Environmental Pollution 157 (2009) 3379–3386

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Chelating agent-assisted electrokinetic removal of cadmium, lead and copper from contaminated soils

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Cadmium, lead and copper were extracted from contaminated soil by integrated electrokinetic and soil washing studies.

ARTICLE INFO

Article history:
Received 3 February 2009
Received in revised form
16 June 2009
Accepted 16 June 2009

Keywords:
Electrokinetic remediation
Soil washing
Chelates
Heavy metals
Phytotoxicity

ABSTRACT

An integrated experimental program was conducted to remove Cd, Pb and Cu from contaminated soil. The chelate agents nitrilotriacetic acid (NTA), diethylenetriamine pentaacetic acid (DTPA) and ethyleneglycol tetraacetic acid (EGTA) were used as washing solutions under different pH conditions and concentrations. Results showed that the extraction efficiency for Cd in decreasing order was NTA > EGTA > DTPA, while for Pb and Cu it was DTPA > NTA > EGTA. The use of higher chelate concentrations did not necessarily result in greater extraction efficiency. Electrokinetic remediation was applied by conditioning anolyte–catholyte pH to neutral values in order to avoid any potential alterations to the physicochemical soil properties. The removal efficiency for Cd was 65–95%, for Cu 15–60%, but for Pb was less than 20%. The phytotoxicity of the treated soil showed that the soil samples from the anode section were less phytotoxic than the untreated soil, but the phytotoxicity was increased in the samples from the cathode section.

1. Introduction

Soils can be contaminated with heavy metals due to agricultural, industrial and military activities. Due to metals toxicity, adverse effects may appear to both soil organisms and plants in situ that are present, threatening soil ecology and agricultural production (Selim and Iskandar, 1999). In Europe, metals such as Cd, Cu, Pb, Cr, Zn, Ni are commonly found at the contaminated sites (Flathman and Lanza, 1998). Unlike organic compounds, toxic metals are not degradable in the environment, and can persist in soils for decades or even centuries (Lestan et al., 2008). Therefore, there is a pressing need to develop effective and economical remediation methods suitable for this class of contaminants. 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 low permeability soils (Shen et al., 2007). Briefly, when a direct current is applied to the soil, the pollutants move towards the electrodes through electromigration, electroosmosis and electrophoresis (Acar and Alshawabkeh, 1993; Wang et al., 2006).

The H^+ and the OH^- ions are generated from the electrodes, and then move across the pore fluid within soil particles towards the cathode and the anode, respectively. 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 precipitated contaminants. The production of OH^- ions at the cathode increase pH which causes the precipitation of the metals, thus preventing their movement and reducing the treatment efficiency (Virkutyte et al., 2002). In order to avoid alkaline precipitation, liquids other than water, such as weak acids and/or complexing or chelating agents, can be used near the electrodes (Li and Li, 2000; Gidarakos and Giannis, 2006). Chelating agents desorb trace metals from solid soil phases by forming strong and water soluble metal-chelant coordination compounds (Lestan et al., 2008). The main parameters affecting soil washing include the mode of extraction (leaching or washing), extraction type and concentration, solution pH, electrolyte, liquid/soil ratio (mL/g), and retention time (Zou et al., 2009). Ethylenediaminetetraacetic acid (EDTA) is one of the most commonly used chelates because of its strong chelating ability for a variety of heavy metals (Sun et al., 2001), but it has also been extensively used in electrokinetic remediation (Reddy and Chinthamreddy, 2003; Yeung et al., 1996). However, its low biodegradability makes it not such a good choice for field applications (Tandy et al., 2004). The chelate agents, nitrilotriacetic acid (NTA), diethylenetriamine pentaacetic acid (DTPA) and ethyleneglycol tetraacetic acid (EGTA) have not been evaluated before in the electrokinetic remediation process. NTA is easily biodegradable, but it is under scrutiny due to possible adverse

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doi:10.1016/j.envpol.2009.06.030

health effects (Ebina et al., 1986). DTPA and EGTA are elongated versions of EDTA, but even stronger chelating agents for soil metal extraction (Hong et al., 2002).

In a previous study, it was found that phytotoxicity increased after electrokinetic remediation, mainly due to the low pH values of the soil (Giannis et al., 2008). Furthermore, the application of electrokinetics altered the physicochemical characteristics of the soil, and the exposed microbial community (Lear et al., 2007). An important prerequisite for electrokinetic methods to be accepted for remediation is to demonstrate that they are effective for purging contaminants and have no negative effect on soil health. Phytotoxicity is described as the intoxication of living plants by substances present in the growth medium, and is based on seed germination and root elongation as a means of providing an easy and inexpensive screening test (Chang et al., 1992).

In order to avoid any alterations of physicochemical soil properties, electrokinetic experiments were conducted by conditioning anolyte–catholyte pH at neutral values. The purpose of this study was to combine integrated approaches, including soil washing batch experiments at the same pH values that prevail in electrokinetics, to investigate the efficiency of the chelate agents (NTA, DTPA, EGTA) in removing heavy metals (Cd, Pb, Cu), to determine the migration of heavy metals under slightly acidic soil conditions during electrokinetics, and to examine soil germination after the electrokinetic process.

