Electrochemical EDTA recycling after soil washing of Pb, Zn and Cd contaminated soil

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ABSTRACT

Recycling of chelant decreases the cost of EDTA-based soil washing. Current methods, however, are not effective when the spent soil washing solution contains more than one contaminating metal. In this study, we applied electrochemical treatment of the washing solution obtained after EDTA extraction of Pb, Zn and Cd contaminated soil. A sacrificial Al anode and stainless steel cathode in a conventional electrolytic cell at pH 10 efficiently removed Pb from the solution. The method efficiency, specific electricity and Al consumption were significantly higher for solutions with a higher initial metal concentration. Partial replacement of NaCl with KNO_3 as an electrolyte (aggressive Cl^- are required to prevent passivisation of the Al anode) prevented EDTA degradation during the electrolysis. The addition of $FeCl_3$ to the acidified washing solution prior to electrolysis improved Zn removal. Using the novel method 98, 73 and 66% of Pb, Zn and Cd, respectively, were removed, while 88% of EDTA was preserved in the treated washing solution. The recycled EDTA retained 86, 84 and 85% of Pb, Zn and Cd extraction potential from contaminated soil, respectively.

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1. Introduction

Metal pollution of soil is widespread across the globe. Acute poisoning may occur in humans due to a high intake of toxic metals, while their presence in the ecological cycles may cause chronic illness due to metal bio-accumulation. In South Eastern Europe, for example, there are more than 1.8 million contaminated sites, of which 240,000 are in need of remedial treatment [1]. However, soil remediation technologies have not been adequately developed. In soil-washing technologies, the solubility and removal of metals can be enhanced by lowering the pH with acids or by adding chelants, which form soluble metal complexes. Acid enhancement changes the soil properties, and is not effective in highly buffered, carbonate soils [2]. On the other hand, chelants do not interact with the soil. Extensive evaluations of numerous chelating agents have shown that ethylenediamine tetraacetate (EDTA) is the most effective for many metals [3]. It is of interest that EDTA has also been used medically to promote removal of especially Pb from the human body.

The development of EDTA-based soil washing technology is currently hampered by the lack of the cost-effective treatments of the spent soil washing solution, preferably including chelant recycling. Although, several approaches have been proposed, none have been commercialised. Ager and Marshall [4] used zero-valent bimetallic mixtures (Mg^0–Pd^0, Mg^0–Ag^0) to precipitate Pb from the solution while liberating EDTA in alkaline pH. Metals liberated from the EDTA complex were cemented to the surfaces of the excess magnesium or removed from the solution as insoluble hydroxides. The method is efficient but could be economically prohibitive. Hong et al. [5] separated Pb from EDTA with Na_2S and $Ca(OH)_2$ under alkaline (pH 10) conditions, resulting in almost complete recovery of metals through precipitation in the form of insoluble metal sulphides. While $Ca(OH)_2$ provided Ca^{2+} ions to compete for the EDTA ligand (by replacing the chelated contaminant metal), Na_2S was used as an anionic precipitant to provide HS^- and S^{2-} to compete with EDTA for the contaminating metals. This method has been found to have limited application due to the hazardous nature of the produced reagents and the sludge, the cost and operational difficulties. Kim and Ong [6] recycled chelant from Pb–EDTA solution by substituting Pb with Fe^{3+} under acidic conditions, followed by precipitation of the released Pb with phosphate (Na_2HPO_4) at near neutral pH. Fe^{3+} ions were then precipitated as hydroxides at high pH using NaOH, thus liberating EDTA. The process, alkaline precipitation, is the simplest way to separate metals from chelant and does not use expensive or hazardous reagents. However, the cost of the process is affected by high reagent consumption: for Pb precipitation a phosphate/Pb molar ratio of about 30 was necessary [6]. Di Palma et al. [7] reduced reagent consumption by evaporating

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the washing solution volume by 75%, precipitation of EDTA under acidic conditions and recycling the residual EDTA using alkaline precipitation, as described above. Juang and Lin [8] tempted electrolytic recovery of Cu and chelant from equimolar EDTA solution in a two-chamber cell separated with a cation exchange membrane Neosepta CM-1 to prevent EDTA anodic oxidation. Iridium oxide coated on titanium (Ti/IrO$_2$) and stainless steel electrodes were used as the anode and cathode, respectively. Under the optimal current density (139 A m^2) and initial catholyte pH of 2.2, the recovery rate of Cu was >95% at sufficiently high Cu–EDTA concentrations. Recovery of other divalent metals, including Pb, from their EDTA solution was possible but less efficient. The method is furthermore prone to operational problems, such as membrane fouling and degradation, and a high feed of the spent washing solution is required to prevent EDTA precipitation in acidic media (protons are generated in the cathode chamber) and deposition on the membrane surface [9].
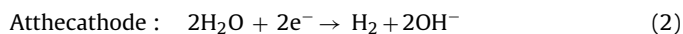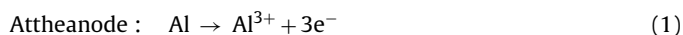
The EDTA recycling procedures described above have been demonstrated on a laboratory scale. In addition to their specific disadvantages, single metal–EDTA solutions were handled in all the mentioned studies. However, most contaminated sites contain multi-contaminated soils. Juang and Wang [9] tested a membrane separated, two-chamber electrochemical treatment for a binary, Pb and Cu, complexed solution and found lower metal recovery and current efficiency than for single metal contamination, regardless of the metal concentration ratios.

