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CATHOLYTE-CONDITIONING ENHANCED ELECTROKINETIC REMEDIATION OF Co AND Pb POLLUTED SOIL

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Abstract

The feasibility of catholyte-conditioning to enhance the electrokinetic (EK) remediation of cobalt and lead polluted soil has been investigated in this study. Electrokinetic experiments were conducted using an EK cell 10 cm in width, 10 cm in height, and 50 cm in length. Plate type electrode of graphite was used as electrode material. Two experiments were conducted under constant voltage condition (2 V/cm). The pH values of the soil significantly affect the removal of Co and Pb ions. Due to electrolysis reaction, soil pH increases near the cathode and without pH conditioning, metals precipitate as hydroxides. This problem is solved by the addition of nitric acid (0.1N) in the catholyte compartment. Significant movement of metals was observed through the soil with high removal efficiency. Results showed that catholyte conditioning using nitric acid increased the removal of cobalt and lead from the soil and, consequently, the maximum removal achieved was 73.84% and 62.88% for cobalt and lead, respectively. These EK tests indicate that the increased experimental time induced a higher removal efficiency of cobalt and lead. The results suggest that longer treatment periods will result in further transport of cobalt and lead in the sample. Also, it indicated that the highest quantities of cobalt and lead moved towards the catholyte, particularly at upper 5 cm. On the basis of the experimental results, we conclude that the electrokinetic remediation, using 0.1N HNO_3 as catholyte-conditioning, is suitable for extracting cobalt and lead from polluted soil.

Key words: catholyte-conditioning, cobalt, enhanced electrokinetic, lead, nitric acid

1. Introduction

Nowadays heavy metals pollution of soils has become a serious environmental problem in the world. Metals originate from a range of human activities including mining operations and landfills. Agricultural lands in the vicinity of these pollution sources have been seriously contaminated by metals (Reddy and Cameselle, 2009). Over the past few decades, several technologies have been applied to remove pollutants all over the world. A significant amount of electrolinetic remediation work for remediating heavy metals are available (Akram and Alshawabkeh, 2009; Probstein and Hicks, 1993; Reddy, 2010; Saichek and Reddy, 2003). In recent decades, laboratory-scale and field scale studies have

shown that electrokinetic remediation can be effectively used to metal removal from soils (Bahemmat et al., 2010; Bulgariu et al., 2006; Ottosen et al., 2001; Reddy and Ala, 2005). A direct-current (DC) electric field is imposed on the contaminated soil. Contaminants migrated by the combined mechanisms of electroosmosis, electromigration, and/or electrophoresis. Electroosmosis is regarded as the phenomenon of water flow induced by application of an electrical field on porous media (Probstein and Hicks, 1993), whereas, electromigration is characterized as the transport of ions under the influence of an electrical field (Acar and Alshawabkeh, 1993). Electrolysis of water is the dominant electron transfer reaction occurring at electrodes during the electrokinetic

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process (Eqs. 1-2). As a result of electrolytic decomposition of electrolytes at the electrodes, H^+ and OH^- ions are generated at the anode and the cathode, respectively during the electrochemical remediation process as follows:

Oxidation at the anode:

$$2H_2O - 4e^- \rightarrow 4H^+ + O_2 \uparrow \qquad (1)$$

Reduction at the cathode:

$$4H_2O + 4e^- \rightarrow 4OH^- + 2H_2 \uparrow \qquad (2)$$
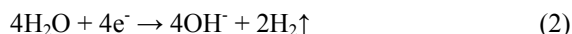
The generated H^+ and OH^- ions migrated through the soil by the DC electric field. Hydrogen ions produced in the process decrease the pH near the anode causing desorption of metallic contaminants from the soil solid phases. Then the dissolved metallic ions are removed from the soil solution by ionic migration and precipitation at the cathode (Acar and Alshawabkeh, 1993). On the other hand, increase in the hydroxide ion concentration causes an increase of the pH near the cathode.

