Using electrocoagulation for metal and chelant separation from washing solution after EDTA leaching of Pb, Zn and Cd contaminated soil

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ABSTRACT

Electrocoagulation with an Al sacrificial anode was tested for the separation of chelant and heavy metals from a washing solution obtained after leaching Pb ($3200\,mg\,kg^{-1}$), Zn ($1100\,mg\,kg^{-1}$), and Cd ($21\,mg\,kg^{-1}$) contaminated soil with EDTA. In the electrochemical process, the sacrificial anode corroded to release Al^{3+} which served as coagulant for precipitation of chelant and metals. A constant current density of $16–128\,mA\,cm^{-2}$ applied between the Al anode and the stainless-steel cathode removed up to 95% Pb, 68% Zn and 66% Cd from the soil washing solution. Approximately half of the initial EDTA remained in the washing solution after treatment, up to 16.3% of the EDTA was adsorbed on Al coagulant and precipitated, the rest of the EDTA was degraded by anodic oxidation. In a separate laboratory-scale remediation experiment, we leached a soil with 40 mmol EDTA per kg of soil and reused the washing solution (after electrocoagulation) in a closed loop. It removed 53% of Pb, 26% of Zn and 52% of Cd from the soil. The discharge solution was clear and colourless, with pH 7.52 and $170\,mg\,L^{-1}$ Pb, $50\,mg\,L^{-1}$ Zn, $1.5\,mg\,L^{-1}$ Cd and 11 mM EDTA.

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1. Introduction

Heavy metal contaminated soil is one of the commonest environmental engineering problems. Removal of metals from soil by means of soil washing using chelants is a potential remediation option, especially for contaminated calcareous soils, where the extraction of metals with acids is impeded by the high soil pH buffer capacity. Chelants form coordinate chemical bonds with metals (complexes) and facilitate their solubilization from the soil into the washing solution.

Ethylenediaminetetraacetic acid (EDTA) has been the chelant most often tested for soil washing, since it forms strong complexes (with a ratio 1:1) with most polluting heavy metals [1] and is relatively inexpensive compared to other chelants (in Europe, it costs about 1.3€ per kg for the technical-grade chemical from a major European manufacturer).

The main obstacle to full scale application and commercialization of soil washing technologies with EDTA remains, however, the subsequent treatment of the washing solution (rich with metal–EDTA complexes) before the waste solution can be safely discharged. Various strategies have been proposed for this. Kim and Ong [2] used trans-complexation: the Pb in the EDTA complex

was replaced with Fe^{3+} at low pH and the Pb was subsequently removed using NaOH as a precipitating agent. The process proved difficult if the EDTA was complexed with more than one metal and the large consumption of chemicals means relatively high operating costs. Ager and Marshall [3] investigated the ability of zero-valent Mg and Pd to substitute metals in EDTA complexes. Zeng et al. [4] proposed the precipitation of heavy metals from the soil washing solution as insoluble sulphides. The sodium sulphide consumed in this process, however, is more expensive than the EDTA. Juang and Wang [5] proposed electrolytic recovery of Pb and Cu from a solution containing EDTA. This process uses sensitive and expensive cation-exchange membranes and is technically quite complicated. Di Palma et al. [6] proposed reverse osmosis for the separation of EDTA complexes from the washing solution. The soil colloidal particles tend to clog the membranes. Tejowulan and Hendershot [7] separated EDTA using an anion exchange resin. These are expensive (>$100 for 500 g). Finzgar and Lestan [8] proposed oxidative decomposition of EDTA complexes in washing solution using advanced oxidation processes (AOP). The treatment was much less effective when the washing solution was either turbid or coloured. Electrochemical (E)AOP [9,10] was more robust but consumed a significant amount of electricity and uses an expensive boron-doped diamond anode. Metals were removed from the soil washing solution by absorption in AOP and mainly by filtration in EAOP.

In the current study, we evaluated electrocoagulation with an Al sacrificial anode for the separation of Pb, Zn and Cd from a washing solution obtained after leaching contaminated soil with EDTA. Elec-

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trocoagulation is a simple and efficient electrochemical method for the purification of wastewaters containing organic or metallic pollutants [11]. When a potential difference is applied between the Al (or Fe) anode and a cathode, Al (or Fe) ions are generated from the anode and hydroxyl ions from the cathode. The reactions for the electrochemical system with an Al anode are as follows:

At the anode, Eq. (1):

$$Al \rightarrow Al^{3+} + 3e^- \qquad (1)$$

At the cathode, Eq. (2):

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad (2)$$

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]. Jiang et al. [13] reported that Al_{13} polymers comprised 43% of all Al hydroxide species, with a long lasting positive charge. Finally, they all transform into amorphous $Al(OH)_3$ and combine to form flocks with a large surface area and considerable absorption capacity for pollutants and for particle aggregation [14,15].

Electrocoagulation has a long history as a water treatment technology, but it has never been accepted as a mainstream technology [16]. Nevertheless, electrocoagulation has been successfully used to treat special wastewaters, such as oil wastes [17], black liquor from the paper industry [12], dye solutions and textile wastewaters [18] and nutrient enriched wastewaters [19]. Although electrocoagulation is primarily used to remove organic and suspended materials from various types of effluents, its use for metal removal, for example Cu, Zn and Cr from electroplating wastewaters [20] and Pb from acidic soil leachate [21] has also been recorded.

This is the first report of the use of electrocoagulation as part of chelant-based remediation of heavy metal contaminated soil. We hypothesized that negatively charged EDTA–heavy metal complexes will absorb on flocks of various monomeric and polymeric positively charged Al hydroxides which form during electrocoagulation, and could afterwards be removed from the soil washing solution by sedimentation and centrifugation. First, we investigated the effect of current density on Pb, Zn, Cd and EDTA removal from the soil washing solution. Second, the feasibility of using electrocoagulation in soil remediation was tested with the recently proposed two-phase soil leaching method with recycling of process waters in a closed loop [8].

