



Application of sequential extraction analysis to electrokinetic remediation of cadmium, nickel and zinc from contaminated soils

Apostolos Giannis^{a,*}, Despina Pentari^b, Jing-Yuan Wang^c, Evangelos Gidaracos^a

^a Department of Environmental Engineering, Technical University of Crete, Politechniopolis, Chania 73100, Greece

^b Department of Mineral Resources Engineering, Technical University of Crete, Politechniopolis, Chania 73100, Greece

^c Residues and Resource Reclamation Centre (R3C), Nanyang Technological University, 50 Nanyang Avenue, 639798 Singapore, Singapore

ARTICLE INFO

Article history:

Received 8 March 2010

Received in revised form 3 August 2010

Accepted 18 August 2010

Available online 26 August 2010

Keywords:

Electrokinetic remediation

Heavy metals

Sequential extraction analysis

Chelate agents

ABSTRACT

An enhanced electrokinetic process for the removal of cadmium (Cd), nickel (Ni) and zinc (Zn) from contaminated soils was performed. The efficiency of the chelate agents nitrilotriacetic acid (NTA), diethylenetriaminepentaacetic acid (DTPA) and diaminocyclohexanetetraacetic acid (DCyTA) was examined under constant potential gradient (1.23 V/cm). The results showed that chelates were effective in desorbing metals at a high pH, with metal–chelate anion complexes migrating towards the anode. At low pH, metals existing as dissolved cations migrated towards the cathode. In such conflicting directions, the metals accumulated in the middle of the cell. Speciation of the metals during the electrokinetic experiments was performed to provide an understanding of the distribution of the Cd, Ni and Zn. The results of sequential extraction analysis revealed that the forms of the metals could be altered from one fraction to another due to the variation of physico-chemical conditions throughout the cell, such as pH, redox potential and the chemistry of the electrolyte solution during the electrokinetic treatment. It was found that binding forms of metals were changed from the difficult type to easier extraction type.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Heavy metal pollution has gradually become one of the major concerns as they are highly toxic and carcinogenic to human beings, animals and plants. The extensive use of waste water irrigation, sewage sludge, pesticide and emissions from vehicle exhausts, mining, smelting and the rapid development of industries without effective control has resulted in a large accumulation of heavy metals in soils [1]. The heavily polluted soils become a long-term source of pollution to groundwater and the ecosystem. It is therefore of great importance to remediate those contaminants in the subsurface [2].

Electrokinetic remediation is one of the most effective in situ or ex situ soil decontamination methods, as it has high removal efficiency and time effectiveness in soil with low permeability [3]. Basically, the electrokinetic technique is based upon the action of an electric field generated between electrodes inserted in the medium, either by applying a low-level DC potential gradient or an electric current [4]. Low-level current induces variations to the physico-chemical and hydrological properties of soil due to many reactions.

The reactions may include electrolysis of water, mineral decomposition, oxidation, reduction and physical–chemical sorption [5]. The H⁺ cations generated at the anode enhance the desorption of the adsorbed metals on the soil surface and at the same time promote the dissolution of the precipitated contaminants. The production of OH⁻ ions at the cathode increases pH which causes the precipitation of the metals, thus preventing their movement and reducing the treatment efficiency [3]. In order to improve the effectiveness of the technique in terms of removing heavy metals from the soil, some researchers have conducted different applications such as conditioning the catholyte pH [6], adding chemical reagents to improve metal solubility [7], using an ion selective membrane to exclude OH⁻ migration from the cathode chamber into the soil [8], and using an electrolyte circulation to control electrolyte pH [9]. Ethylenediaminetetraacetic acid (EDTA) is one of the most commonly used chelates because of its strong chelating ability for a variety of heavy metals, but it has also been extensively used in electrokinetic remediation [7,10] and its low biodegradability makes it not such a good choice for field applications. From our data, little attention has been given to the chelate agents – nitrilotriacetic acid (NTA), diethylenetriaminepentaacetic acid (DTPA) and diaminocyclohexanetetraacetic acid (DCyTA) – as electrolyte solutions in order to extract heavy metals through the electrokinetic process and to change the form of the heavy metals. NTA is an easily biodegradable agent while DTPA and DCyTA are strong metal chelators over a wide pH range [11].

* Corresponding author. Tel.: +30 2821037789; fax: +30 2821037850.

E-mail addresses: apostolos.giannis@enveng.tuc.gr (A. Giannis), gidarako@mred.tuc.gr (E. Gidaracos).

Little attention has been given to adsorption/desorption of heavy metals by the electrokinetic process, and especially to the dependency of metal removal efficiencies upon their physico-chemical states and the prevailing chemical conditions. To determine the nature of any given system in terms of chemical species present and their relative mobilities, sequential extraction analysis has been suggested [12]. This consists of several steps that allow one to determine the speciation of the contaminating metals, and may help to assess the risk of continued contamination in the long term [13]. Besides, residence time of heavy metals in soil is directly related to their bioavailability. Heavy metals present their highest bioavailability immediately after application to soil. Such time effect is ascribed to the reactions between metal ions and soils, which mainly include complexation, surface adsorption, exchange reactions, chelation, and precipitation of metal ions in the soil particle surface or diffusion into the mesopores and macropores of soil leading to the conversion of highly soluble forms into less soluble ones [14]. If heavy metals exist as exchangeable or adsorbed forms on the surface of clay, organic matter and oxides with weak bonding strength, they tend to be easily moved and dispersed. However, metals complexed with organic ligands or in crystal lattices are not easily separated or mobilized. Only a few electrokinetic studies have investigated a detailed chemical speciation of heavy metals or how the metals are held (remained and bound) to the soil constituents [15].

The aim of this study was to examine the electrokinetic removal of cadmium, nickel and zinc from contaminated soil. In this aspect, the chelate agents (NTA, DTPA and DCyTA) were used to enhance heavy metal extraction from the soil. Moreover, sequential extraction analysis was used to evaluate the speciation of metals during the electrokinetic process in five soil fractions, as affected chelate agents, pH and redox. The selected metals (Cd, Ni and Zn) were used in this study because they are mobile and can easily transport across the pore fluid within soil particles.

