

Electrokinetic remediation of Cd contaminated soil at field condition

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Abstract

Electrokinetic removal of heavy metals from contaminated soils seems an innovative approach for their remediation. However, employing that method in calcareous soils and soils with great adsorption capacity for heavy metals needs to be studied thoroughly. In this research a clayey loam soil spiked with Cd used to investigate electrokinetic remediation in three depths (0, 15 and 30 cm) at four plots at field condition. All experiments were imposed with a constant voltage gradient of 1 V/cm for 2, 4 and 6 days at a field in Marand area, North West of Iran. The soil contained large amount of Cd (24, 21, 17 mg/kg in 0, 15 and 30 cm depths respectively). The results indicated that the removal efficiencies for Cd were significantly influenced by time duration. Maximum metal removal efficiency of Cd for three depths (0, 15 and 30) were 30.2%, 62.3% and 85% respectively. High lime content (13%) of the examined soil appears hindered the removal efficiency. In addition, the pH changes along the soil plots showed an increasing trend from the anode to the cathode.

Keywords: Cadmium, Electrokinetic, Heavy metal, Removal, Soil

1. Introduction

Recently, heavy metal contamination has caused serious environmental and human health problems in abandoned mine and industrial sites (Baek *et al.* 2009; Kim *et al.* 2009; Ađca 2014; Melegy 2014; Tabatabaei *et al.* 2014). Electrokinetic soil remediation methods have gained interest since these methods are well suited for fine-grained soils where other methods as, e.g. soil washing or pump and treat methods are impractical or impossible to use (Shen *et al.* 2007). Even though soil washing is an effective technology to remove heavy metals from sandy or silt soil (Kim *et al.* 2009). Electrokinetic remediation is effective to remove organic compounds, heavy metals and radionuclides from soil, mine tailings, sludge and sediment (Acar and Alshwabkeh 1996; Acar *et al.* 1995; Reddy *et al.*, 2001; Baek *et al.* 2009). In metal removal using the electrokinetic process, a hydrogen ion is produced at the anode due to the hydrolysis reaction of water. The hydrogen ion is transported toward the cathode by an electric field and is exchanged with cationic metals such as zinc and nickel onto soil surface. The desorbed metal ions

are moved toward the cathode by electromigration. Generally, an acidic solution is preferred to extract or desorb cationic metals from soil, which means higher removal efficiency (Baek *et al.* 2009). The control of soil pH using various methods is a common choice to enhance the removal efficiency of pollutants in the electrokinetic process (Baek *et al.* 2009; Reddy and Chinthamreddy 1999; Kim *et al.* 2001; Sah *et al.* 1998; Vengris *et al.* 2001). Consequently, various researchers have tried adding different solutions, such as weak acids and/or complexing or chelating agents, to enhance metal solubility near the cathode and improve remedial efficiency (Eykholt 1994; Yeung *et al.* 1996). Among these solutions, ethylenediamine tetraacetic acid (EDTA) has shown great promise. EDTA has been also employed to treat heavy metal-contaminated soil using conventional soil flushing/washing, as in studies by Amrate *et al.* (2005), Amrate and Akretche (2005) and Kimura *et al.* (2007). Chelating agents such as EDTA have been shown to form strong metal-ligand coordination compounds and are highly effective in remediating heavy metal-contaminated soils (Lestan *et al.* 2008; Popov *et al.* 2003). Yeung *et al.* (1996) have studied the effect of EDTA on enhancing removal of lead from kaolinite spiked samples characterized by a high acid/base buffer capacity. Results of the study have shown that approximately 90% of the contaminant can be migrated toward the anode and accumulated within 15% of soil. This study investigated the feasibility of electrokinetic remediation of Cd contaminated soil in three time duration (2, 4 and 6 days) at field condition.

2. Materials and methods

2.1. Soil and sampling

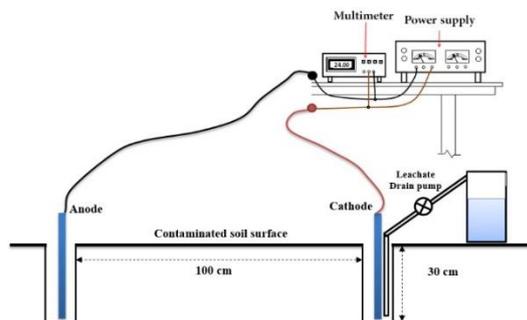
The soil used in this study was spiked by irrigation with Cd ($(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (50 mg kg⁻¹) solution, in a field, around Marand city, North West of Iran. Thereafter, contaminated plots irrigated with cadmium nitrate-free water for 10 days to created balance to heavy metals adsorption on soil particles (Sah and Chen 1998). Initial concentrations of Cd at three depths were 24, 21 and 17 mg kg⁻¹, respectively after contamination. Table 1 lists the basic physical and chemical characteristics of the samples collected from this site.