One of the major problems encountered in the EK removal of heavy metals from soil is the precipitation of metal oxide/hydroxide near the cathode, where soil pH significantly increases due to production of hydroxide ion at the cathode (Baek et al., 2009). Where the pH changes significantly within a very short distance, creating a region called the pH front. Generally, this pH front is close to the cathode because the migration velocity of the hydrogen ions is higher than that of the hydroxide ions (Lee and Yang, 2000; Zhou et al., 2005). The pH front acts as a barrier for the removal of heavy metals, such as copper, lead, and zinc, from the soil during EK because the solubilities of most heavy metals are relatively low when the soil pH is high (Pavel and Gavrilescu, 2008; Zhou et al., 2003). The change in soil pH can change the chemical speciation of contaminants, rendering them immobile (Yeung and Gu, 2011). These precipitation reactions can be hindered by different enhancement techniques such as using purging solutions (HNO_3, citric acid, HCl) or complexing agents (EDTA) and special electrodes and membranes (Virkutyte et al., 2002; Yeung et al., 1996).

Specific objectives of reservoir conditioning include: (1) precipitation of metal contaminants should be avoided and/or precipitates should be solubilized and mobilized; (2) electrical conductivity of the specimen should not be increased excessively in a short duration so as to avoid diminishing of the advective transport of contaminant by electroosmosis prematurely; (3) the electrolysis reaction at the cathode should possibly be depolarized to avoid the generation of OH^- ions and their transport into the specimen (Yeung and Gu, 2011). Accordingly, controlling soil pH is very important for the success of electrochemical remediation. The purpose of electrode reservoir conditioning is to maintain the pH of catholyte within appropriate ranges specific to the

contaminants being remediated. Cobalt is commonly obtained from Ni, Pb, Cu, and Fe ores as a by-product. The main industrial use of cobalt is in the production of high-grade steels, alloys, superalloys, and magnetic alloys. Acid conditions increase the availability of Cobalt as Co^{2+}. Cobalt was found to accumulate in hydrous oxides of Fe and Mn in soils (Bradl, 2005). As the soil pH is raised, Cobalt solubility decreases because of increased chemisorption on oxides and silicate clays, complexation by organic matter, and possibly precipitation of $Co(OH)_2$. Lead is the most abundant element among the heavy metals with an average content of approximately 15 ppm (Bradl, 2005). Under alkaline conditions, lead in the soil may become sediments of hydroxides [$Pb(OH)_2$] and carbonates ($PbCO_3$).

Soil pH determines the concentrations of hydroxide and carbonate in the soil solution, which play a crucial role in the formation of heavy metal complexes in soil (Virkutyte et al., 2002). To date, a very few studies have been reported the feasibility of electrokinetic remediation cobalt in real polluted soil. Unlike cobalt, numerous studies that use ideal soils such as kaolin spiked with a selected single contaminant (e.g. lead) to understand the contaminant transport processes have been reported. However, only a limited number of studies have been reported on real-world soils contaminated with a wide range of aged contaminants. Also, in literature, few studies have been encountered on the electro-remediation of heavy metals from natural polluted soil and compared its removal efficiencies in different depths.

In this study, we investigated the capability of electrokinetics with catholyte conditioning (0.1N HNO_3) for the simultaneous remediation of aged polluted soil with cobalt and lead at laboratory scale. Comparison of residual concentration of cobalt and lead after electrokinetic treatment was performed in two different depths and four different times.

2. Materials and methods

2.1. Soil sampling

Soil was taken from the site of a mine and several hundred kilograms were mixed. The soil had been polluted with cobalt and lead, and contained several other heavy metals at elevated concentrations due to the mining activity on the site. At the laboratory, the soil was sieved and the fraction smaller than 2 mm was used in electrokinetic experiments. Selected physicochemical properties of the soil were measured and are listed in Table 1.

The soil sample was submitted to a physicochemical characterization: pH, Electrical conductivity, moisture, texture and cation exchange capacity (CEC). The organic carbon (OC) content was determined by oxidation with 1 N potassium dichromate in acidic medium. Particle size distribution was determined by the hydrometer

method. Soil pH and EC were measured by employing a pH meter and EC meter. $CaCO_3$ content was determined by following equation (Eq. 3) (Sparks, 1996):

$$CaCO_3 \ (\%) = \frac{\left[\left(10 \times N_{HCl} \right) - \left(R \times N_{NaOH} \right) \right] \times 0.05 \times 100}{W_t} \quad (3)$$

where N_{HCl} is the normality of the HCl solution, R is the volume of NaOH solution used (ml), N_{NaOH} is the normality of the NaOH solution, and W_t is the weight of air-dried soil (g).