2. Materials and methods

2.1. Chemicals and soil preparation

All reagents used in the experiments were of analytical grade. The chelate agents, NTA (99%), DTPA (98%) and DCyTA (98%), were purchased from Fluka. The heavy metals, cadmium nitrate ($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$; 99%), nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; 98.5%) and zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; 99%), were obtained from Fluka, and were used without any further purification. For the sequential extraction analysis the following agents were used: HNO_3 (Fluka; 65%, w/w), H_2O_2 (Riedel-de Haen; 30%, w/w), NaOH (Riedel-de Haen; 99%), acetic acid (Merck; 99.8%, w/w), hydrofluoric acid (Fluka; 40%, w/w), sodium acetate (Riedel-de Haen; 98%), ammonium acetate (Riedel-de Haen; 98%), and hydroxylamine hydrochloride (Riedel-de Haen; 99%).

The test soil was sampled from an agricultural area of Chania, Crete. The soil sample was air-dried, coarsely ground and sieved (<2 mm) to remove stones and large particles. Then, it was mixed to ensure uniformity and stored in plastic bags at room temperature. The particle size distribution was 56% sand, 35.5% silt and 8.5% clay [16], and the main mineral constituents were quartz (9.5%), illite (46.5%), kaolinite (42%) and albite (2%). The specific gravity of the soil was 2.38 [17] and the cation exchange capacity was 0.62 meq/g [18]. The organic content was determined as 1.53% [19]. Soil pH and redox potential were measured by a pH meter (Crison pH 25) with a ratio of 1:2.5 soil to water [20]. For the electrokinetic experiments, the soil was artificially contaminated (spiked) with $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ for Cd(II), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ for Ni(II) and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ for Zn(II). The slurry mixture (700 g soil and 700 mL metal solution) was

mixed mechanically for 20 d. The mixture was then allowed to settle for more than 5 d, in order to complete adsorption in the soil samples. Finally, the contaminated soil was rinsed with distilled water. After mixing, the sample was allowed settling and two separated levels were formed: the clear supernatant phase and the settled soil particles. The supernatant phase contained the metals that were not adsorbed onto the soil particles. To eliminate the free metals, this procedure was repeated three times. The analytical procedure for the spike method used in this study was similar to that used in previous electrokinetic research [21]. The final Cd, Ni and Zn concentrations in the soil were 115, 290 and 1200 mg/kg, respectively.

2.2. Experimental procedure

The electrokinetic test set-up used in this study has been described in a previous electrokinetic research [22]. The electrokinetic experiments were carried out in a rectangular Plexiglas column which included a soil cell, two electrode compartments, a power supply and a multimeter. The soil cell was 35 cm long with a cross-section of 10 cm \times 10 cm. The two electrode compartments (with 300 mL working volume) were placed at the end of each soil cell. Two cylinder graphite electrodes (diameter: 3 cm, length: 10 cm) were used as the working electrodes. Two pierced Plexiglas plates, each 0.5 cm thick and separated by a paper filter, were placed between the soil cell and the electrode compartments to prevent soil leakage from the soil cell to the electrode compartments.

Three different experiments were conducted to evaluate the influence of the chelate agents NTA, DTPA and DCyTA as purging solutions. These experiments were performed mainly to observe the efficiency of the chelates as electrolyte solutions when flushed in sequence to remove cadmium, nickel and zinc from the soil. The initial concentration of the anolytes was 10^{-3} M NTA, 10^{-3} M DTPA and 10^{-3} M DCyTA, while the concentration of the catholytes was 10^{-1} M NTA, 5×10^{-2} M DTPA and 5×10^{-2} M DCyTA, respectively. For each electrokinetic test, approximately 3600 g of dry soil was mixed with 1200 mL of deionized water in a polyethylene container, thoroughly by hand for several minutes, in order to achieve homogeneity. The ratio of the sample weight to the volume of water was 3 g:1 mL. The slurry was placed inside the cell (tamped using a hand compactor so that the amount of void space was minimized) and a constant DC voltage gradient of 43 V was applied in all experiments for a treatment time of 23 d. During the treatment, electrolyte pH and redox potential were measured daily in the electrode compartments. Also, the pH and the redox of the soil were monitored at six different distances from the anode: 2.5, 8.5, 14.5, 20.5, 26.5 and 32.5 cm. Moreover, after 3, 7, 13, 18 and 23 d of experimental time, soil samples were taken from these positions. The samples were oven dried and the USEPA 3051 microwave-assisted acid digestion method was used for the metals' extraction. Metal concentrations were determined using flame AAS.

Batch experiments were performed to evaluate the Cd, Ni and Zn extraction efficiency using water at different pH values. These tests were performed to simulate the conditions prevalent during electrokinetic experiments to better understand the interactions between soil-metals and interpret the results of the electrokinetic experiments. For the batch experiments, 2 g of the spiked soil were added to 40 mL of the washing solutions (10^{-2} M NaNO_3 as background electrolyte), and the flasks (polyethylene) were placed on a shaker table for 4 h at room temperature ($24 \pm 1^\circ\text{C}$) (liquid/soil ratio was 20 mL/g). The pH values of the suspension specimens were adjusted to the target values by adding HNO_3 or NaOH. Triplicate experiments were conducted to verify the reproducibility of the testing procedure. After shaking, each suspension was centrifuged at 3900 rpm for 15 min, and the supernatant was filtered through a 0.45 μm filter, acidified and stored for analysis.