Table 1. Soil properties and heavy metals concentrations

Parameters	Content
pH (saturation extract)	7.8
Organic matter content (%)	1.86
Cation exchange capacity (cmol _c kg ⁻¹)	21.2
Clay content (%)	30
Equivalent calcium carbonate (%)	13
Cd metals (mg kg ⁻¹)	
– Depth 0	25
– Depth 15	22
– Depth 30	18

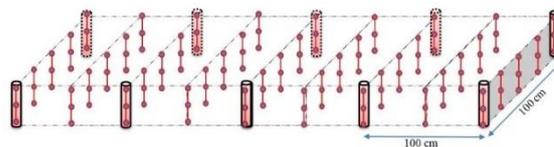
2.2. Experimental set-up

Electrokinetic processing was performed using a field setup, which constitutes a DC electric power supply, two graphite electrodes, multimeter. Graphite electrodes with a diameter of 3 cm and 30 cm high, were used in the field. A schematic view of electrokinetic set-up is shown in Fig. 1. All treatments were conducted with a constant voltage gradient of 1V cm⁻¹ for 2, 4 and 6 days in saturation condition.

**Figure 1.** Schematic of electrokinetic Set-up in the field

2.3. Measurement and analyses

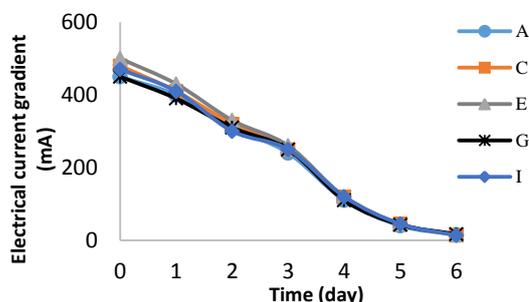
Prior to hold the experiments, Soil pH, EC and initial Cd content were determined in spiked soil. During the experiments, which were operated under a constant voltages condition, the cell current was measured with a digital multimeter. At the end of a specific experimental run time (2, 4 and 6 days), the soil sample was immediately collected from the plots in three depths (Fig. 2). Each sample was measured for soil pH and Cd content. The distribution of Cd content was measured by mixing 5 g of dry soil and 25 ml of 4 M HNO₃, heated (70–80 °C) for 16 h. After cooling, samples were filtered through coarse acid-washed cellulose filters, and total acid-extractable metals were determined with atomic absorption spectrometric analysis (Sposito *et al.* 1982; Richards *et al.* 1998; Turer and Genc 2005).

**Figure 2.** Sampling points in the experimental plots

3. Results and discussion

3.1. Electrical current

The electrical current gradient changes during the test on five series of electrodes are shown in Fig. 3. On the first day, due to the production of H⁺ (acid) in front of the anode by electrolysis of water, ions dissolution and extension of acidic front to the cathode, the path electrical conductivity was more and higher electrical current gradient was observed. But with time passes, ions transfer to the electrodes with opposite charge by the ion migration (ion depletion) caused reduction in path electrical conductivity and electrical current gradient decreased. In this study, the electrical current gradient was decreased gradually in all five electrode series and reached from 470 mA at the start of the experiment to 15 mA at the end of the sixth day. Changes in the electrical current gradient also have been reported by Altin and Degirmenci (2005), Altaee and *et al.* (2008) and Al-Hamdan and Reddy (2008).

**Figure 3.** Changes in the gradient of the electric current during the test

3.2. Soil pH

Fig. 4 shows the pH distributions across the soil plots after the experiments, where 1 is the slice closest to the anode and 5 the slice closest to the cathode. Considering that the soil had a pH of 7.8 before the experiment, the soil pH after the experiment decreased greatly at the anode across the soil due to extension of the acid-front towards the cathode by migration advection and diffusion. Soil pH after the experiment increased at the cathode across the soil due to Electro-migration of OH⁻ ions towards the anode (Yuan and Chiang 2008; Yuan *et al.* 2009). It was also observed that soil pH in the cathode region had not been significantly affected by electrolyte pH, but had been in the anode region. Pamukcu (1997) and Al-Hamdan and Reddy (2008) reported that the main reason why pH in the soil at cathode end is lower compared with its value in the cathode compartment is the continuous consumption of

OH⁻ due to generation of Cd(OH)₂ in the soil at that location. Compared with the pH profile for Series A, C, E, G and I series, the pH values for B, D, F and H series were constant through the entire soil sample except for the region closest to the anode and cathode, approximately. This is the reason why a relatively small amount of H⁺ and OH⁻ entered the soil when these series not located in the site of electrode placement.