Table 1. Selected physicochemical properties of soil

Soil property	
Sand (%)	56
Silt (%)	22
Clay (%)	22
pH	8.2
Electrical Conductivity (ds m^{-1})	1.493
Organic Carbon (%)	0.86
Soil Saturation Percent (%)	38.88
CEC (cmol$_+$ kg^{-1})	21.9
Carbonate Content (%)	12.07
Pb (mg kg^{-1} soil)	2500
Co (mg kg^{-1} soil)	19.83

2.2. Electrokinetic set up

The experimental apparatus is shown schematically in Fig. 1. Electrokinetic experiments were conducted in a $50 \times 10 \times 10$ cm^3 plexiglass cell. The two electrode compartments (with 1000 mL working volume) were placed at each end of the sample compartment. On both sides, two graphite plate electrodes (10 cm × 5 cm × 1 cm) were used to apply the electric field. Two sheets of filter paper (Whatman 42) were used to isolated soil particles and the electrolyte solution reservoirs. The total length of the soil column was 30 cm.

The solutions in the electrode compartments were stirred continuously. Each electrode compartment was changed (refreshed) daily.
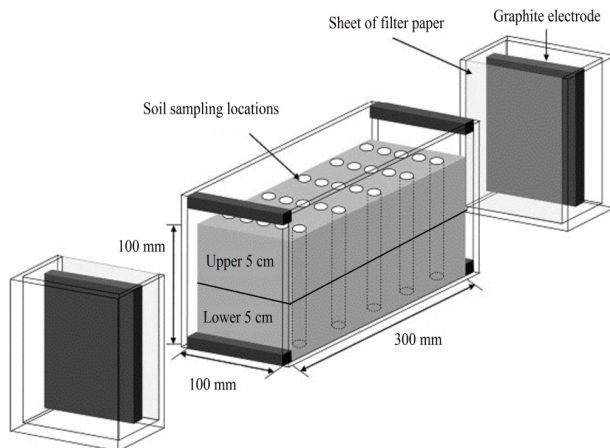
Fig. 1. Schematic of the electrokinetic cell apparatus

2.3. Experimental conditions

Initially, for each electrokinetic test, approximately 5 kg of dry soil were saturated with 2 L of water (according to saturation percent) and mixed in a polyethylene container with a stainless spatula. After saturation, the electrokinetic cell was compactly filled with the saturated soil. Experimental conditions are summarized in Table 2. Exp. 1 is a conventional electrokinetic experiment, and in Exp. 2 used 0.1N HNO$_3$ as a catholyte-conditioning fluid to control the catholyte pH (6-7) which enhance desorption of Co and Pb from soil. A constant voltage gradient of 2 V/cm was applied to the electrode, and the electrokinetic process was carried out for 20 d.

Table 2. Experimental condition of electrokinetic process

Exp. no.	Anolyte purging solution	Catholyte purging solution	Duration (days)	Electric potential (V/cm)
1	Distilled water	Distilled water	5, 10, 15, 20	2
2	Distilled water	0.1N HNO$_3$	5, 10, 15, 20	2

2.4. Analytical procedure

During the electrokinetic treatment, the electric current was measured hourly, and the soil pH was measured daily at five different locations: 5, 10, 15, 20 and 25 cm from the anode. Moreover, after 5, 10, 15 d of experimental time, soil samples were taken from same positions by a glass tube. Also, the soil samples taken from both upper 5 cm and lower 5 cm at these location after 20 d. The samples were oven dried and then digested by HNO$_3$ (4N) (Richards et al., 1998). The solution samples from the acid digestion procedures were analyzed using an AAS (Shimadzu, Japan). Also, removal efficiency of metal ions by electrokinetic is defined as following equation (Eq. 4):

$$\text{Removal efficiency } (\%) = \frac{C_0 - C_f}{C_0} \times 100 \quad (4)$$

where, C_0 is initial metals concentration (mg kg^{-1}) of soil, and C_f is the final concentration of metals (mg kg^{-1}) after electrokinetic treatment in soil.

