below the critical Cu concentration ( $140 \text{ mg kg}^{-1}$ ) set in EU legislation [24]. For comparison, using the EDTA solution only once removed less than half of the Cu from the soil and such remediation did not meet the legislative criteria. The EDTA lost due to the absorption and washing solution treatment was similar to that measured after extractions of original soils (Table 2).

During remediation with recycled EDTA, some Al released from the EDTA complex may be deposited in the soil. However, after extraction (continuous soil extractions, Table 2) the concentration of Al in the soil was even slightly lower ( $17.5 \pm 1.1 \text{ g kg}^{-1}$ ) than before ( $18.6 \pm 0.6 \text{ g kg}^{-1}$ ). This result indicates that the quantity of Al extracted from the soil (by original Na<sub>2</sub>-EDTA and protonated EDTA) was higher than the quantity of Al released from Al-EDTA. Furthermore, although Al is known to reduce plant growth in acid soils, in which Al<sup>3+</sup> cations disturb root growth and function, it is naturally present in the soil and non-toxic in pH-neutral conditions [25].

## 4. Conclusions

Electrochemical treatment of soil washing solution obtained after EDTA extraction of Cu contaminated soil, using an Al anode in a conventional electrolytic cell at pH 10, efficiently separated EDTA and Cu, which was almost quantitatively removed from the treated washing solution by electro-deposition on the cathode. Electrochemical treatment separated EDTA in an active form—the EDTA solution retains most of its Cu extraction potential. Minor part of EDTA was lost from washing solution during electrochemical treat-

ment and due to absorption onto the soil solid phases during soil extraction. Electrochemical treatment of the washing solution has potential for technically simple and effective recycling and reuse of EDTA as a part of Cu soil washing technologies.

### Acknowledgement

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