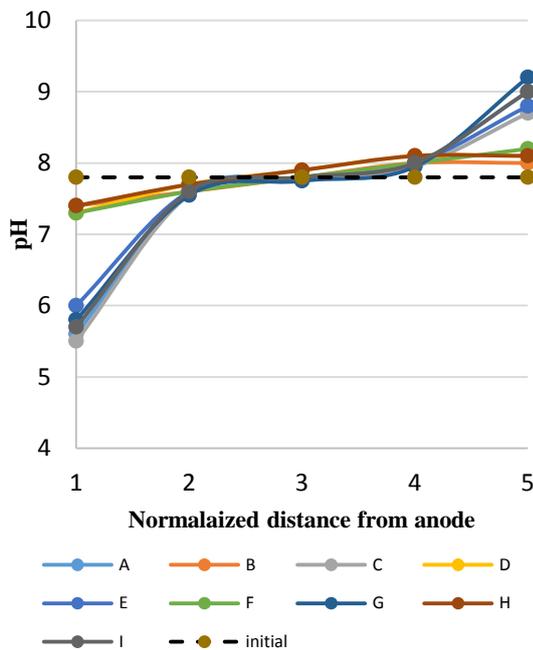


Figure 4. pH distribution in soil plots after electrokinetic treatment

3.3. Cd content in the Soil

Figures 5 and 6 show the residual Cd concentration in experimental plots in series A and B samples after applying electric current for six days. Due to the same trend of Cd concentration in the sampling series matches to the electrodes location, series A is shown in Fig. 5 as an example of Cd concentration of these Series. For Cd concentration in series between the electrodes also Cd concentration of B series is given as an example in Fig. 6. Different Cd initial concentrations were observed in the above figures. The reason for this could be severe absorption of Cd in the upper layers of the soil during adding of cadmium nitrate solution. In fact, the distance between the initial concentration and residual concentration in the figures 5 and 6 shows the amount of Cd removal. The amount of Cd removal from soil was increased with increasing duration of electrical current application. As can be seen in the figures the highest removal of Cd observed nearby the anode and an increase in Cd concentration was observed near the cathode. Reduction in soil pH at the anode by production of H⁺ in water electrolysis can enhance the precipitation of heavy metals. Conversely, an increase in pH in the cathode due to production of OH⁻ leads to the precipitation of heavy metals (Giannis and Gidaracos 2005). Similar results about the influence of pH near the anode and cathode on the removal of heavy metals have reported by Zhou *et al.* (2005) and kim *et al.* (2011). As seen in Figures 5 and 6, a

significant difference in the removal of Cd was observed among the electrode series and series between the electrodes. In series between the electrodes due to the lack of H⁺ production at the outset of the plot, higher Cd removal efficiency was not observed as the series based on the location of the electrodes, and the highest Cd removal of this series observed in the middle of plots.

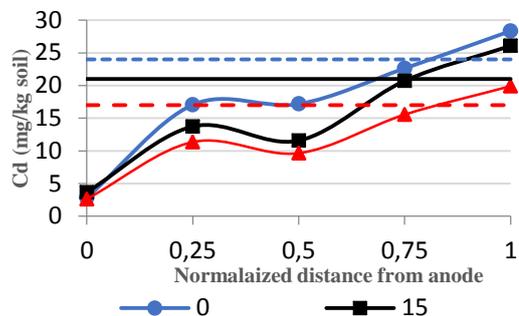


Figure 5. Distribution of Cd in soil plot (sampling series A) after electrokinetic treatment

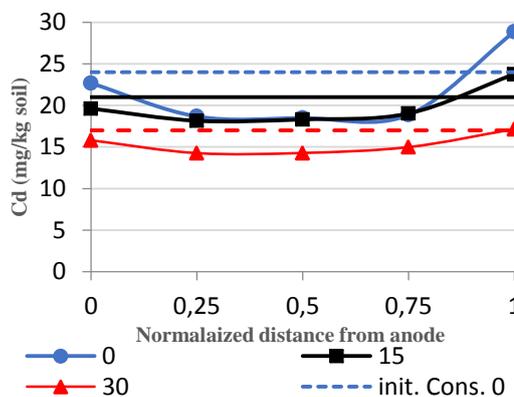


Figure 6. Distribution of Cd in soil column after electrokinetic treatment

Table 2 shows the removal efficiency of Cd in the soil section after electrokinetic remediation in three time duration and three depths. Between all experiments, 3rd depths had highest Cd removal efficiency. In general, the removal efficiency of Cd from soil increased with increasing electrical current application time, but, the increasing in Cd removal efficiency gradually declined because of decreasing in the electrical current gradient with time (Fig. 3). High lime content (13%) of the examined soil appears hindered the removal efficiency. Similar results have been noted in carbonate soils by Altin and Degirmenci (2005).

4. Conclusions

Electrokinetic remediation have good heavy metal removal efficiency in the field conditions. In this study a total of 18.01 percent of cadmium removed from soil. Although there was a large amount of lime (13%) in the soil. Increasing in the time duration of applied electric current enhanced the removal of Cd from the soil, meanwhile increasing trend of removal efficiency declined with increasing time. Electrokinetic remediation of Cd contaminated soil in deeper depths was more efficient than

the surface soil. Results also showed that electrokinetic remediation caused change in the soil pH near the anode and cathode electrodes. Decreasing in the soil pH near anode electrode enhanced the heavy metal removal efficiency and maximum removal efficiency showed near the anode electrode.

Table 2. Mean removal efficiency for Cd in different time duration at 3 depths

Time duration (day)	Sampling depth (cm)	Mean Cd removal efficiency (%)
2	0	9.4
	15	13.1
	30	13.3
4	0	14.7
	15	17.9
	30	18.2
6	0	20.3
	15	22.4
	30	24.2

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