2. Materials and methods

2.1. Soil samples and analysis

Soil was collected from the 0 to 30 cm surface layer of a vegetable garden in the Mežica Valley, Slovenia. The Mežica Valley has been exposed to more than 300 years of active lead mining and smelting. Soils in the valley, including 6600 ha of agricultural land, are polluted primarily with Pb but also with Zn and Cd.

For standard pedological analysis, the pH in soils was measured in a 1/2.5 (w/v) ratio of soil and 0.01 M $CaCl_2$ solution suspension. Soil samples were analyzed for organic matter by modified Walkley–Black titrations [22], cation-exchange capacity (CEC) by the ammonium acetate method [23] and soil texture by the pipette method [24]. The following values were obtained: pH 6.57, organic matter 14.2%, CEC 20.7 mg 100 g^{-1} of soil, sand 51.0%, silt 42.5%, and clay 6.5%. The soil texture was sandy loam.

2.2. Electrolytic cell

The electrolytic cell consisted of an Al anode and two stainless-steel cathodes, with an electrode distance of 10 mm. The overall anode surface was 63 cm^2. The surface area ratio between the cathodes and anode was 1:1. Electrodes were placed in 500 mL of the soil washing solution in a magnetically stirred 1 L flask. Current densities were adjusted (from 16 to 128 mA cm^{-2}) and the cell voltage was 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 °C.

2.3. Electrochemical treatment of the soil washing solution

To obtain the washing solution, we placed 4.5 kg of air-dried soil in a 15 cm diameter soil columns (two replicates) and leached the soil with a 5000 mL aqueous solution of 40 mmol EDTA (disodium salt) per kg of soil for 64 h. Approximately 3000 mL of the washing solution per column was collected.

For each treatment (three replicates) 500 mL of the washing solution (obtained after soil leaching as described above) was transferred into the electrolytic cell. Current densities used were 16, 32, 64 and 128 mA cm^{-2}. Samples (20 mL) of washing solution were collected at intervals from 4 to 45 min of contact time in the electrode cell and the pH and EC were measured. Contact time was calculated as the ratio of the electrode cell volume to the volume of the washing solution and multiplied by the operation time (initially 30 min of operation time equalled 3.78 min of contact time). At the end of the electrochemical treatment, the cathodes were etched with 30 mL of 65% HNO_3 to dissolve deposited Pb, Zn and Cd and clean the cathode. Concentrations of HNO_3 dissolved metals were determined by atomic absorption spectrophotometry (AAS) as described below. Samples were centrifuged at $2880 \times g$ for 30 min. The supernatant was stored in the cold for the further analysis of Pb, Zn, Cd, Al, Fe, Ca and EDTA concentrations. Al hydroxide flocks and other precipitated matter remained in pellets after centrifugation. To determine the percentage of Pb, Zn, Cd and Al, a sample was taken from the pellet, dissolved in *aqua regia* and metals were analyzed by AAS. To determine the EDTA, part of the pellet was suspended in 200 mL of deionized water and acidified with 37% HCl (to approx. pH 1.5) to obtain fine, homogenous suspension. The percentage of Pb, Zn, Cd and EDTA that was removed from the washing solution by electrodeposition and electrocoagulation or remained in the treated washing solution was calculated.

The specific energy consumption (SEC) of the electrochemical treatment of the washing solution was calculated using the following equation (Eq. (3)):

$$SEC = \frac{U \times I \times t}{m} \qquad (3)$$

where U is the voltage measured during the treatment (in V), I the applied electrical current (in A), t the operation time (in h) and m the amount of pollutants (Pb, Zn and Cd) removed from the washing solution (in g). SEC was expressed in kWh g^{-1}.

The Al anodes were weighed before and after electrochemical treatment of the washing solution to determine the amount of Al consumed during the process.

2.4. Coagulation with $AlCl_3$ dosing

A weight of 2292 mg of $AlCl_3$ was dosed in 100 mL of the washing solution and stirred for 30.24 min (reaction time). The concentration of Al was the same as the concentration dissolved from the Al anode at 32 mA cm^{-2} (4638 mg L^{-1} Al^{3+}) when the contact time

Table 1
Effect of current density applied in electrolytic cell on voltage between electrodes, specific energy consumption (SEC) of electrochemical treatment, Al anode consumption and balance of EDTA after treatment of the washing solution using electrocoagulation with an Al sacrifice anode.

Current density (mA cm^{-2})	Process parameters				EDTA (% of initial)	
	Voltage (V)		SEC (Wh g^{-1})	Al anode consumption (g)	Solution	Electrocoagulated
	Initial	Final				
16	4.25 ± 0.07	16.3 ± 2.3	[a]46 ± 6	[a]2.11 ± 0.34	[a]52.3 ± 8.8	[a]12.5 ± 2.3
32	5.75 ± 0.52	22.1 ± 7.8	[a]70 ± 11	[a]2.32 ± 0.41	[a]51.3 ± 0.7	[ab]14.2 ± 3.6
64	7.67 ± 0.23	25.6 ± 10.7	[b]148 ± 52	[a]2.51 ± 0.78	[a]47.1 ± 6.9	[ab]14.3 ± 1.5
128	12.5 ± 1.2	24.1 ± 8.9	[b]164 ± 21	[a]2.49 ± 0.85	[a]50.1 ± 16.6	[b]16.3 ± 2.6

Means ($n = 3$) followed by the same letter are not significantly different according to the Duncan test ($P < 0.05$).

of the electrochemical reaction equalled the reaction time of the dosing experiment. The precipitate was then removed from the solution with centrifugation at 2880 × g for 30 min, and the concentrations of Pb, Zn and Cd in solution were analyzed using AAS. AlCl$_3$ was dosed, since it was not possible to add Al as an Al hydroxide solution due to its low solubility.