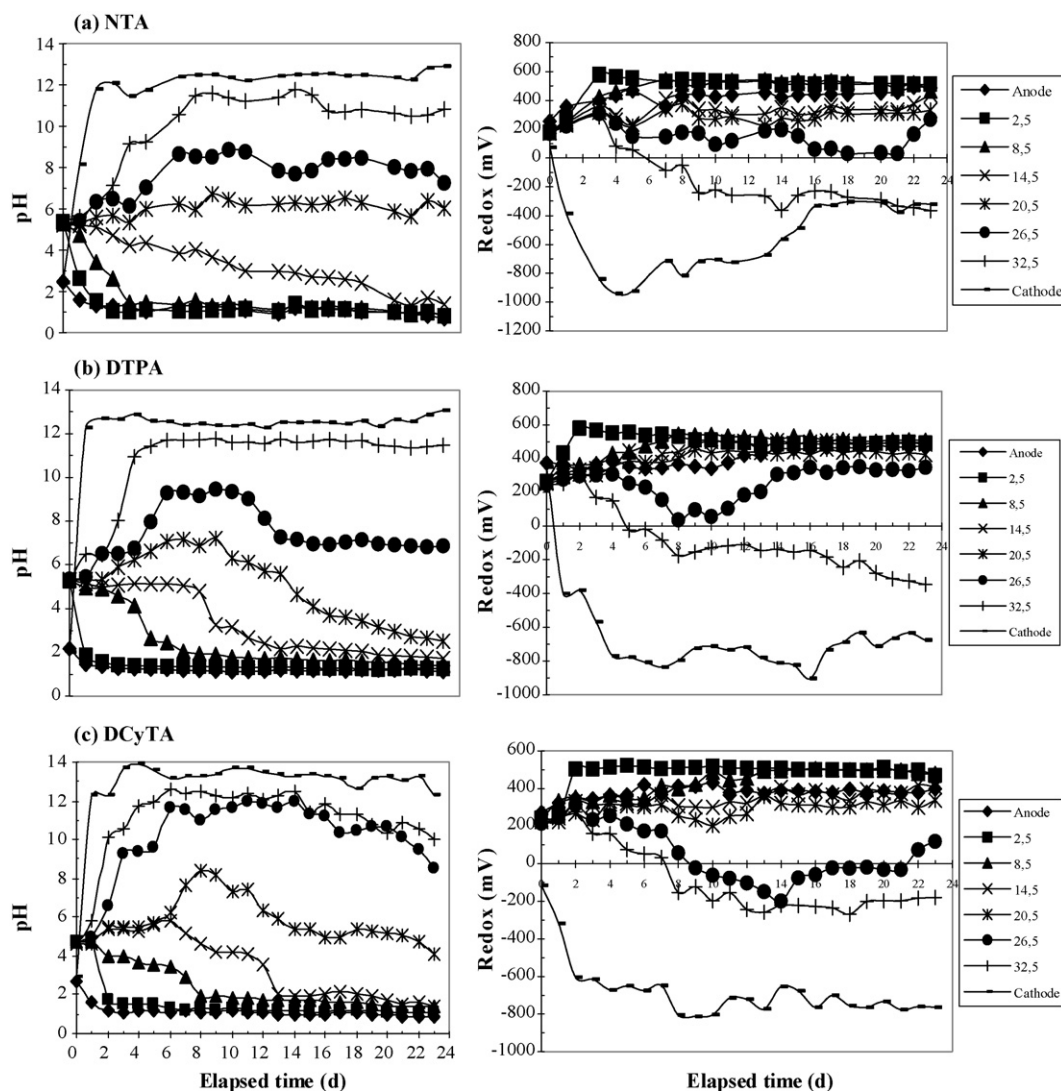


Fig. 1. pH and redox variations in the soil cell during the electrokinetic experiments.

2.3. Sequential extraction analysis

To determine metal fractionation in the soil, a five-step sequential extraction analysis was carried out. The sequential chemical extraction procedures can help in assessing the potential mobility and solubility of metals in contaminated soils. The adopted procedure closely followed the scheme proposed by Tessier et al. [12]. However, these fraction designations may not apply to freshly and/or heavily contaminated soils that contain small amounts of organic matter [23]. Therefore, the five fractions could be categorized as: (1) exchangeable and soluble forms, (2) carbonates and easily soluble oxides/hydroxides (weakly adsorbed) under slightly acidic conditions, (3) Fe–Mn oxides and additional soluble oxides/hydroxides, (4) organic matter and metals associated with easily oxidizable solids or compounds, (5) residual and strongly held complexes. The detailed extraction procedure for the five fractions is described in Chen et al. [24].

3. Results and discussion

3.1. Variations of pH and redox

Fig. 1 shows the pH and redox variations profiles in the soil and electrode compartment of all the three experiments. The pH

and the redox of the soil column were monitored daily at six distances from the anode: 2.5, 8.5, 14.5, 20.5, 26.5 and 32.5 cm. pH and redox distribution of the treated soil as a function of time depends on the initial pH of the soil system, the acid/base buffer capacity of the soil system, the chemical composition of the reservoir solution, and the direction of electro-osmotic flow [10].

When voltage potential was applied to the electrokinetic cell, the electrolysis of water generated H^+ at the anode and OH^- at the cathode. The electrolyte solutions used (NTA, DTPA and DCyTA) in the electrode compartments had no buffer capacity, resulting in a low pH near the anode and a high pH near the cathode. During the first day of each experiment, the anode compartment pH quickly decreased to 1.5–2, while the pH in the cathode compartment increased to 12. These values were almost constant during the experiments. H^+ and OH^- ions migrated through the soil towards the opposite electrode, forming an acidic and a basic front. Indeed, the acid front favored desorption of the metallic species that contributed to the transfer of charge. Regarding the soil pH, Fig. 1 indicates that at the beginning of the experiments the soil pH was lowered from the initial value of 5.25 to approximately 2 at the section near the anode and increased to 12 at the section near the cathode. The acidic front generated at the anode gradually moved through the soil towards the cathode, and lowering the pH close

to 2 in half of the sections close to the anode (three out of the six sections). At the next section, the soil pH was not changed from the initial one, but pH was increased to above 8 at the two sections close to the cathode. Acar and Alshawabkeh [25] found that the H^+ ions dominate the electrokinetic system chemistry because the mobility of H^+ is 1.75 times greater than that of OH^- ions. Similarly, redox followed the pH variations. In the soil cell, oxidizing conditions prevailed close to the anode (about 400 mV) and in the middle of the cell (200 mV), except for the area close to the cathode (-200 mV) where reducing conditions prevailed. The higher redox values near the anode are due to the depletion of electrons from the anode through the external power source, and the lower redox values at the cathode are due to the input of electrons from the power source [26].

The pH and redox variations were not affected by the electrolyte solutions NTA, DTPA and DCyTA. By comparing the pH and redox profiles of the three experiments, it seems that they followed almost the same distributions. This was mainly due to the low buffering capacity of NTA, DTPA and DCyTA [20]. Despite the high concentrations of catholyte solutions, these could only partially neutralize the OH^- anions generated at the cathode electrode, resulting in reducing conditions after some hours of treatment. Under these conditions, the high pH causes a metal ion to complex with the chelates [5].