In order to overcome problems with the use of a cation exchange membrane and EDTA precipitation, we proposed a novel electrochemical treatment of spent washing solution in a conventional single chamber electrolytic cell (without membrane) under alkaline conditions (pH 10) using a sacrificial Al anode. We demonstrated the method feasibility for treatment of spent washing solution with a single toxic metal, Pb [10] and Cu [11] and their EDTA complexes. The theoretical explanation of the proposed method is given in the section below.

In this study, the feasibility of the proposed electrochemical method for simultaneous removal of Pb, Zn and Cd, and EDTA recovery from a washing solution obtained after EDTA extraction of multi-metal contaminated soil was evaluated. This is an innovation, since simultaneous treatment of EDTA complexes with several metals is ineffective with currently proposed methods [9] and the recent electrochemical method using a sacrificial Al anode has not yet been tested [10,11]. The factors governing the specific electricity consumption and specific Al consumption after electrocorrosion of the anode were examined. Strategies to improve the efficiency of the EDTA recycling were investigated.

2. Theoretical background

The experimental set-up for electrochemical EDTA recovery from a spent soil washing solution is explained in Section 3.3. When a potential difference is applied between the Al anode and a cathode, Al ions are generated from the anode and hydroxyl ions from the cathode:

$$\text{At the anode}: \quad \text{Al} \rightarrow \text{Al}^{3+} + 3e^- \tag{1}$$

$$\text{At the cathode}: \quad 2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^- \tag{2}$$

Al^{3+} and OH$^-$ ions react further to form various monomeric Al hydroxides, such as Al(OH)$^{2+}$, Al(OH)$_2$$^+$ or Al$_2$(OH)$_2$$^{4+}$ and polymeric Al hydroxides, such as Al$_6$(OH)$_{15}$$^{3+}$, Al$_7(OH)_{17}$$^{4+}$, Al$_8(OH)_{20}$$^{4+}$, Al$_{13}O_4(OH)_{24}$$^{7+}$ or Al$_{13}$(OH)$_{34}$$^{5+}$ [12]. Finally, they all transform into amorphous Al(OH)$_3$ and combine to form flocks with a large surface area and considerable absorption capacity. Due to the high Al reactivity (electro-positivity), Al is oxidized at the anode preferentially to EDTA oxidation.

Table 1
Selected properties of two contaminated soils (A and B) used for extractions.

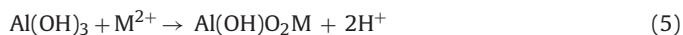| Soil properties	Soil A	Soil B
pH (CaCl$_2$)	6.57	7.0
Organic matter (%)	14.2	7.2
CEC (mmol C$^+$ 100 g^{-1})	20.7	20.3
Sand (%)	51.0	38.5
Silt (%)	42.5	55.4
Clay (%)	6.5	6.1
Texture	Sandy loam	Silty loam

To allow electrochemical EDTA recycling from the spent washing solutions, metals (M) are liberated from the complex with EDTA, possibly on the outside of the electric double layer of the cathode:

$$\text{M-EDTA}^{2-} \rightarrow \text{M}^{2+} + \text{EDTA}^{4-} \tag{3}$$

Metals are reduced and deposited onto the cathode,

$$\text{M}^{2+} + 2e^- \rightarrow \text{M}_{(s)} \tag{4}$$

precipitated as insoluble hydroxides or absorbed and co-precipitated on Al hydroxide flocks:

$$\text{Al(OH)}_3 + \text{M}^{2+} \rightarrow \text{Al(OH)O}_2\text{M} + 2\text{H}^+ \tag{5}$$

While M are removed from the spent washing solution (mostly by electro-deposition), the EDTA remained preserved in the solution. Al(OH)$_3$ is typically amphoteric and, under the alkaline conditions (pH 10) maintained during electrolysis, forms negatively charged Al hydroxide:

$$\text{Al(OH)}_3 + \text{OH}^- \rightarrow \text{Al(OH)}_4^- \tag{6}$$

This negative charge of Al hydroxide flocks explains why negatively charged EDTA is not removed and remains recycled in the washing solution. EDTA is presumably recycled as Al–EDTA complex, since Al ions form in abundant concentrations during electro-corrosion of the Al anode and since they are not electrodeposited (the reduction potential Al^{3+}/Al is very low, −1.66 V, [13]). Furthermore, the stability of Al–EDTA complex formation has been reported to be higher in a solution with pH 9 than in solutions with pH 7 and 4 [14] while the stability of, for example, the Pb– and Cu–EDTA complex slightly decreases in solutions with pH > 9 [15].

3. Materials and methods

3.1. Soil properties

Soils were used from two locations in the Mežica Valley, Slovenia, which has been exposed to more than three hundred years of active lead mining and smelting. The first soil (soil A) was collected from the top 30 cm layer of a vegetable garden and it contained 3980 ± 60 mg kg^{-1} Pb, 1170 ± 60 mg kg^{-1} Zn and 26 ± 1 mg kg^{-1} Cd. The second soil (B) was collected from abandoned arable land, now used as pasture, and was contaminated with 1431 ± 39 mg kg^{-1} Pb, 587 ± 14 mg kg^{-1} Zn and 12 ± 0 mg kg^{-1} Cd. Standard pedological analysis was made on homogenized soil samples (Table 1). The pH in the soils 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 Walkley–Black titrations [16], cation exchange capacity (CEC) by the ammonium acetate method [17] and soil texture by the pipette method [18].