2.5. Two-phase soil leaching using EDTA and electrocoagulation

A two-phase soil remediation method using EDTA for soil leaching and electrocoagulation with a sacrificial Al anode was simulated in a laboratory-scale experiment. Air-dried soil (4.5 kg) was sieved (5 mm mesh) and placed in a 15 cm diameter column 28 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 40 mmol EDTA per kg of soil in 3 L unbuffered tap water. The washing solution was circulated in the first (leaching) phase (peristaltic pump, flow rate 15 mL min^{-1}) solely through the soil (pathway A, Fig. 3) for 64 h. In the second (rinsing) phase, the washing solution circulated through the soil after treatment of the solution in an electrode cell (current density, 32 mA cm^{-2}) and removal of metals and EDTA by centrifugation (electrocoagulated material) and by periodically etching the cathode with 65% HNO$_3$ (electrodeposited metals), shown in Fig. 3 as pathway B. 20 mL samples of washing solution were collected from the column outlet after each 4 h of operation time and pH, EC and Pb, Zn, Cd, Al, Fe, Ca and EDTA concentrations were determined. Approximately 40% of the total initial water was added to the system during remediation, to compensate for water loss during the process (sampling, evaporation, electrolysis). At the end of remediation (when removal of Pb, Zn and Cd from the washing solution had become inefficient), the soil column was dismantled. Samples were taken from different soil layers (profile) for further determination of Pb, Zn, Cd, Al, Fe and Ca residual in soil after remediation.

2.6. EDTA determination

Samples of washing and soil rinsing solution were centrifuged at 2880 × g for 30 min and EDTA determined spectrophotometrically according to the procedure of Hamano et al. [25].

2.7. Metal determination

Air-dried samples of non-leached and leached soil (1 g) were ground in an agate mill, sieved through a 160 μm mesh and digested in a glass beaker on a hotplate with 28 mL of *aqua regia* solution (HCl and HNO$_3$ in a 3:1 ratio (v/v)) for 2 h at 110 °C. Condensation of the evaporating fumes was achieved via circulation of cool tap water through glass tubes placed on top of the glass beakers. After cooling, the digested samples were filtered through Whatman no. 4 filter paper and diluted with deionised water up to 100 mL. Concentrations of Pb, Zn, Cd Al, Fe and Ca were analyzed by flame (acetylene/air) AAS with a deuterium background correc-

tion (Varian, AA240FS). Metals in the washing solution and in HNO$_3$ solutions (dissolved electrocoagulated and otherwise precipitated or electrodeposited metals) 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 recovery percentages were 126 ± 2, 114 ± 20, 113 ± 0, 98 ± 2, 90 ± 4 and 70 ± 4%, and the limits of quantification (LQ) were 0.1, 0.01, 0.02, 0.06, 0.01 and 0.3 mg L^{-1} for Pb, Zn, Cd, Fe, Ca and Al, respectively. Reagent blank and analytical duplicates were also used where appropriate to ensure accuracy and precision in the analysis.

2.8. 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. Treatment of EDTA soil washing solution with electrocoagulation

The concentrations of major metals present in the soil washing solution before treatment in the electrolytic cell were 1420 ± 200 mg L^{-1} Pb, 260 ± 30 mg L^{-1} Zn, 9 ± 1 mg L^{-1} Cd, 1120 ± 40 mg L^{-1} Ca and 220 ± 50 mg L^{-1} Fe. The initial EDTA concentration was 18,100 ± 1600 mg L^{-1} (48.5 ± 4.0 mM) and the pH of the washing solution was 7.1. The molar ratio between major cations in the soil washing solution and EDTA was 1:1.13.

The EDTA mass balance (Table 1) revealed that approximately one-half of initial EDTA remained in the washing solution after electrochemical treatment, irrespective of the current density applied. Less than 20% of EDTA was removed from the washing solution by electrocoagulation adsorbed on Al hydroxide flocks. The 33.6–38.6% of EDTA that is missing from the balance (Table 1) was presumably degraded by anode oxidation. Johnson et al. [26] reported that EDTA was anodically oxidized into many compounds, including CO$_2$, formaldehyde and ethylenediamine. Fig. 1 shows that, during electrochemical treatment, the EDTA concentration decreased in the soil washing solution coincidently with increasing concentrations of electrocoagulated chelant.

Metals were removed from the washing solution either in complexes with EDTA after electrocoagulation or by electrodeposition, precipitation as insoluble hydroxides, or absorption and co-precipitation on Al hydroxide flocks after being released from anodically oxidized EDTA.

As shown in Fig. 2A, electrochemical processes efficiently removed Pb from the washing solution (up to 95% of the initial concentration). The mass balance (Table 2) indicates that the majority of Pb was removed by electrodeposition on the cathode, as reported earlier by Meunier et al. [21] for Pb removal from acidic

Table 2
Balance of Pb, Zn and Cd after treatment of the soil washing solution using electrocoagulation with an Al sacrifice anode.

Current density (mA cm^{-2})	Solution (%)	Electrodeposited (%)	Electrocoagulated + precipitated (%)	Recovery (%)
Pb				
16	[a]4.26 ± 0.02	[a]78.6 ± 3.9	[a]2.17 ± 0.56	85.0 ± 4.5
32	[a]3.80 ± 2.40	[a]73.6 ± 5.9	[a]3.38 ± 0.54	80.8 ± 8.8
64	[a]5.46 ± 2.39	[a]68.9 ± 6.9	[a]4.33 ± 1.40	78.7 ± 10.7
128	[a]5.75 ± 0.75	[a]69.8 ± 8.5	[a]11.51 ± 0.72	87.1 ± 10.0
Zn				
16	[a]29.4 ± 1.5	[a]26.4 ± 4.3	[a]41.6 ± 8.4	97.4 ± 14.2
32	[ab]30.3 ± 4.4	[a]20.6 ± 6.1	[ab]43.6 ± 6.2	94.5 ± 16.7
64	[b]35.8 ± 6.6	[a]12.1 ± 6.0	[b]53.4 ± 3.7	101 ± 16
128	[c]39.9 ± 1.6	[a]14.4 ± 8.8	[c]55.9 ± 1.4	110 ± 12
Cd				
16	[a]33.5 ± 3.3	[a]18.8 ± 5.9	[a]30.9 ± 5.5	83.2 ± 14.7
32	[a]30.6 ± 2.9	[a]18.2 ± 8.2	[ab]31.2 ± 2.1	80.0 ± 13.2
64	[b]36.4 ± 1.5	[a]11.8 ± 5.6	[ab]34.2 ± 5.6	82.4 ± 12.7
128	[c]40.2 ± 0.3	[a]23.1 ± 13.6	[b]35.9 ± 3.8	99.2 ± 17.7