3. Results and discussion

3.1. Distribution of soil pH after electrokinetic treatment

As described above, the anode region becomes acidic due to H$^+$ generation and the cathode region becomes alkaline due to OH$^-$ generation during EK processes. The variation in the pH of the soil specimen was measured directly using a pH probe during electrokinetic remediation and is shown in Fig. 2.
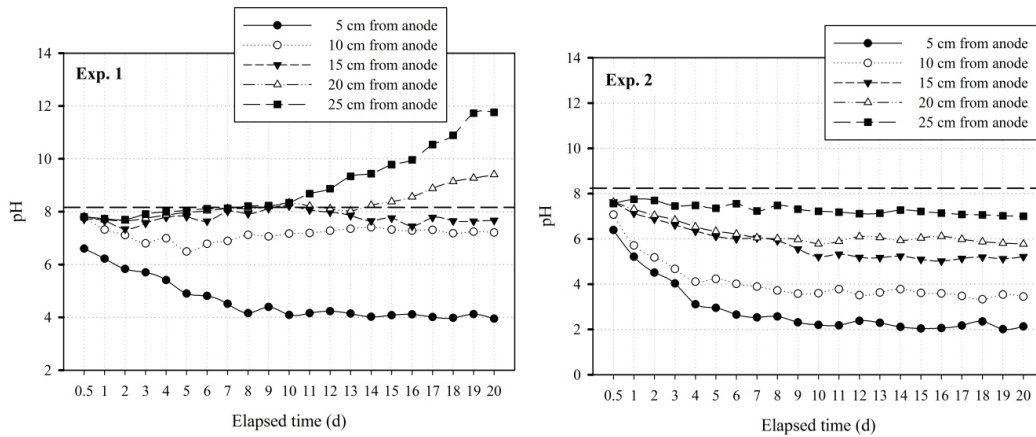
Fig. 2. The variation of pH of soil during electrokinetic experiment

In Exp. 1, where conditioning was not performed, the pH changed to below 4 from the initial 8.2 near the anode and above 12 near the cathode (25 cm from anode).

These results are in accordance with the findings reported in various studies (Bahemmat et al., 2010; Kim et al., 2009). In typical electrokinetic remediation without electrolyte conditioning (Exp. 1), the H^+ ions were transported towards the cathode by electromigration and electroosmosis, while OH^- was moved towards the anode. However, H^+ travels at a velocity 1.8 times faster than OH^- (Acar and Alshawabkeh, 1993). Whereas H^+ enhanced desorption of heavy metals, OH^- significantly declined the mobility of the metal ions because of $Me(OH)_2$ precipitation (Lee and Yang, 2000). It is pivotal, to maintain an acidic pH in the soil and to prevent hydroxide precipitation (Yeung and Gu, 2011). The transport of the base front from the cathode compartment to the soil has several unfavorable effects that result in a decrease in the effectiveness of the electrokinetic remediation (Virkutyte et al., 2002).

Acidic electrolytes such as HNO_3, has been used for this purpose. Electrolyte pH conditioning is a feasible and convenient way to adjust soil pH during EK process. In Exp. 1 without catholyte pH conditioning, the pH in the section of soil close to the cathode quickly increased to above initial pH at 10 d. For Exp. 2 with catholyte pH conditioning, the pH in the section of soil close to the anode was even decreased to about 2 in the later stage. In the experiment without catholyte conditioning, soil pH increased from 2 close to the anode to more than 11 close to the cathode. This is a typical soil pH variation for EK remediation (Acar and Alshawabkeh, 1993; Reddy, 2010; Saichek and Reddy, 2003).

The pH in the central section of the soil ranged between the values found at the anode and the cathode. The pH increased as the soil became far away from the anode, and the pH in the middle of the soil cell maintained about at the initial value of 8.2. The much lower soil pH near anode in Exp. 2 than in Exp. 1 was ascribed to the production of more H^+ at anode in Exp. 2 with higher current (Fig. 3), which exceeded the buffering capacity of anolyte. The pH distribution in Exp. 2, where conditioning was performed, was rather even. In relation to pH, as it was expected, the catholyte presented predominantly an alkaline pH and the anolytes an acid pH which varied between 3 and 4, if they are not controlled (Lee and Yang, 2000).