3.2. Soil extraction

To obtain soil washing solutions of various Pb, Zn and Cd concentrations, we placed 0.5 kg of air-dried soil (A and B) and 1000 mL of aqueous solution with different EDTA (disodium salt) concentrations (from 7.5 to 50 mM EDTA) in 1.5 L flasks. Soil was extracted on

a rotating shaker (3040 GFL, Germany) for 24 h at 16 rpm. Approximately 850 mL of the washing solution was obtained from each flask after separation of the washing solution from the solid soil phase by centrifugation at 2880 × g for 10 min. Fine particles were removed from the washing solutions by filtration (filter paper 80 g m^{-2}).

To concentrate metals in the washing solutions (used to assess factors important for specific electricity and Al consumption), we used the same washing solution for two or three extractions of the fresh soil.

3.3. Treatment of the washing solutions in the electrolytic cell

The electrolytic cell was composed of electrodes placed in a 1 L glass flask in which 500 mL of washing solution was magnetically stirred. The Al anode was placed between two stainless steel cathodes (distance = 10 mm). The overall anode surface was 63 cm^2 and the surface area ratio between the cathodes and anodes was 1:1. The electrode cell was cooled using a cooling mantle and tap water to keep the temperature of the treated washing solution below 35 °C. Electrical current densities were adjusted to one of four determined values: 64, 96, 192 and 288 mA cm^{-2}. The cell voltage was measured with a DC power supply (Elektronik Invent, Ljubljana, Slovenia). The contact time of electrochemical treatment was calculated by Eq. (7):

$$t_{con} = \frac{t_{op} \cdot V_{con}}{V_{op}} \tag{7}$$

where t_{con} is the contact time of the washing solution in the electrolytic cell, t_{op} is the operation time of the experiment, V_{con} is the volume of the electrolytic cell and V_{op} is the volume of the washing solution in the experiment. Initially, 30 min of operation time equalled 3.78 min of contact time.

During the process, the pH of the washing solution was regulated to pH 10 by drop-wise addition of 5 M NaOH and 96% H$_2$SO$_4$. The voltage during electrolysis was regulated below 8 V by the addition of 5 M NaCl and 1 M KNO$_3$ as electrolytes. Twenty mL samples of treated washing solution were collected periodically and centrifuged at 2880 × g for 10 min. The concentration of Pb in the supernatant was measured after each sample was taken and electrolysis was stopped when the concentration and removal rate of Pb from the treated washing solution were no longer significant. To study the possible effect of FeCl$_3$ addition to the washing solution on EDTA recycling and metal removal efficiency, the molar concentrations of Pb, Zn and Cd in the used washing solution were first determined. The same molar concentration of FeCl$_3$ was added to the washing solution and magnetically stirred for 2 h before electrochemical treatment.

3.4. Use of recycled EDTA solution

The recycled EDTA solution for further soil extractions was obtained after electrochemical treatment (contact time 26.5 min) of the washing solution obtained after extraction of soil B with 30 mM kg^{-1} EDTA. The concentration of recycled EDTA was measured and a fresh washing solution with the same EDTA concentration was prepared. To compare the efficiency of recycled and fresh EDTA solutions, 50 g of soil B was extracted with 100 mL of each, in five replicates, using a rotating shaker (24 h, 16 rpm).

3.5. EDTA determination

The concentration of EDTA in the samples was determined spectrophotometrically according to the procedure described by Hamano et al. [19]. The method involves the reaction of EDTA in washing solution with Fe^{3+} under acidic conditions to produce
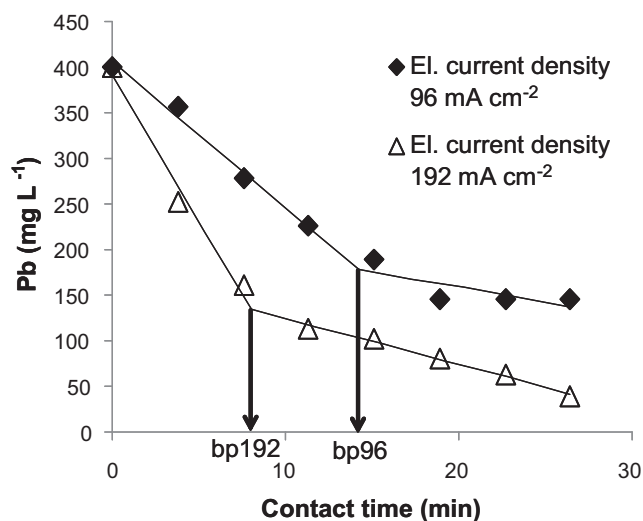

Fig. 1. An example of determination of the "breaking point".

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}.

3.6. Metal determination

Air-dried soil samples (1 g) were ground in an agate mill, sieved through a 160 μm mesh and digested in a microwave oven (CEM, MDS-2000) in 12 mL of *aqua regia* (20 min at 175 °C). The digestions were conducted in triplicate. After cooling, digested samples were filtered through Whatman no. 4 filter paper and diluted with deionized water up to 100 mL. The pseudo-total concentration of Pb, Zn, Cd and Fe were determined by flame (acetylene/air) AAS with a deuterium background correction (Varian, AA240FS). The metal concentration in the solutions was 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 limit of quantification for Pb, Zn, Cd and Fe were 0.1, 0.01, 0.02 and 0.06 mg L^{-1}, respectively. Reagent blank and analytical duplicates were also used where appropriate, in order to ensure accuracy and precision in the analysis.