Means ($n = 3$) followed by the same letter are not significantly different according to the Duncan test ($P < 0.05$).

soil solutions. Electrodeposition of Pb was possible only after Pb^{2+} was released from the EDTA complex. At the given conditions, all Pb in the washing solution was complexed to EDTA and initially occupied more than 15% of the available EDTA. In the solution after electrochemical treatment, the share of EDTA complexed to Pb was reduced to only approximately 1.5% (calculated from the data in Tables 1 and 2). This indicates that if Pb^{2+} was released from the EDTA after anodic oxidation of the EDTA, then anodic oxidation of EDTA–Pb complexes must have been preferential to oxidative degradation of other EDTA complexes (or acidic, more or less protonated EDTA species). Another possible mechanism for Pb^{2+} release is trans-complexation; the substitution of Pb in the EDTA complex

with other metals. A probable candidate is Al^{3+}, which indeed has a lower complex formation stability constant (Ks) than Pb (log Ks 16.3 and 18.0 at 20 °C and ionic strength $\mu = 0.1$ for Pb and Al, respectively [27]) but was formed in abundant concentrations during corrosion of the Al anode.

The rate of heavy metals removal and the share of electrocoagulated heavy metals increased with the current density applied (Fig. 2 and Table 2). After electrochemical treatment, up to 40% of the other two polluting metals, Zn and Cd, remained in the washing solution. The rest was removed, primarily by electrocoagulation (Fig. 2 and Table 2). Several competitive reactions occurred simultaneously in the soil washing solution during electrochemical
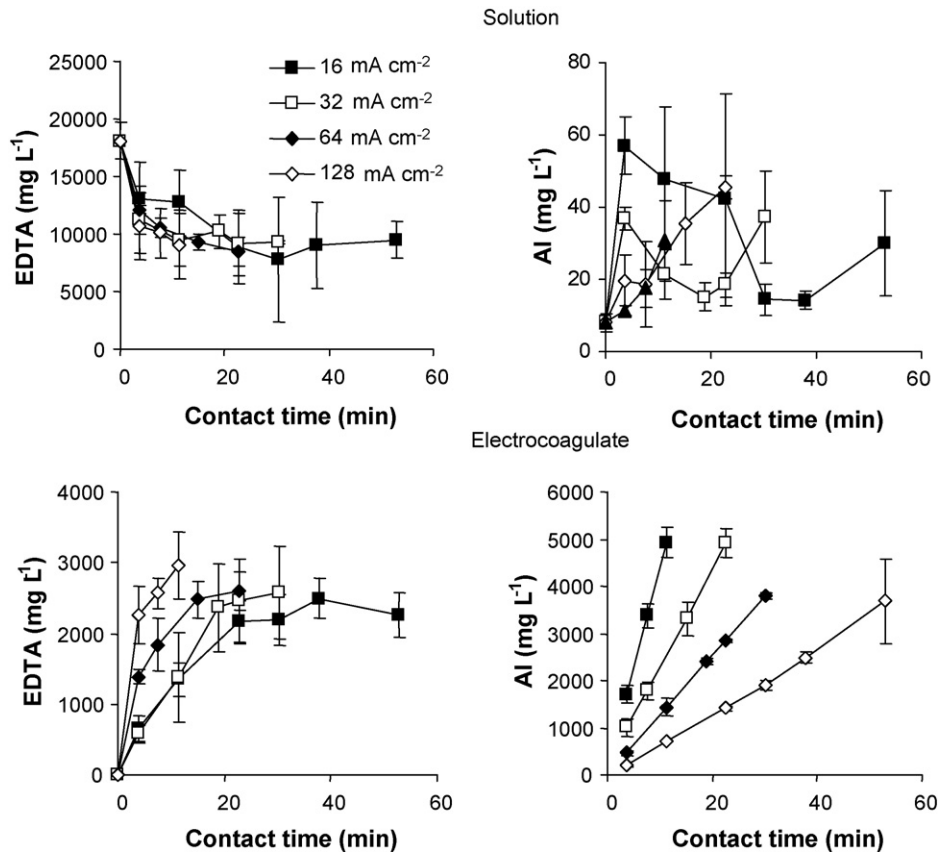