3.2. Distribution of cadmium, nickel and zinc in the soil cell

The distribution of Cd, Ni and Zn across the soil cell for the duration of the electrokinetic experiments using the chelate agents NTA, DTPA and DCyTA is presented in Fig. 2. Soil samples were analyzed after 3, 7, 13, 18 and 23 d of treatment. The chelate agents NTA, DTPA and DCyTA are anionic complexes which migrated from the cathode to the anode through the soil-aided desorption of metals and the formation of anionic complexes. The stability constants of Cd with NTA are: 9.5 ($Cd-NTA^-$) and 4.67 ($Cd-HNTA^-$), with DTPA: 19.0 ($Cd-DTPA^{3-}$) and 2.3 ($Cd-HDTPA^{2-}$), and with DCyTA: 19.88 ($Cd-DCyTA^{2-}$). Likewise, the stability constants of Ni with NTA are: 11.42 ($Ni-NTA^-$) and 4.88 ($Ni-HNTA^-$), with DTPA: 20.2 ($Ni-DTPA^{3-}$) and 5.59 ($Ni-HDTPA^{2-}$), and with DCyTA: 20.20 ($Ni-DCyTA^{2-}$). Last, the stability constants of Zn with NTA are: 10.44 ($Zn-NTA^-$) and 3.28 ($Zn-HNTA^-$), with DTPA: 18.29 ($Zn-DTPA^{3-}$) and 4.33 ($Zn-HDTPA^{2-}$), and with DCyTA: 18.60 ($Zn-DCyTA^{2-}$) [27].

Using NTA as a purging solution, it was observed that after 3 d of treatment the metals accumulated in the middle of the cell. Due to the low pH close to the anode, cadmium, nickel and zinc desorbed from the soil particles surface, dissolved into the pore fluid as Cd^{2+} , Ni^{2+} and Zn^{2+} , and were transported through the soil by electromigration towards the cathode. In order to confirm this assumption, batch washing experiments were performed. Fig. 3 presents the extraction of Cd, Ni and Zn with water at different pH values. The removal efficiency of Cd and Zn was high at pH 2 (more than 85%) while Ni removal was 79%. At pH 3, the extraction efficiency was much lower, 32, 23 and 45% for Cd, Ni and Zn, respectively. At pH more than 4, the extraction of metals was lower than 6% indicating that metals were associated to the soil surface.

As observed in Fig. 2, the use of 10^{-1} M NTA in the cathode favored the formation of $Cd-NTA^-$ and $Ni-NTA^-$ complexes which migrated towards the anode. These conflicting directions forced the metals to accumulate in the middle of the cell. From the stability constants, it can be noticed that the NTA thermodynamically prefers to form complexes with nickel when both nickel and cadmium are present. Therefore, when NTA enters the soil from the cathode compartment, it first forms complexes with nickel. After the Ni has migrated further into the soil towards the

anode, the new NTA molecules entering the soil will then complex with Cd. After 13 d of treatment, the pH values in more than the half cell were lower than 3, therefore the metals existed in the dissolved phase as Cd^{2+} , Ni^{2+} and Zn^{2+} and migrated towards the cathode. When the $Cd-NTA^-$ and $Ni-NTA^-$ complexes entered under such conditions, they were inclined to dissociate with Cd and Ni, and complex with H^+ . By the end of the experiment 96% of Cd and Zn, and 91% of Ni had been mobilized and transferred towards the cathode. Despite a very effective clean up of the metals from the half cell, only a small amount of the metals moved into the cathode compartment (less than 3%) because the metals precipitated as hydroxides or had re-adsorbed onto the soil particles.

In the case of DTPA, Fig. 2 shows that only $Ni-DTPA^{3-}$ complexes were formed after 3 d of treatment and migrated towards the anode. More than 50% of Ni was desorbed near the cathode to the pore fluid. It seems that DTPA prefers to complex with Ni and only a small amount of $Cd-DTPA^{3-}$ and $Zn-DTPA^{3-}$ complexes were formed. Probably, using 5×10^{-2} M DTPA as catholyte solution was insufficient to form significant complexes with the metals. At the beginning of the experiment, the pH of the soil sections close to the anode was less than 3, and the metals existed in the dissolved phase. Specifically, nickel existed as Ni^{2+} close to the anode and $Ni-DTPA^{3-}$ close to the cathode, and therefore the two fronts met in the middle of the cell where there was an increase of nickel concentration. After 13 d of treatment and until the end of the experiment, Cd and Zn accumulated close to the cathode due to a high pH while nickel concentrated at the pH "jump" point. For this reason, a relatively low level of metals removal was observed. Similarly to DTPA, DCyTA desorbed a small amount of cadmium and zinc near the cathode forming anionic complexes which migrated towards the anode. The low pH at the end of the experiment favored desorption/dissolution of the metals, so they migrated towards the cathode, where they accumulated due to high pH. Even though DCyTA has high stability constants with the metals, only small amounts of metals were desorbed. It should be mentioned that DCyTA is a relatively large ligand and has low ionic mobility, therefore the amount of DCyTA electromigration into the soil from the cathode may have been insufficient, resulting in inadequate chelation with the metals [28].

Comparing the three electrokinetic experiments, it appears that the order of heavy metals transfer efficiency followed the order $Cd > Zn > Ni$. In addition, slight differences can be observed between the distribution of Cd and Zn for all three experiments. The mobility of Cd and Zn through the soil followed the same pattern [29]. These findings are consistent with previous studies conducted in lab-scale electrokinetic experiments with chelate agents conditioning the cathode compartment. Reddy and Chinthamreddy [7] and Kim et al. [30] have reported that initially the majority of the metals accumulated in the middle of the cell but, after oxidizing conditions prevailed, metals migrated close to the cathode due to precipitation. On the contrary, Yeung and Hsu [31] attempted to remediate a cadmium contaminated soil, and the majority of cadmium migrated towards the anode. They have reported that after treatment, the soil pH was lower than 5 only in the section close to the anode, and cadmium mainly existed as $Cd-EDTA^-$.

The undesirable accumulation of heavy metals close to cathode does not disqualify the electrokinetic extraction technique as an effective in situ soil remediation technology. It simply complicates the application logistics of the technique. The problem can be solved by careful planning of the process or using the technique in combination with other remediation technologies [31]. The key to successful electrokinetic removal of heavy metals from the soil is to keep the metals in the dissolved phase. Detailed discussion on the control of electrolyte pH to keep metals in the dissolved phase is given by Giannis et al. [21].