3.7. Calculation of the specific electricity consumption

Specific electricity consumption (q) for treatment of the washing solution was calculated using the following equation (Eq. (8)):

$$q = \frac{U \cdot I \cdot t}{m} \tag{8}$$

where U is the voltage measured during the experiment (in V), I the applied electrical current (in A), t the operation time at "breaking point" (in h) and m the amount of metals (Pb, Zn, Cd and Fe) (in g) removed from the washing solution in operation time t. The "breaking point" was determined by segmented regression using package "segmented" in program R [20] using data on the metal (Pb, Zn, Cd and Fe) concentrations change vs. time. Regression indicated two segments of linear relation, as shown in Fig. 1. The "breaking

Table 2
Removal of Pb, Zn and Cd from soils (A and B) and metal concentrations in used washing solutions before electrochemical treatment. Solutions (π, #) were obtained after dilution of the original ones with deionized water, and solutions ([2, 3, 4]) after repeated extraction of the fresh soil.

Solution, EDTA (mmol kg^{-1})	Soil (% of removed metal)			Soil solution (metal concentrations mg L^{-1})				
	Pb	Zn	Cd	Pb	Zn	Cd	Fe	ΣPb,Zn,Cd,Fe
Soil A								
60, π	65	37	52	1298	216	6.8	238	1759
75, π, #	81	44	61	1615	260	8.0	520	2403
100[2]	62	36	55	2484	423	14	624	3545
Soil B								
15	41	21	35	369	81	2.4	32	484
15[2]	38	20	34	690	151	4.8	10	856
25[4]	29	14	23	1036	216	6.4	33	1291
50[2]	45	25	38	802	188	5.3	268	1263
50[3]	38	20	35	1020	231	7.4	195	1453
100[2]	53	26	39	956	198	5.4	375	1534

[2] Used twice for soil extraction.
[3] Used three times for soil extraction.
[4] Used four times for soil extraction.
2-times diluted solution.
π 3-times diluted solution.

point" represents the threshold contact time at which the rate of electrochemical metal removal from the washing solution falls significantly. To calculate specific electricity consumption, the contact time at "breaking point" was recalculated to operation time by Eq. (7) and q expressed in W h g^{-1}.

The Al anode was weighed before and after treatment of the washing solution to determine the amount of electro-corroded Al. The specific consumption of Al during the treatment was calculated by dividing the amount of consumed Al (in g) by the amount of metals (Pb, Zn, Cd and Fe) (in g), removed from the washing solution in the "breaking point" time.

3.8. Statistics

A linear mixed model for longitudinal data [21,22] was used in statistical analysis of the data from the electrochemical treatment of different washing solutions. The specific electricity consumption was modelled as a function of electrical current density, initial metal (Pb, Zn, Cd and Fe) concentration and initial EDTA concentration. The data was taken as longitudinal, because there were several consecutive measurements in time on each washing solution sample.

Analysis of variance with Duncan's test was used for comparison of the average EDTA consumption due to different kinds of pH adjustment. In the last two experiments, the t-test was used for comparison of the average metals (Pb, Zn and Cd) reduction in the two different treatments (with or without FeCl$_3$; fresh or recycled EDTA).

All statistical analyses were done in R programme [20].

4. Results and discussion

4.1. Soil metal removal

As shown in Table 2, soil extractions (soil A and B) with EDTA removed between 29 and 81% of Pb, 14 and 44% of Zn and 23 and 61% of Cd from the solid soil phases into the liquid phase. Metals in soil are not entirely accessible to chelants, especially in soils rich in organic matter, such as ours (Table 1). Zn was the least extractable. This could be partly explained by the stability constants (log K_s) of EDTA complex formation. For example, log K_s of EDTA–Pb is 18.0 (at 25 °C and ionic strength $\mu = 0.1$), while log K_s for EDTA–Zn is lower: 16.5 [23]. Another possible reason for the low Zn removal is the high percentage of non-extractable Zn bound to the residual soil fraction (65%), as found in Mezica soil [24]. Most of the Pb was found in the

more labile organic matter and carbonate fraction (55% and 25%, respectively). A modified Tessier's sequential extraction procedure was used in the cited study [24], in order to investigate the distribution of toxic metals among different soil fractions (from more to less labile): soluble in soil solution, exchangeable from soil colloids, bound to soil carbonates, bound to Fe and Mn oxides, bound to organic matter, and present in the residual fraction obtained after the digestion of the residual soil sample with *aqua regia*.

4.2. Specific electricity and Al consumption

Initial metal and EDTA concentration and current density were studied as primary factors governing the specific electricity consumption, q (Wh per g of Pb, Zn, Cd and Fe removed) and specific Al consumption during electrochemical treatment. We prepared 12 soil washing solutions with different initial total concentrations of metals (Pb, Zn, Cd and Fe), ranging from 485 to 3545 mg L^{-1}, and EDTA concentrations ranging from 2140 to 20,642 mg L^{-1} (Table 2). Each of these washing solutions was exposed to electrical current densities of 64, 96, 192 mA cm^{-2}, and three of them also to 288 mA cm^{-2}.

q and specific Al consumption (m_{Al}) were strongly linearly correlated variables, linear regression model for q is (Fig. 2):

$$q = -2.40 + 14.08\, m_{Al} \tag{9}$$

$r^2 = 0.98$, the confidence interval for the model parameters are: [−5.35, 0.56] for the intercept and [13,15] for the slope. Specific Al consumption is influenced by the initial metal concentration in the same way as q. The difference between specific Al consumption obtained during the experiment (broken line) and theoretical specific Al consumption calculated using Faraday's law (continuous line) is shown in Fig. 2. According to Treacy et al. [14], the presence of EDTA in an alkaline solution results in an increase of anodic dissolution of Al, which is consistent with our results. Another possible reason for the observed discrepancy between the theoretically predicted and observed specific Al consumption is that the geometry of the electrolytic cell assembly and conditions of operation were probably not optimal [25].