Fig. 1. Removal of Al and EDTA from the soil washing solution using electrocoagulation with an Al sacrificial anode as a treatment method. EDTA and Al concentrations in the washing solution treated with different current densities (16–128 mA cm^{-2}) are shown in the upper two graphs. EDTA and Al concentrations in the electrocoagulate precipitated from the washing solution are shown in the lower two graphs. Error bars represent standard deviation from mean value ($n = 3$).
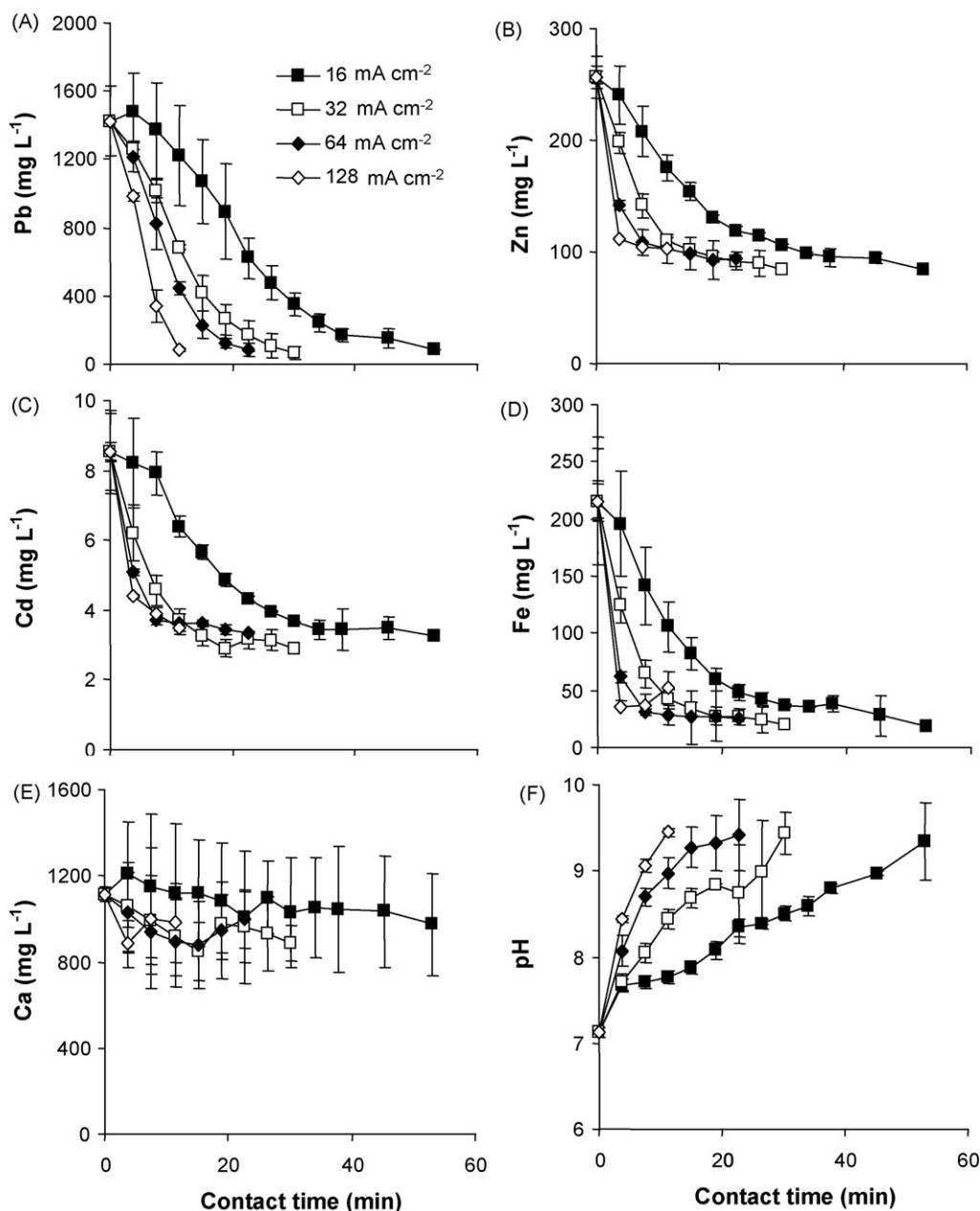
Fig. 2. Pb, Zn, Cd, Fe and Ca concentrations and pH of the soil washing solutions treated with different current densities (16–128 mA cm^{-2}). Electrocoagulation with an Al sacrificial anode was used to remove heavy metals from the soil washing solution. Error bars represent standard deviation from mean value ($n = 3$).

treatment, which could resulted in insufficient removal of Zn and Cd. Metal cations were removed by electrodeposition by cathodic reduction according to Eq. (4).

$$Me^{z+} + ze^- \leftrightarrow Me_{(s)} \qquad (4)$$

where Me is the metal and z the valence of the metal. Metal cations can be simultaneously or successively reduced and electrodeposited on the cathode, depending on their electronegativity (tendency to accept electrons). Since Cd and Zn are less electronegative than Pb, the observed preferential electrodeposition of Pb was expected. Insufficient removal of Zn and Cd from the washing solution could also be linked to the pH of the soil washing solution. The theoretical pH for metal precipitation as insoluble hydroxides [28] is significantly higher for Zn and Cd than for Pb (pH 8.5, 9.4, 6.5, respectively) and also higher than the pH of the washing solution (Fig. 2F) during the contact period of intensive Zn

and Cd removal from the washing solution (Fig. 2B and C). Zn and Cd could therefore be removed from the washing solution either by electrocoagulation as EDTA complexes or by absorption of released cations (after anodic EDTA oxidation or trans-complexation) on Al hydroxide flocks, according to the reaction in Eq. (5):

$$Al(OH)_3 + Me^{2+} \leftrightarrow Al(OH)O_2Me + 2H^+ \qquad (5)$$
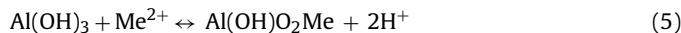
Eq. (5) is analogous to that proposed by Meunier et al. [21] for the removal of metals by absorption on Fe hydroxides. However, the pH of the treated washing solution increased over time (Fig. 2F) since the electrochemical system generated enough OH$^-$ at the electrode to counteract the H$^+$ released by the formation of Al hydroxides as a net final product [29]. Cinazares et al. [30] reported that Al hydroxide precipitate forms and influences coagulation between pHs 5 and 9. Outside this range at pH > 9 only ionic Al species have to be considered to explain the electrocoagulation results. Ionic

Al species might be less efficient absorbents than Al hydroxide precipitate—another possible reason for insufficient removal of Zn and Cd. Whether Zn and Cd removal could be improved by controlling the pH of the soil washing solution during electrochemical treatment remains to be investigated further.

Of other major metals, the concentration of Fe in the washing solution decreased in a fashion similar to Pb (Fig. 2D), the concentration of Ca remained fairly stable during the treatment (Fig. 2E), while the concentration of Al increased at first as expected but then fluctuated with fairly large deviations (Fig. 1). These fluctuations are perhaps explained by the complex precipitation kinetics, during which the Al^{3+} and OH^- generated at the anode and cathode react to form various monomeric and polymeric species, as described in Section 1. The concentration and rate of electrocoagulated and precipitated Al increased almost linearly through the electrochemical treatment (Fig. 1).