3.2. Variation of current density

Fig. 3 shows the comparison of current variation with elapsed time for Exp. 1 and Exp. 2. The development of the current density is demonstrated for 24 h that it is average of 20 d. The ions move in consequence of the process of electromigration and electro-osmosis, and as the concentration of ions reduce in the soil with treatment time, decreasing the current intensity (Reddy and Ala, 2005).

In Exp. 2, the electrical current was higher than in Exp. 1 in the same time. Kim et al. (2009) reported that under a constant current the introduction of hydrogen ions into the soil by acidic circulation using HNO_3 can decrease the voltage gradient and resistance of the soil and enhance the dissolution of soil minerals. At the very beginning, current density increased rapidly and peaked at 26 mA cm^{-2}. Then, the current decreased, dropping to a value below 2 mA cm^{-2} within the first 20 h. Finally, the electric current stabilized at a low value that ranges from 1 to 2 mA cm^{-2} with increased treatment time. The maximum and minimum current recorded in the 6 h and 24 h were, respectively, about 26 and 1.4 mA cm^{-2}.

The changes in current density were almost similar in all days because each electrode compartments changed (refreshed) daily and solute ions in those depleted. The increase of current intensity is attributed to significant H^+ and OH^- ions generated at the anode and cathode, respectively, due to electrolysis of water (Acar and Alshawabkeh, 1993). The increase of ion concentration in the electrode compartments results in the decreasing of the electric resistance and therefore, increasing of the

electric current (Reddy and Ala, 2005; Reddy and Karri, 2006).

Furthermore, the increased mobility of ions in the soil as a result of dissolution of precipitated salts and desorption of adsorbed ions (Reddy et al., 2011) also contributes to the electric current. Also, the OH^- ions electrogenerated at the cathode will increase the soil pH close to the cathode end. High pH decreases the solubility of metal ions, forming precipitates that diminish the total amount of ions available to transport (Virkutyte et al., 2002).
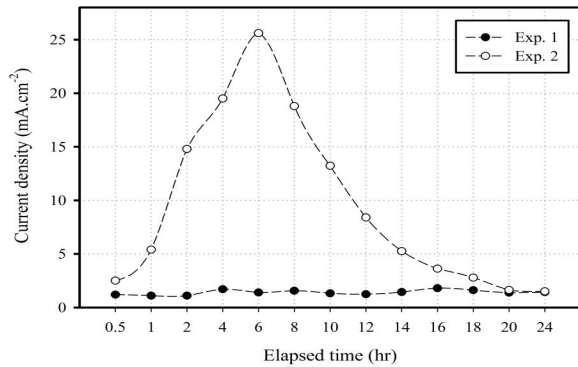

Fig. 3. Example of typical evolution of daily current density during electrokinetic treatment

It results in a decreasing electric current intensity. The increase in extraction of the heavy metals and other ions caused a decrease in the electrical resistance of the soil. Thus, the current density increased gradually over a period of 6 h, decreased suddenly, and remained low thereafter. In general, the current values initially increased to a maximum value within a short time and then reduced and stabilized.

For Exp. 2 test, current increased rapidly within the first 6 h of the testing and then started to decrease and stabilize thereafter. As the ions migrated towards the electrolyte compartments, however, the current gradually declined. After approximately 20 h of voltage gradient application, the current for Exp. 1 and Exp. 2 tests stabilized at almost the same level (i.e., 1 mA). High current was measured due to the partial solubilization of salt precipitates resulting in higher ionic concentration in pore-water (Virkutyte et al., 2002; Saichek and Reddy, 2003).

However, with increased elapsed time, these ions are depleted as they migrate into the electrolyte compartments (Reddy and Karri, 2006). At the same time, ions constantly generated near the anode had high mobility and were transported through the soil due to different transport processes including electromigration and electroosmosis (Acar and Alshawabkeh, 1993).