The q of the electrochemical process exponentially decreased with increasing initial total metal concentration in the washing solutions and also with EDTA concentration (Fig. 3A and B). The log transformation of the q data was therefore considered to be a dependent variable in the linear mixed effects model (Eq. (10)). The electrical current density, the initial metal concentration and initial EDTA concentration were included in the linear mixed model
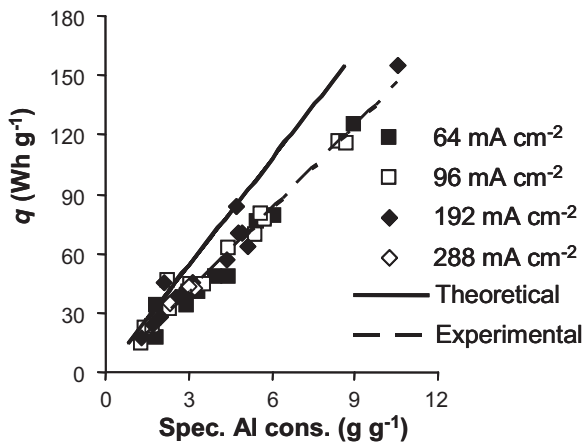
Fig. 2. Specific Al consumption (per g of total metals (Pb + Zn + Cd + Fe) removed) and specific electricity consumption (q) during electrochemical treatment of soil washing solutions at different current densities. The continuous line represents the theoretical amount of specific Al consumption (according to Faraday's law). The broken line represents the linear model (as explained in the text) of experimentally obtained specific Al consumption.

as independent variables (X). The analysis of variance shows that only the initial metal concentration of the washing solution has a significant influence on q ($P = 0.0009$), there is no statistical significance influence of the initial EDTA ($P = 0.1512$) nor of the electrical current density ($P = 0.4172$).

The final linear mixed effects model is:

$$\ln(q) = \beta_0 + \beta_1 X + T + \varepsilon \qquad (10)$$

where β_0 and β_1 are parameters of the model, T represents the random influence of each sample and ε represents the random residuals of the model. The estimates for the two model parameters presenting the intercept and fixed effect of the initial metal concentration of the washing solution are:

$$\ln(q) = 4.69 - 0.0008X \qquad (11)$$

The restricted maximum likelihood estimation method (REML) was used for calculations [26]. A higher initial concentration of Pb, Zn, Cd and Fe by 100 mg L^{-1} decreased q by 8.0% (with a 95% confidence interval between 4.2% and 11.8%). The influence of EDTA in the linear mixed effects model is not significant, because of the strong correlation between EDTA and the initial concentration of metals.

Higher initial metal (mostly Pb, Table 2) and EDTA concentrations in the washing solutions presumably decrease the q by increasing the driving force for mass transfer during electrolysis, and thus facilitating the current efficiency of electrodeposition of metals on the cathode. Similar to our results, higher economic current efficiency at higher metal concentrations were observed by Juang and Lin [8] for the treatment of metal–EDTA solutions in a two-chamber electrolytic cell separated with a cation exchange membrane.

4.3. EDTA oxidation control

At the beginning of the electrochemical treatment of the used washing solutions (listed in Table 2), the initial potential between the electrodes was high, up to 30 V, due to the lack of electrolytes. Later during the process, the potential started to increase again due to Al anode surface passivisation by an oxide/hydroxide layer. This layer forms during electrolysis in neutral as well as in acidic and alkaline media, although the oxide composition and structure are different [27]. In order to increase the process current efficiency and to break down the passive layer, we applied a single dose of
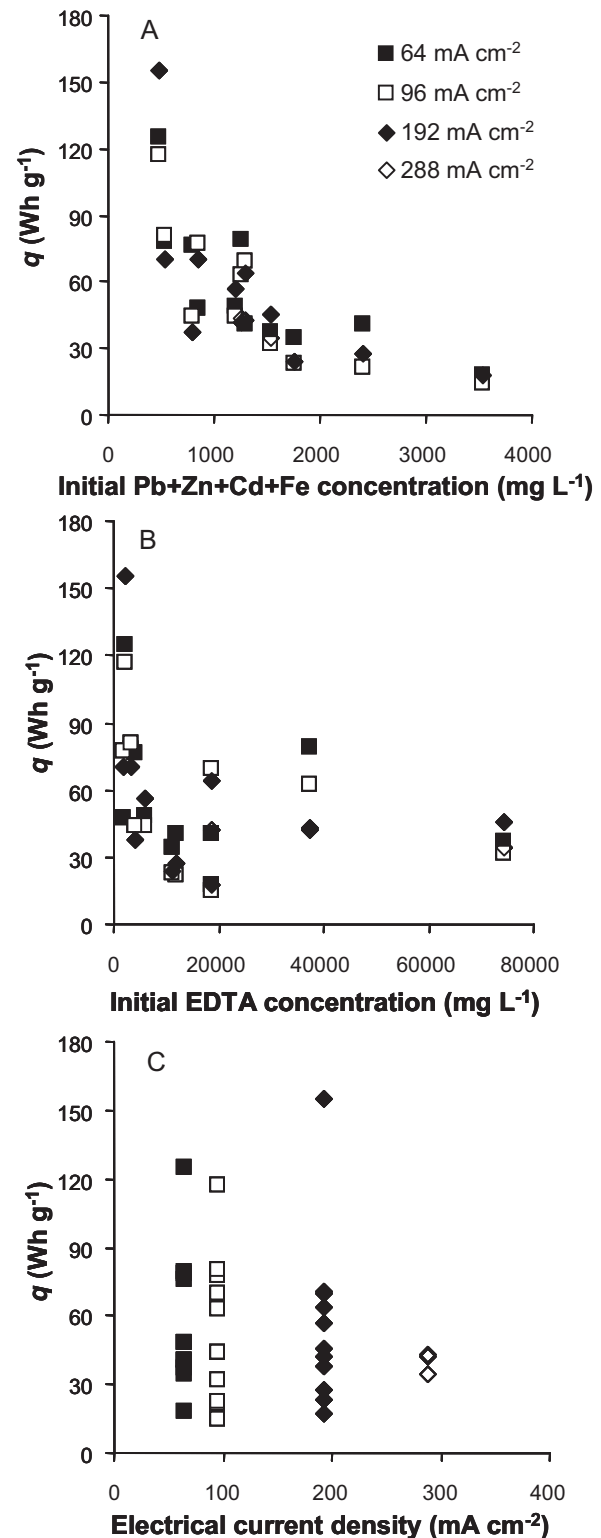