The voltage between the electrodes increased significantly during the treatment (Table 1). This was partly due to a decrease in the electro-conductivity of the washing solution from an initial $5.8\,mS\,cm^{-1}$ to approximately $4\,mS\,cm^{-1}$. Some electrolytes were apparently removed from the washing solution by electrocoagulation or other electrochemical processes. Passivisation of the electrode surfaces could also be responsible for the voltage increase. The anode was passivisated by the formation of Al oxides and the cathode by electrodeposited matter. The amount of Al consumed from the Al sacrificial anode during electrocoagulation (Table 1) directly depends on the treatment time and slightly increased with applied current density. Likewise, the operating cost of the electrochemical treatment of the soil washing solution is directly related to the specific energy consumption (SEC). SEC is defined as the amount of electrical energy consumed per unit mass of pollutants (Pb, Zn and Cd in the present case) removed. As expected and shown in Table 1, the SEC increased with the current densities applied. Some of the energy loss at higher current densities was due to heating of the treated solution. In subsequent experiments and for laboratory-scale simulation of soil remediation, we used a current density of $32\,mA\,cm^{-2}$, based on the favorable SEC and due to significantly slower kinetics of heavy metal removal in treatment with $16\,mA\,cm^{-2}$ (Fig. 2).

Electrocoagulation is an alternative to more commonly used dosing of Al (or Fe) salts to remove pollutants, and particulate impurities, from wastewaters. To compare the efficiency of the two methods, the same amount of Al was dosed in the washing solution (as $AlCl_3$) as dissolved from the Al anode in the electrochemical treatment (current density $32\,mA\,cm^{-2}$). Only 4.8% of Pb, 2.3% of Zn, and 0.7% of Cd were removed with $AlCl_3$. Electrocoagulation was therefore far more effective (Fig. 2 and Table 2). The results of the two methods could partly be explained by differences that exist between various hydrolyzing Al species formed in an aqueous solution at different pH, which can have a strong influence on the coagulation efficiency [29,30]. Namely, the pH increased during electrocoagulation (Fig. 2F), whereas it decreased during $AlCl_3$ dosing by 4 units, to 3.13, as a consequence of the acidic proteolytic reactions of Al salt. The metal removal efficiency with direct $AlCl_3$ dosage was also probably lower because metals were complexed with the EDTA. During electrocoagulation, however, part of the Pb, Zn and Cd were released from the EDTA; either after anodic oxidation of the EDTA or after trans-complexation of the metals.

3.2. Two-phase soil remediation using EDTA leaching and electrocoagulation

In addition to difficulties with treatment of wastewaters containing complexed EDTA, the retention of toxic EDTA and EDTA–heavy metal complexes through absorption by soil mineral
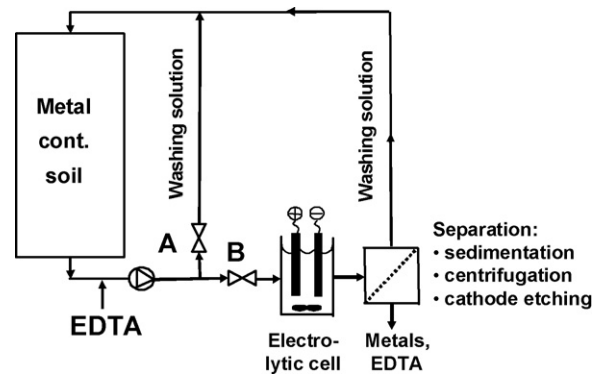

Fig. 3. Flow sheet of the two-phase soil remediation method using EDTA for heavy metal leaching and an Al sacrificial anode for electrochemical treatment and reuse of washing solution in a closed loop. (A) Leaching phase: washing solution first circulates solely through soil and (B) rinsing phase: washing solution treatment, soil rinsing phase in which the washing solution circulates through the soil and electrochemical cell.

surfaces and organic matter [31] is another important problem of soil washing remediation technologies. A vast consumption of clean water would be required for their removal from the soil. To overcome these problems, we recently proposed a two-phase soil remediation method [8]. In the first (leaching) phase, the soil is leached with EDTA solution (washing solution) to mobilize contaminating metals. In the second phase, the washing solution is treated to remove the heavy metals and EDTA. The clean solution is then used to rinse the soil in a closed loop and remove the remaining EDTA and its complexes retained (adsorbed) in the soil after the first (leaching) phase (Fig. 3). Since the washing solution is recycled, the method requires very little additional process water. Within this remediation method we evaluated the feasibility of using electrocoagulation with a sacrificial Al anode for treating the washing solution in the second (rinsing) phase (pathway B, Fig. 3). In a laboratory-scale simulation, 40 mmol EDTA per kg of soil was used for metal extraction and a constant current density of $32\,mA\,cm^{-2}$ was applied in the electrolytic cell. The electro-conductivity of the washing solution decreased from 5.6 to $2.4\,mS\,cm^{-1}$ during the remediation, due to electrocoagulation of the electrolytes. Some may also be adsorbed in the soil. The initial voltage was 5.3 V and increased up to 20 V several times during the process, mostly due to passivization of the electrodes. At these points, the electrodes were removed from the electrolytic cell. The cathode was etched with nitric acid to remove electrodeposits and the anode scrubbed with polishing paper to remove Al oxides. The voltage at the end of the remediation was 10.6 V. The pH increased from an initial 7.08 to a final 7.52 (Fig. 4G). This pH increase was smaller than observed previously in the electrochemical treatment of soil washing solution (Fig. 2F). Soils have a considerable pH buffer capacity and percolation of the washing solution through the soil (Fig. 3) prevented a further pH increase. The concentrations of Pb, Zn, Cd, EDTA and also Fe and Ca in the washing solution decreased with operation time (Fig. 4). The concentration of Al fluctuated (Fig. 4F), as observed previously in the treatment of washing solution. The final, discharge solution was clear, colourless, containing $170\,mg\,L^{-1}$ Pb, $50\,mg\,L^{-1}$ Zn, $1.5\,mg\,L^{-1}$ Cd and $4150\,mg\,L^{-1}$ (11 mM) EDTA. At the end of the remediation experiment, 110 g of hydroxide sludge was generated from the washing solution treatment.