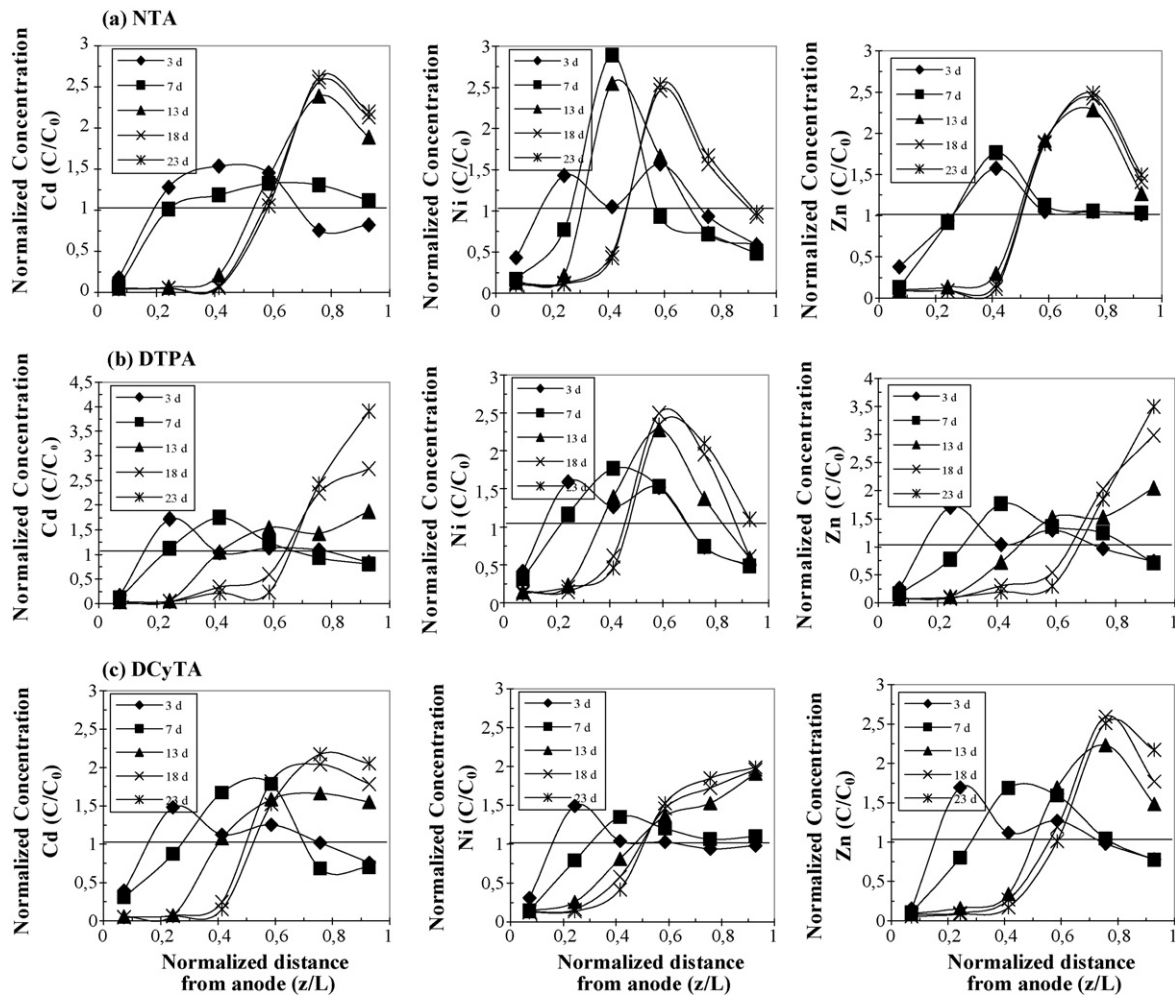


Fig. 2. Distribution of Cd, Ni and Zn profiles across the soil cell during the experimental time.

3.3. Speciation of Cd, Ni and Zn in the electrokinetic cell

Figs. 4–6 indicate the quantity of metals extracted in each step of the sequential extraction analysis. It is well known that the electrokinetic process alters metal speciation in soils and the process is strongly influenced by the pH. When metals were added to the soil, 59% of cadmium existed in exchangeable and soluble form,

while the remainder existed in tightly adsorbed forms. Significant amounts of nickel (80%) were strongly adsorbed by Fe–Mn oxides, while zinc distribution was 22 and 21% in exchangeable and carbonate forms, and more than 46% in Fe–Mn oxides. For all three metals, as the organic matter in soil was about 1.5%, the heavy metal adsorption in the organic fractions was low. Likewise, the residual fractions were less than 6% due to the fresh contaminated soil. By sequential extraction analysis, it was proved the high adsorption capacity of exchangeable, carbonates and Fe–Mn oxides fractions in freshly contaminated soil.

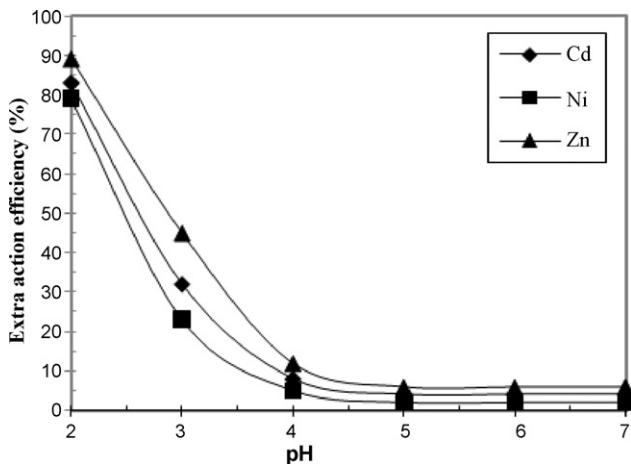


Fig. 3. Extraction efficiencies of Cd, Ni and Zn based on batch washing experiments.