Fig. 3. Specific electricity consumption (q) after treatment of soil washing solutions with different initial metal (Pb + Zn + Cd + Fe) concentrations, different initial EDTA concentrations and at different electrical current densities. Discriminate relations of q with initial metal concentrations (A), EDTA concentrations (B) and electrical current densities (C) are presented.
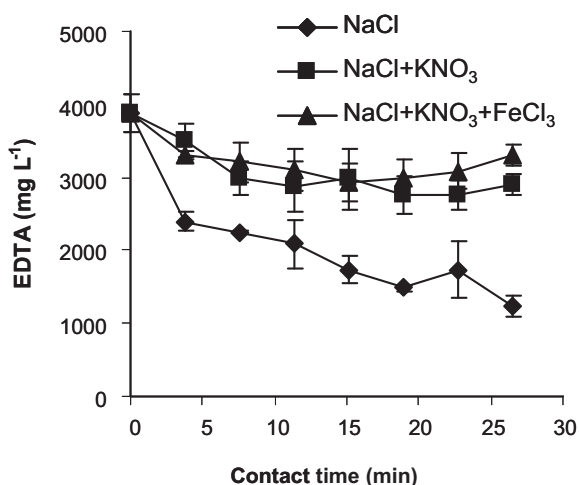
Fig. 4. Concentration of EDTA in the washing solution obtained after extraction of soil B during electrochemical treatment (current density 192 mA cm^{-2}) using three different regimes of pH control and electrolyte addition: (1) NaCl, (2) NaCl + KNO$_3$, and (3) NaCl + KNO$_3$ + FeCl$_3$. Error bars represent standard deviation from the mean value (n = 3). The coefficient of variation was between 0.2 and 14 (n = 3).

Cl$^-$ (10 mL of 5 M NaCl per L of soil washing solution (soil B)) at the beginning of the process. This decreased and kept the voltage below 8 V. However, the addition of NaCl to the electrolytic chamber is followed by anodic formation of hypochlorite radicals (ClOH$^\bullet$), which are strong oxidants [28] and degrade organic compounds (R) such as EDTA:

$$\text{At the anode:} \quad H_2O + Cl^- \rightarrow ClOH^\bullet + H^+ + 2e^- \quad (12)$$

$$R + ClOH^\bullet \rightarrow RO + H^+ + Cl^- \quad (13)$$

Consequently, up to 67% of initial EDTA was lost from the treated washing solutions (Fig. 4).

To preserve the EDTA during the electrochemical process and, at the same time, to control the electric potential, we compared three different regimes of electrolyte addition. Washing solution with 3743 mg L^{-1} EDTA, and 867, 154 and 4.7 mg L^{-1} of Pb, Zn and Cd, respectively, was used in these and further experiments. We first applied the same regime as used initially: we adjusted the pH of the washing solution (500 mL) to 10 (1 M NaOH) before we started the electrolysis and then immediately lowered the voltage to 8 V with a single-dose application of NaCl (10 mL, 5 M). The second regime involved the addition of 4 mL of 5 M NaOH after we started electrolysis. This not only increased and set the pH value to 10 but also decreased the initial voltage to about 25 V. We then added KNO$_3$ (8 mL, 1 M) as electrolyte, which lowered the voltage to 15 V. Further use of KNO$_3$ was not efficient in voltage reduction, probably because this electrolyte could not prevent the formation of the insulative oxide/hydroxide layer on the anode. An additional 5 mL of 5 M NaCl was necessary to break the oxide/hydroxide layer and decrease the voltage to 8 V. Later during the process, only small amounts of NaCl were applied to control the voltage at 8 V. The third treatment regime involved the addition of FeCl$_3$ (1.27 g L^{-1}) 2 h before electrolysis. The starting potential between the electrodes was 17 V, the addition of NaOH (7 mL) adjusted the pH to 10 and lowered the voltage to 12 V; KNO$_3$ (2 mL) lowered it further to 11 V. During the process, small amounts of NaCl again kept the voltage at 8 V. As explained below, FeCl$_3$ was included in the third regime to help improve the efficiency of Zn and Cd removal from the treated washing solution.