Leaching on average removed 53% Pb, 26% Zn and 52% Cd from the soil, while concentrations of other major metals (Fe, Ca, Al) remained almost unchanged (Fig. 5). Interestingly, significantly more Pb was removed from the top soil layers. This again could point towards trans-complexation of Pb in the EDTA complex with
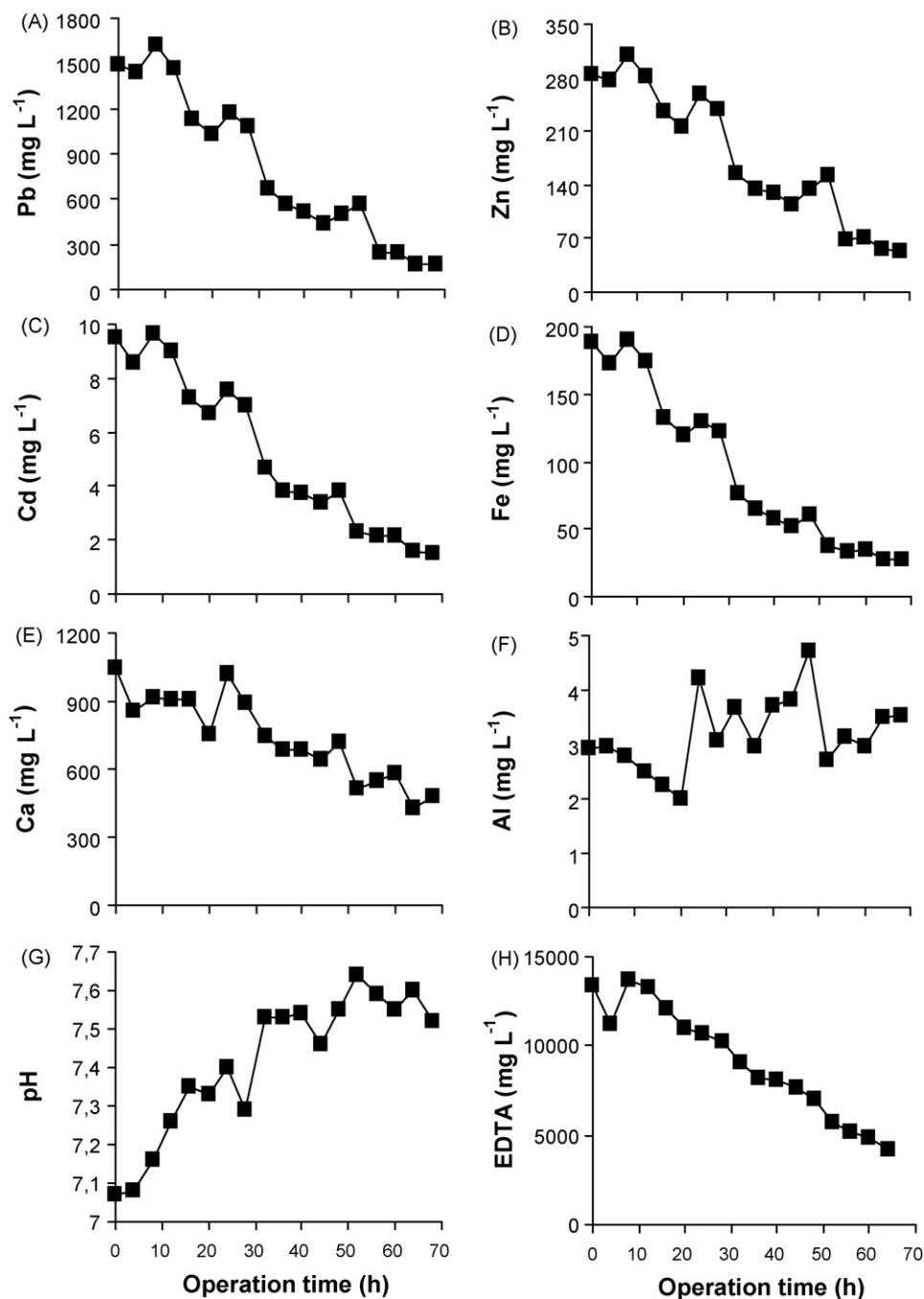
Fig. 4. Concentrations of Pb, Zn, Cd, Fe, Ca, Al and EDTA, and pH of the soil washing solution during the second, washing solution treatment/soil rinsing phases of the two-phase soil remediation method. Electrocoagulation with an Al sacrificial anode was used for the soil washing solution treatment.

Al, as discussed earlier (Section 3.1). EDTA–Al could then extract some additional Pb from the soil, due to the higher Ks of the EDTA–Pb formation, while the affinity of the EDTA for Al, Zn and Cd is quite similar (log Ks 16.3, 16.5, 16.4 at 20 °C and $\mu = 0.1$ for EDTA–Al, –Zn and –Cd, respectively [27].

The removal efficiency of heavy metals from soil was as expected, since metals in soil are generally not entirely accessible to chelants, even at a high chelant-to-metal ratio [32]. Zn was the least extractable. This was also observed in our previous studies, for soils from the same contaminated site. The low extractability was explained by the specific Zn fractionation in the soil. A high percentage of total Zn content was bound to the residual soil fraction of sequential extractions [9].

In the remediation experiment, Zn and Cd were removed from the washing solution much more efficiently (Fig. 4B and C) than after electrochemical treatment of the soil washing solution (Fig. 2B and C). This could be a consequence of the significantly lower pH of the washing solution during the remediation experiment (Figs. 2F and 4G) and, consequently, more efficient electrocoagulation processes (discussed in Section 3.1).