During the entire duration of the experiments, the pH in the soil decreased near the anode and increased near the cathode as discussed in Section 3.1. The heavy metal speciation analysis was used to understand the changes in Cd, Ni and Zn concentrations in the soil specimen at different times and locations. In the case of the NTA experiment, after 3 d of treatment, it was observed that exchangeable and soluble cadmium easily migrated from the anode area towards the cathode. The chelate agent NTA, under the influence of the electric field, entered into the soil, generating a complex with exchangeable forms of Cd as Cd–NTA⁻, and migrated towards the anode. At the end of the experiment, the exchangeable Cd concentration decreased to a very low level in more than half the cell and Cd accumulated in the cathode area mostly as immobile hydroxyl complexes and precipitates due to the high pH, as well as binding to Fe–Mn oxides.

In the untreated soil, Ni was mainly bound to Fe–Mn oxides. Even though Ni was initially Fe–Mn bound prior to treatment, it

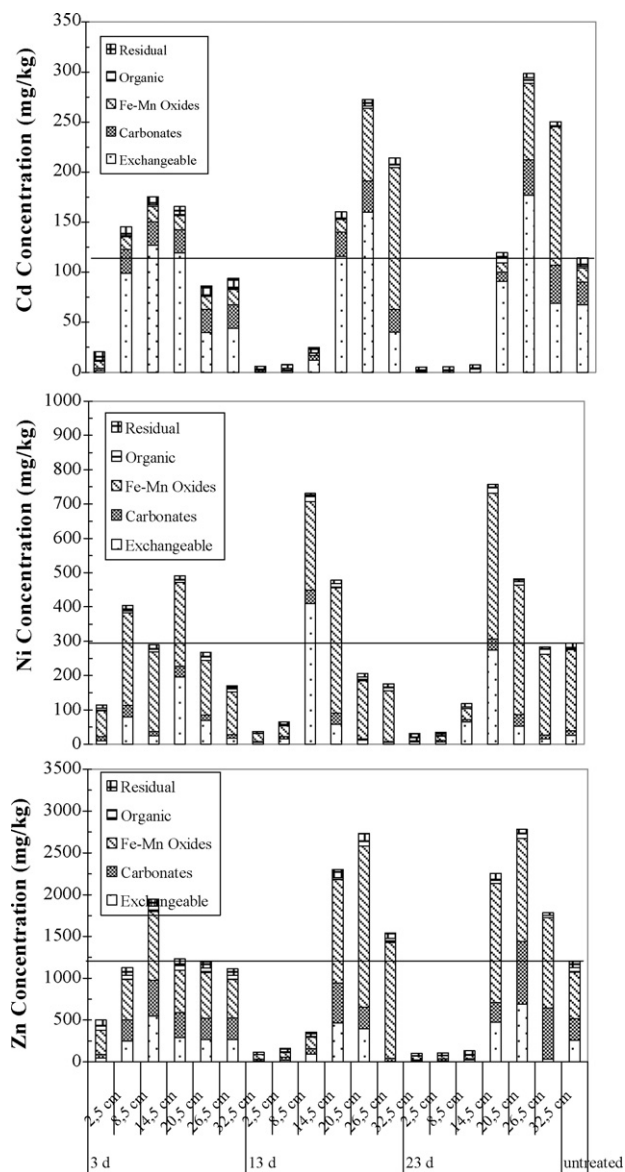


Fig. 4. Speciation of Cd, Ni and Zn during and after electrokinetic remediation with NTA.

could be dissolved and migrated towards the cathode area. Close to the cathode, NTA created Ni-NTA^- complexes which migrated towards the anode, increasing the exchangeable and soluble forms of Ni in the middle of the soil cell. At the end of experiment, Ni accumulated close to the cathode as exchangeable and soluble forms as well as being bound to Fe–Mn oxides. As seen from Fig. 2, the distribution of Zn in the soil followed Cd distribution, but Zn speciation was different from Cd. Due to the low pH close to the anode, exchangeable and soluble Zn easily migrated towards the cathode, resulting in an additional increase of Fe–Mn oxides in the middle of the cell. The extended electrokinetic application caused accumulation of Zn close to the cathode area, mainly bound to Fe–Mn oxides and carbonates. One study performed by Zhou et al. [32] on Cu–Zn contaminated red soil also showed that soil-exchangeable and carbonate-fraction metal concentrations reduced to different fractions. The results indicate that the forms of the metals could be altered from one fraction to another fraction due to a variation of physico-chemical conditions throughout the cell, such as pH, redox potential, and the local chemistry of both liquid and solid phases during the electrokinetic treatment.

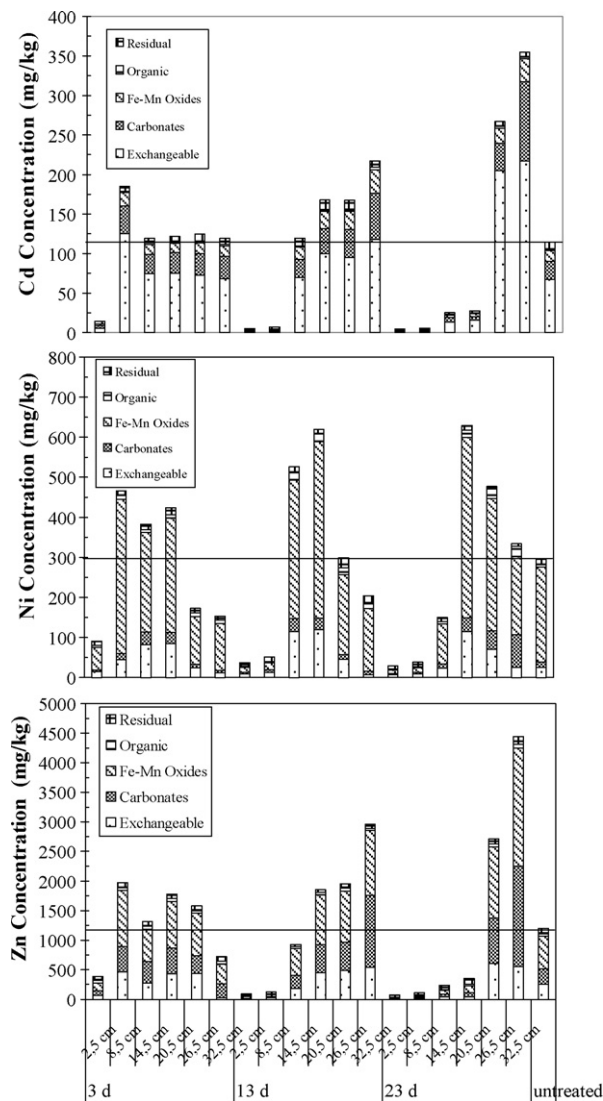


Fig. 5. Speciation of Cd, Ni and Zn during and after electrokinetic remediation with DTPA.