2. Materials and methods

2.1. Soil preparation and physicochemical analysis

The soil used in this study was obtained 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 (ASTM D422), 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 (ASTM D854-92) and the cation exchange capacity was 0.62 meq/g (EPA 9080). Soil pH and redox potential were measured by a pH meter (Crison pH 25) with a ratio of 1:2.5 soil to water, and the initial values were 5.04 and 345 mV, respectively (ASTM D4972). The soil was artificially contaminated (spiked) with cadmium nitrate ($Cd(NO_3)_2 \cdot 4H_2O$) for Cd(II), lead nitrate ($Pb(NO_3)_2$) for Pb(II) and copper nitrate ($Cu(NO_3)_2 \cdot 3H_2O$) for Cu(II). All reagents used in this study were of analytical grade. The slurry mixture (700 g soil and 700 mL metal solution) was mixed mechanically for 20 days. The mixture was then allowed to settle for more than 5 days, in order to complete adsorption in the soil samples. Finally, the contaminated soil was rinsed with distilled water. After mixing, the sample 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 final Cd, Pb and Cu concentrations in the soil were 145, 455 and 1005 mg/kg, respectively.

2.2. Soil washing experiments

Batch experiments were performed to evaluate the Cd, Pb and Cu extraction efficiency using four different washing solutions (NTA, DTPA, EGTA, acetic acid) and water at different pH values and different solution concentrations (Table 1). 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 ± 1 °C) (liquid/soil ratio was 20 mL/g). Preliminary kinetic studies showed that 4 h were sufficient to reach steady state conditions. The pH values of the suspension specimens were adjusted to the target values by adding HAc 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 with concentrated HNO_3, and stored for analysis. The concentrations of the metals Cd, Pb and Cu were measured by atomic absorption spectrometry (AAS) (Perkin-Elmer Analyst, 100A).

Table 1
Soil washing experiments.

Reagents	Concentrations	pH	Washing time (hr)
NTA	10^{-1} M, 5×10^{-2} M, 10^{-2} M, 5×10^{-3} M	3, 5, 7	4
EGTA	5×10^{-2} M, 5×10^{-3} M, 10^{-3} M	3, 5, 7	4
DTPA	5×10^{-2} M, 5×10^{-3} M, 10^{-3} M	3, 5, 7	4
HAc	1 M, 10^{-1} M, 10^{-2} M	3, 5, 7	4
H_2O	–	3, 5, 7	4

2.3. Electrokinetic experiments

The electrokinetic experiments were performed in a rectangular Plexiglas column which included a soil cell, two electrode compartments, a power supply and a multimeter. Giannis et al. (2008) have already described this set up in detail. The soil cell was 17 cm long with a cross section of 10 cm × 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.

Three different experiments were conducted to evaluate the influence of NTA, DTPA and EGTA as purging solutions. The basic information of the experiments is shown in Table 2. For each electrokinetic test, approximately 1800 g of dry soil was mixed with 600 mL of 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 anolyte was maintained at $pH > 6$ by dosing appropriate volumes of 2 M NaOH to buffer the hydrogen cations formed at the anode, and the catholyte was maintained at $pH < 6$ by adding 10 M acetic acid to buffer the hydroxyl anions formed at the cathode. In this way, the slightly acidic conditions were maintained at the soil cell and the metal precipitation was prevented. The sample was placed inside the cell and a constant DC voltage gradient of 22 V was applied in all experiments for a treatment time of 23 days. During the treatment, the electric current as well as the electrolyte pH and redox potential were measured daily in the electrode compartments. Also, the pH and the redox of the soil were monitored at three different distances from the anode: 2.5, 8.5 and 14.5 cm. Moreover, after 3, 7, 13, 18 and 23 days 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 (Perkin-Elmer Analyst, 100A).

2.4. Phytotoxicity tests

The three plant species monocotyl Sorgho (*Sorghum saccharatum*), dicotyls garden cress (*Lepidium sativum*) and mustard (*Sinapis alba*) were used for seed germination assays. After the electrokinetic experiments, the treated soil of the cell was separated into three equal segments (close to the anode (0–5.5 cm), middle of the cell (5.5–11.5 cm), close to the cathode (11.5–17 cm)) and subsequently preserved in glass bottles. The standard Phytotoxkit microbiotest (MicroBioTests Inc., Belgium) was selected on the basis of the rapid germination of the seeds and growth of the roots. The standard Phytotoxkit measures two kinds of effect: the decrease in seed germination and the decrease in root growth, compared to the germination and root growth in a control soil (ISO, 1992). Each soil segment was placed in a PVC plate with dimensions 21 cm × 15.5 cm × 0.8 cm. About 30 mL of distilled water were added for water saturation of the soil at the beginning of the tests. Then, ten seeds from each type of plant used were placed on a filter paper installed on the soil sample. The plate was capped and kept in a dark incubator at 25 °C for 3 days. Then the germinated seeds were counted and root length was measured by means of a ruler to the closest millimeter. All samples were run in duplicate while the control soil measurements were taken in triplicate.

The germination index (GI) was evaluated according to Zucconi et al. (1981) and Komilis et al. (2005), using the following equations:

$$\text{Relative seed germination}(\%) = \frac{\text{Number of seeds germinated in sample}}{\text{Number of seeds germinated in control}} \times 100$$

$$\text{Relative root elongation}(\%) = \frac{\text{Mean root elongation in sample}}{\text{Mean root elongation in control}} \times 100$$

$$\text{GI} = \frac{(\%\ \text{Seed germination})(\%\ \text{Root elongation})}{100\%}$$

Table 2
Experimental conditions for electrokinetic experiments.

Test	Voltage applied (V)	Soil saturation	Anolyte	Catholyte	Duration (days)
I	22	H_2O	10^{-3} M NTA	10^{-1} M NTA	23
II	22	H_2O	10^{-3} M DTPA	5×10^{-2} M DTPA	23
III	22	H_2O	10^{-3} M EGTA	5×10^{-2} M EGTA	23