The results of analysis of variance and Duncan's test showed significant differences ($P < 0.0000$) between all three-treatment regimes. As shown in Fig. 4, the first regime, when the pH was adjusted prior to electrolysis and the voltage lowered with a single-

dose application of NaCl, it resulted in the destruction of 68% (95% confidence interval is between 63 and 73%) of the initial EDTA. Adjusting the pH after the start of electrolysis and partial replacement of NaCl with KNO$_3$, which is not chemically aggressive toward EDTA, showed less destruction of the chelant. During the second regime, 25% of the EDTA (95% confidence interval is between 20 and 30%) was destroyed and the third treatment regime resulted in a decrease in EDTA concentration of 15% (95% confidence interval is between 9 and 20%).

Although, small additions of Cl$^-$ seem necessary to maintain the reactive surface of the Al anode and thus the loss of EDTA due to Cl oxidation could not be prevented entirely, our results indicate that optimization of electrolyte additions and perhaps the design of a more effective electrolytic cell (to reduce the double electric layer and enhance the diffusion of electrolytes towards the electrodes) could further improve not only EDTA recovery but also the process economics.

4.4. Zn and Cd removal

Fig. 5 shows that during electrolysis (treatment with NaCl and KNO$_3$), Pb was recovered from the treated soil washing solution (soil B) in preference to Zn and Cd. At the end of the treatment, 98, 49 and 56% of Pb, Cd and Zn were removed, respectively. In our previous study [10], 80% of Pb was electro-deposited on the cathode (Eq. (4)) (80%) and the rest was removed from the solution by precipitation, in alkaline conditions mostly absorbed on Al-hydroxide flocks (Eq. (5)). The electrodeposition and removal of metals from the washing solution are governed by Eqs. (3) and (4). The EDTA reduction rate at the cathode (Eq. (3)) should be lower for metal–EDTA complexes with higher log K_s. However, the formation constant of Cd–EDTA (18.2 at 25 °C and ionic strength μ = 0.1, [23]) is only slightly higher than the log K_s of Pb–EDTA (18.0), while log K_s for Zn–EDTA (16.5) is lower. Nevertheless, Zn removal from the treated washing solution was significantly less efficient than that of Pb (Fig. 5). It appears that the reduction tendency of metals (Eq. (4)) and not their log K_s of EDTA complex formation is pivotal for metal recovery. Furthermore, central metal ions in the EDTA complex, which are easily reducible in the electric field near the cathode, should leave the chelant more easily. Indeed, the reduction potentials of free metal ions: −0.13 V for Pb^{2+}/Pb > −0.40 V for Cd^{2+}/Cd > −0.76 for Zn^{2+}/Zn [13], explain the preferential removal of Pb.

To enhance Zn and Cd removal, we applied FeCl$_3$ to the used washing solution (in a concentration equimolar to the total initial concentration of Pb, Zn and Cd) before electrochemical treatment. The use of FeCl$_3$ did not improve the removal of Pb (Fig. 5) but the reduction of the Zn and Cd concentrations was significantly different between the two treatments (P = 0.0118 for Zn and P = 0.0007 for Cd). The lower impact on Cd was probably due to the already low initial Cd concentration in the washing solution.

The addition of FeCl$_3$ acidified the media to pH 3. Under acidic conditions, Fe^{3+} is known to replace other metals (Pb, Zn and Cd) in a complex with EDTA [7], due to the high log K_s of Fe–EDTA formation (25.1, [23]). Under alkaline conditions during the electrolysis, the released Pb, Zn and Cd either precipitated onto the cathode or as insoluble hydroxides (Eqs. (4) and (5)). During the electrolyis, Fe^{3+}, which is easily reducible (with a reduction potential of free Fe^{3+}/Fe^{2+} ions 0.77 V) leaves the complex with EDTA (Eqs. (3) and (4)) and EDTA formed complexes with Al, which electro-corroded from the sacrificial anode. Al is electropositive, with a reduction potential of Al^{3+}/Al ions −1.66 V and therefore with a very low tendency to leave the chelant in the electric field near the cathode. The above mechanism explains the results shown in Fig. 5.
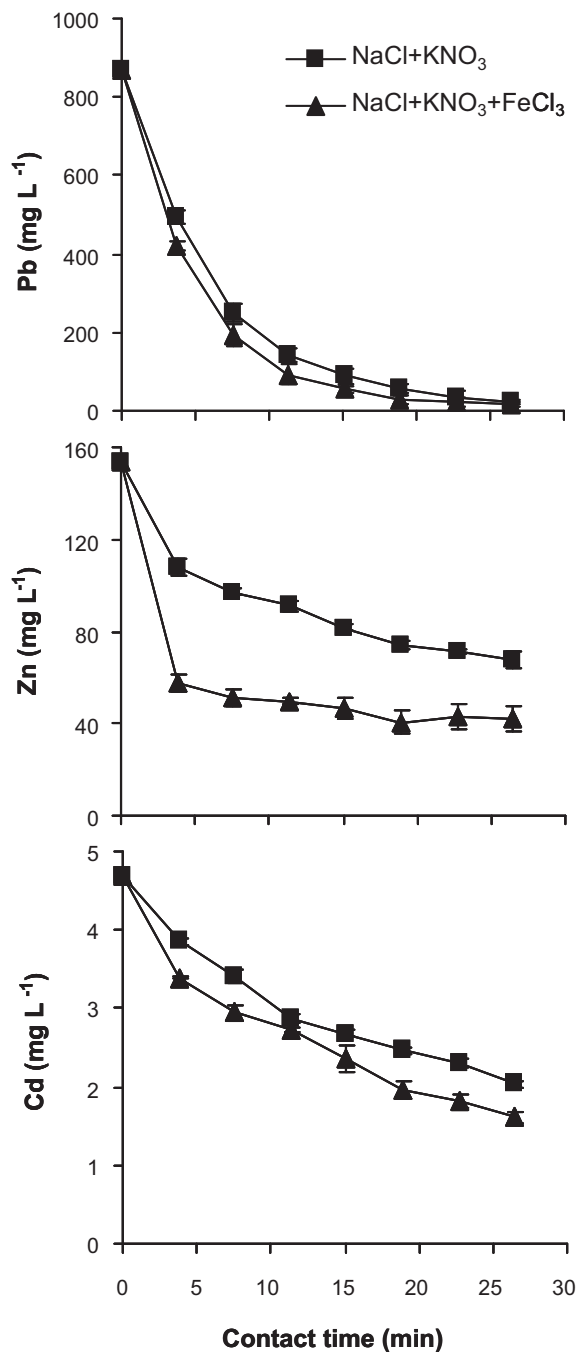
Fig. 6. Pb, Zn and Cd removed from soil (soil B) after extractions with fresh and recycled EDTA solutions. Error bars represent standard deviation from the mean value ($n = 5$).