Similar to NTA, the experiments with DTPA and DCyTA as electrolyte solutions showed an accumulation of the metals close to the cathode, following electrokinetic treatment. Cd existed mainly in exchangeable bound forms, Ni was bound to Fe–Mn oxides, and Zn immobilized to bound Fe–Mn oxides and carbonates. The distributions of the heavy metals based on the sequential extraction analyses showed that the greater migration of the metals occurred under induced electric potential if the metals initially existed in exchangeable and soluble forms [23]. Moreover, the distribution of the metals suggests that the electrolyte conditioning system was capable of dissolving heavy metals by generating complexes with the exchangeable forms of the metals. In all three metals, the location close to the cathode – where the oxidizing conditions changed to reducing conditions – favored metals to bind with Fe–Mn oxides. As seen from Fig. 1, the redox potential close to the cathode was about -200 mV. Under these conditions, Fe–Mn oxides are more powerful and have the capacity to adsorb a great amount of metals [33]. In summary, the mass balance recovery from the sequential extraction analysis was checked for Cd, Ni and Zn. The recoveries varied in the ranges of 89–110%. Hence, the sum of the five fractions was reasonably similar to the total metal contents.

Knowledge of chemical speciation is important in evaluating the mobility and the toxicity of heavy metals. According to the metal

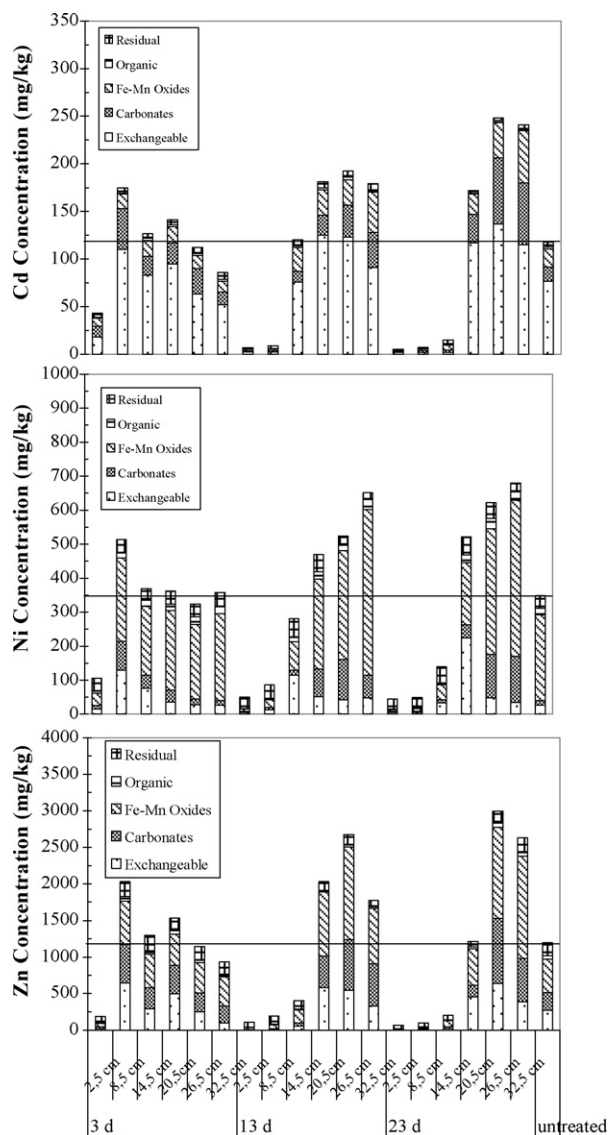


Fig. 6. Speciation of Cd, Ni and Zn during and after electrokinetic remediation with DCyTA.

speciation in the soil after the electrokinetic treatment, the metals Cd and Zn present in release fractions (hydroxides, exchangeable and carbonates). The summation of these fractions can be used to assess the environmental available components [34]. Although the results may be misleading, since a freshly prepared (spiked) soil can never represent an aged, complex natural contamination. Ideally, one would support and verify sequential extraction data with other speciation techniques (e.g. X-ray diffraction spectroscopy) [35]. Despite the problem outlined, this study yields valuable insight as to whether significant redistribution occurs during sequential extraction and which of the soil properties might play the important role in the electrokinetic treatment.

4. Conclusions

In this work, the distribution of Cd, Ni and Zn was examined during and after the electrokinetic remediation using NTA, DTPA and DCyTA. The main mechanisms affecting the migration of metals were the low pH close to the anode and the electrolyte solution close to the cathode. At the end of the experiments, most of the metals accumulated at the cathode area due to the prevailing low pH

in half the soil cell. Finally, sequential extraction analyses showed that the binding forms of metals could be altered from one fraction to another. After treatment, cadmium existed in the exchangeable fraction, nickel was bound to Fe–Mn oxides, and zinc immobilized to Fe–Mn bound oxides and carbonates.