Approximately 31% of the initial EDTA concentration remained in the washing solution after remediation (Fig. 4H) and 20% of the EDTA was removed by electrocoagulation (precipitated with the Al hydroxide sludge). More EDTA was electrocoagulated than in experiments with washing solution (Table 1). Whether the EDTA in the washing solution and the EDTA adsorbed in the Al hydrox-
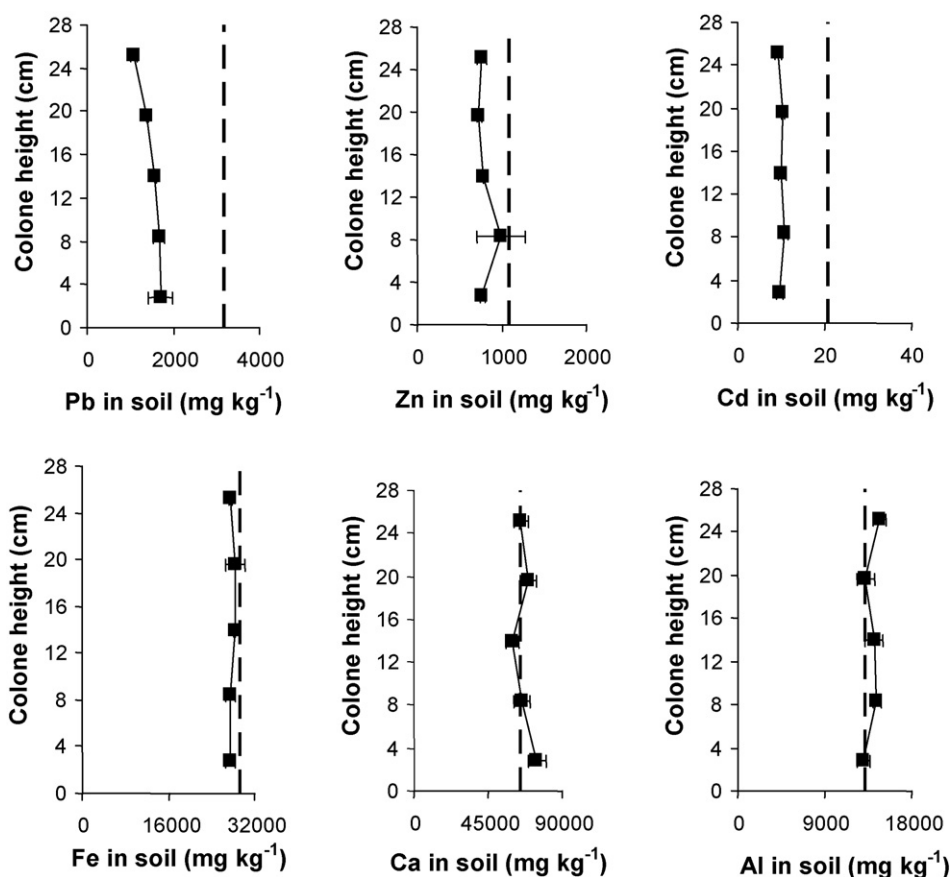
Fig. 5. Pb, Zn, Cd, Fe, Ca and Al concentrations through the soil profile in soil column before (dotted line) and after (solid line) remediation with the two-phase soil remediation method. Soil was leached with 40 mmol EDTA per kg of soil.

ide sludge could be recycled in an active form and reused for soil remediation remains to be studied.

An accurate evaluation of the costs associated with soil remediation would require a pilot-scale experiment (after further process optimization). However, EDTA and electricity consumption (which represent the major part of the total costs) can be extrapolated from our laboratory-scale remediation experiment. Leaching 1 ton of soil would thus require 15 kg of EDTA. At a price of 1.3€ per kg EDTA this translates into 19.6€. Treatment of the washing solution (without appropriate scale-up of the equipment) would require 15110 h at a constant current of 1 A and an average voltage of 8 V. This is 121 kWh and at an approximate cost of 0.1€ per kWh translates into 12.1€. The approximate EDTA and electricity cost would therefore be 31.7€ ton^{-1} of dry soil. The cost of electricity alone is approximately 2.5-times lower than the 31€ ton^{-1} estimated for the electricity consumption of two-phase soil leaching using EAOP and a boron-doped anode for washing solution treatment [9]. The soil was almost identical in the two studies (from the same contamination site). Furthermore, more Pb, Zn and Cd were removed from the soil in our current study, because of the higher EDTA concentration applied.

4. Conclusions

The results of our initial study indicate that electrocoagulation with a sacrificial Al anode could become a feasible option for the treatment of soil washing solutions containing EDTA complexes with Pb, Zn, Cd, and also as part of a two-phase (soil leaching, soil rinsing) soil remediation method. After leaching with 40 mmol EDTA per kg of soil, Pb, Zn and Cd were partly removed from the soil, indicating that the heavy metals were not entirely accessible

to the chelant. After electrochemical treatment, heavy metals were easily removed from the washing solution as insoluble precipitates and as electrodeposits on a cathode.

Electrocoagulation with an Al sacrificial anode is characterized by simple equipment, brief retention time and easy operation, which would contribute to reducing the operating cost in a large scale application. The method is energy efficient and the cost of the chelant, rather than the cost of electricity, might become a limiting factor for its use. In this respect, the possibility of recycling and reusing part of the EDTA from the washing solution and perhaps also from the hydroxide sludge seems very important and merits further investigation. In the end, however, the method failed to remove the EDTA entirely from the washing solution, and an additional cleansing strategy seems essential.

In addition to EDTA recycling, in further studies, process parameters such as the use of Al and Fe sacrificial anodes, pH control in the electrolytic cell, inter-electrode distance and geometry of the electrolytic cell will be optimized for washing solutions from soil leaching and soil extraction remediation options.

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