nificant, mainly due to the low variability of replicates ($P = 0.0003$ for Pb, $P = 0.0000$ for Zn and Cd, coefficient of variation = 3.7%). The small decrease in soil metal extraction efficiency can be explained by complexation of EDTA to Al in the recycled washing solution. The stability constant of Al–EDTA (log K_s = 16.3) is significantly higher than the stability constants of (differently protonated) Na–EDTA complexes in the fresh washing solution, with log K_s values less than 2 [23]. The replacement of the central metal ion in the complex depends on the stability of the complex, so washing solutions with EDTA complexes with higher log K_s have lower potential to extract metals from the soil [6].

Based on our experimental results, Pb–, Zn– and Cd–EDTA spent washing solution can be recycled without losing much of the EDTA extraction capabilities. Recycling would reduce the amount of EDTA required and the volume of wastewater generated during the remediation process. However, at the end of the process, both toxic EDTA and metals need to be removed completely for safe wastewater discharge. One way this could be achieved by electrochemical advanced oxidation processes using, for example, a boron-doped diamond anode for complete EDTA degradation and removal of metals from the waste solution by (electro) precipitation [24].

5. Conclusions

The following conclusions can be drawn from our work:

- The efficiency of toxic metal extraction from contaminated soils with EDTA follows the order: Pb = Cd > Zn.
- Electrochemical treatment of the spent soil washing solutions using a sacrificial Al anode at pH 10 is suitable for solutions with an initial metal concentration >1500 mg L^{-1}, due to the lower specific electricity and Al consumption.
- Using KNO$_3$ as electrolyte instead of chemically aggressive Cl ions prevents EDTA destruction during the electrochemical treatment of the soil washing solution.
- Lead is efficiently removed during electrolysis, due to the high reduction potential of Pb^{2+}/Pb. Acidification of the spent soil washing solution and the addition of FeCl$_3$ before electrochemical treatment at pH 10 significantly enhance removal of also Zn and Cd from the treated solution.
- Electrochemical treatment separated the EDTA in an active form—the EDTA solution retains most of its Pb, Zn and Cd extraction potential.

Fig. 5. Pb, Zn and Cd removal from the soil washing solution (soil B) during electrochemical treatment (current density 192 mA cm^{-2}) using two different regimes of pH control and electrolyte addition: (1) NaCl + KNO$_3$ and (2) HCl + KNO$_3$ + FeCl$_3$. Error bars represent standard deviation from the mean value ($n = 3$). The coefficient of variation was between 0.3 and 26 ($n = 3$).

4.5. Efficiency of recycled EDTA solution for removal of soil metals

To test the efficiency of the recycled EDTA (we applied the third electrochemical treatment regime, Section 4.3) for extraction of Pb, Zn and Cd from the soil (soil B), we compared the recycled and freshly prepared EDTA solutions. Both solutions had the same EDTA concentration of 3377 mg L^{-1} (9.1 mM) and pH adjusted to 4.6 (the pH of the fresh EDTA solution). As shown in Fig. 6, the recycled EDTA removed 9, 5 and 7 percentage points less Pb, Zn and Cd, respectively, compared to the freshly prepared solution. Although the differences were slight, they were nonetheless statistically sig-
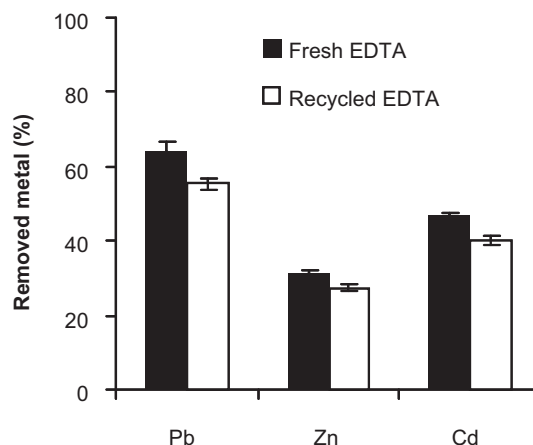
Applying the measures evaluated in our study significantly increases the feasibility of electrochemical recycling and reuse of EDTA from spent soil washing solutions containing several contaminating metals, as a part of soil washing technologies.

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