References

- [1] W.Y. Shi, H.B. Shao, H. Li, M.A. Shao, S. Du, Progress in the remediation of hazardous heavy metal-polluted soils by natural zeolite, *J. Hazard. Mater.* 170 (2009) 1–6.
- [2] T. Li, S. Yuan, J. Wan, L. Lin, H. Long, X. Wu, X. Lu, Pilot-scale electrokinetic movement on HCB and Zn in real contaminated sediments enhanced with hydroxypropyl- β -cyclodextrin, *Chemosphere* 76 (2009) 1226–1232.
- [3] J. Virkutyte, M. Sillanpaa, P. Latostenmaa, Electrokinetic soil remediation—critical overview, *Sci. Total Environ.* 289 (2002) 97–121.
- [4] S. Amrate, D.E. Akretche, C. Innocent, P. Seta, Removal of Pb from a calcareous soil during EDTA-enhanced electrokinetic extraction, *Sci. Total Environ.* 349 (2005) 56–66.
- [5] O. Hanay, H. Hasar, N.N. Kocer, Effect of EDTA as washing solution on removing of heavy metals from sewage sludge by electrokinetic, *J. Hazard. Mater.* 169 (2009) 703–710.
- [6] E. Gidarakos, A. Giannis, Chelate agents enhanced electrokinetic remediation for removal cadmium and zinc by conditioning catholyte pH, *Water Air Soil Poll.* 172 (2006) 295–312.
- [7] K. Reddy, S. Chinthamreddy, Sequentially enhanced electrokinetic remediation of heavy metals in low buffering clayey soils, *J. Geotech. Geoenviron.* 129 (2003) 263–277.
- [8] W.-S. Kim, S.-O. Kim, K.-W. Kim, Enhanced electrokinetic extraction of heavy metals from soils assisted by ion exchange membranes, *J. Hazard. Mater.* 118 (2005) 93–102.
- [9] H.-H. Lee, J.-W. Yang, A new method to control electrolytes pH by circulation system in electrokinetic soil remediation, *J. Hazard. Mater.* 77 (2000) 227–240.
- [10] A.T. Yeung, C.N. Hsu, R.M. Menon, EDTA-enhanced electrokinetic extraction of lead, *J. Geotech. Eng.* 122 (1996) 666–673.
- [11] J. Hong, P.N. Pinturo, Desorption-complexation-dissolution characteristics of adsorbed cadmium from kaolin by chelators, *Water Air Soil Pollut.* 86 (1996) 35–50.
- [12] A. Tessier, P.G.C. Campbell, M. Bisson, Sequential extraction procedure for the speciation of particulate trace metals, *Anal. Chem.* 51 (1979) 844–851.
- [13] S.-O. Kim, K.-W. Kim, Monitoring of electrokinetic removal of heavy metals in tailing-soils using sequential extraction analysis, *J. Hazard. Mater.* 85 (2001) 195–211.
- [14] M. Jalali, Z.V. Khanlari, Effect of aging process on the fractionation of heavy metals in some calcareous soils of Iran, *Geoderma* 143 (2008) 26–40.
- [15] A.Z. Al-Hamdan, K. Reddy, Transient behavior of heavy metals in soils during electrokinetic remediation, *Chemosphere* 71 (2008) 860–871.
- [16] ASTM, Standard Test Method for Particle-Size Analysis of Soils: ASTM D 422-63, ASTM International, West Conshohocken, PA, 2007.
- [17] ASTM, Standard Test Method for Specific Gravity of Soil Solids by Water Pycnometer: ASTM D 854-02, ASTM International, West Conshohocken, PA, 2002.
- [18] USEPA, Cationic Exchange Capacity of Soil (Ammonium Acetate): Test Methods for Evaluation Solid Waste, Physical/Chemical Methods. SW-846, Method 9080, USEPA, Washington, DC, 1986.
- [19] ASTM, Standard Test Methods for Moisture, Ash, and Organic Matter of Peat and Other Organic Soils: ASTM D 2974-07, ASTM International, West Conshohocken, PA, 2007.
- [20] ASTM, Standard Test Method for pH of Soils: ASTM D 4972-01, ASTM International, West Conshohocken, PA, 2007.
- [21] A. Giannis, A. Nikolaou, D. Pentari, E. Gidarakos, Chelating agent-assisted electrokinetic removal of cadmium, lead and copper from contaminated soils, *Environ. Pollut.* 157 (2009) 3379–3386.
- [22] A. Giannis, E. Gidarakos, A. Skouta, Transport of cadmium and assessment of phytotoxicity after electrokinetic remediation, *J. Environ. Manage.* 86 (2008) 535–544.
- [23] K. Reddy, C.Y. Xu, S. Chinthamreddy, Assessment of electrokinetic removal of heavy metals from soils by sequential extraction analysis, *J. Hazard. Mater.* 84 (2001) 279–296.
- [24] X. Chen, Z. Shen, Y. Lei, B. Ju, W. Wang, Enhanced electrokinetic remediation of Cd and Pb spiked soil coupled with cation exchange membrane, *Aust. J. Soil Res.* 44 (2006) 523–529.
- [25] Y. Acar, A. Alshawabkeh, Principles of electrokinetic remediation, *Environ. Sci. Technol.* 27 (1993) 2638–2647.
- [26] K. Reddy, S. Chinthamreddy, A. Al-Hamdan, Synergistic effects of multiple metal contaminants on electrokinetic remediation of soils, *Remediation J.* 11 (2001) 85–109.
- [27] A.E. Martell, R.J. Motekaitis, Determination, Use of Stability Constants, 2nd ed., Wiley, New York, 1992.
- [28] K. Reddy, S. Danda, R. Saichek, Complicating factors of using ethylenediamine tetraacetic acid to enhance electrokinetic remediation of multiple heavy metals in clayey soils, *J. Environ. Eng.* 130 (2004) 1357–1366.
- [29] T. Vengris, R. Binkiene, A. Sveikauskaitė, Electrokinetic remediation of lead-, zinc- and cadmium-contaminated soil, *J. Chem. Technol. Biotechnol.* 76 (2001) 1165–1170.

- [30] D.-H. Kim, B.-G. Ryu, S.-W. Park, C.-I. Seo, K. Baek, Electrokinetic remediation of Zn and Ni-contaminated soil, *J. Hazard. Mater.* 165 (2009) 501–505.
- [31] A.T. Yeung, C.N. Hsu, Electrokinetic remediation of cadmium-contaminated clay, *J. Environ. Eng.* 131 (2005) 298–304.
- [32] D.-M. Zhou, C.-F. Deng, L. Cang, A. Alshwabkeh, Electrokinetic remediation of a Cu–Zn contaminated red soil by controlling the voltage and conditioning catholyte pH, *Chemosphere* 61 (2005) 519–527.
- [33] M.E. Sumner, *Handbook of Soil Science*, CRC Press, Boca Raton, FL, 2000.
- [34] J.-F. Peng, Y.-H. Song, P. Yuan, X.-Y. Cui, G.-L. Qiu, The remediation of heavy metals contaminated sediment, *J. Hazard. Mater.* 161 (2009) 633–640.
- [35] W. Calmano, S. Mangold, E. Welter, An XAFS investigation of the artefacts caused by sequential extraction analyses of Pb-contaminated soils, *Fresen. J. Anal. Chem.* 371 (2001) 823–830.