3.3. Cobalt and lead distribution after electrokinetic treatment

Extraction of the remaining cobalt and lead in the soil samples was performed according to the Section 2.3. General remediation results are given in Tables 3 and 4. Table 3 includes normalized concentrations of Co and Pb (C/C_0) in the soil, after the unenhanced electrokinetic treatment (Exp. 1), and Table 4 shows the details of the normalized concentrations of Co and Pb (C/C_0) in the soil, after the catholyte-conditioning enhanced electrokinetic (Exp. 2), under the different time. As shown in Tables 3 and 4, results indicated that the electrokinetic remediation efficiency of cobalt can be largely enhanced by catholyte conditioning. At the case of unenhanced electrokinetic (Exp. 1), only 15.46% of cobalt was removed.

The cobalt concentrations in the soil (Table 4) decreased compared to the initial concentration and the lowest concentrations were found in Exp. 2 near the anode. In some sections metal concentrations increased compared to the initial concentrations ($C/C_0 > 1$), because of the accumulation of metals.

The migration and transport of the cobalt was higher under condition of catholyte conditioning using an acidic solution because cations including metal ions can be easily desorbed into the pore solution from a soil surface in an acidic condition (Ouhadi et al., 2010; Xiu and Zhang, 2009). Hence, these desorbed metal ions can easily be transported by electromigration under an electric field (Probstein and Hicks, 1993; Virkutyte et al., 2002).

The lead removal efficiencies were 21.23% and 38.14% for Exp. 1 and Exp. 2, respectively. Similar to the results for cobalt removal, catholyte conditioning with an acidic solution helped to enhance lead removal efficiency.

Table 3. Normalized concentrations of heavy metals (C/C_0)[*] in the soil, after the electrokinetic treatment[**] (**Exp. 1**), under the different time

Normalized concentrations of heavy metals (C/C_0)										
	Cobalt						Lead			
	Distance from anode (cm)						Distance from anode (cm)			
Time (d)	5	10	15	20	25		5	10	15	20	25
5	0.885	1.111	0.864	1.099	0.785		0.849	0.895	0.967	1.091	0.950
10	1.011	0.996	1.022	0.859	0.750		0.759	0.890	0.964	1.132	0.873
15	0.868	0.922	0.892	0.812	0.873		0.683	0.868	0.879	0.958	0.837
20	0.811	0.757	0.934	0.912	0.811		0.674	0.778	0.860	0.890	0.734

[*]C_0: Initial concentration; C: Final concentration
[**]Mean values of the five replicates.

Table 4. Normalized concentrations of heavy metals (C/C$_0$)[*] in the soil, after the electrokinetic treatment[**]
(**Exp. 2**), under the different time

	Normalized concentrations of heavy metals (C/C$_0$)										
	Cobalt						*Lead*				
	Distance from anode (cm)						*Distance from anode (cm)*				
Time (d)	5	10	15	20	25		5	10	15	20	25
5	1.093	1.071	0.809	0.774	0.904		0.761	0.969	0.919	1.076	0.804
10	0.776	1.220	1.061	1.021	0.773		0.603	1.234	0.852	0.739	0.758
15	0.461	0.818	0.818	0.901	0.604		0.474	0.939	0.910	0.790	0.760
20	0.262	0.883	0.366	0.964	0.395		0.371	0.674	0.678	0.696	0.672

[*]*C$_0$: Initial concentration; C: Final concentration*
[**]*Mean values of the five replicates.*

For all experiments, lead accumulated in the cathode section because Pb^{2+} ions from the anode compartment met OH$^-$ from the cathode compartment and precipitated as Pb(OH)$_2$, and were partially removed from the anode section because lead in the electrokinetic process became cationic and moved towards the cathode, most probably as free Pb^{2+} ions in the pore fluid (Lee and Yang, 2000). In catholyte conditioning using an acidic purging solution, the overall cobalt and lead removal efficiencies were 42.58% and 38.14%, respectively.

In Exp. 1 where catholyte conditioning was not performed, the cobalt removal efficiency was lower than that for catholyte conditioning: 15.4%, and 38.1%, respectively. According to Chung and Kang (1999), the transport of lead (II) at low levels of concentration is slower because almost all of the lead is adsorbed to the soil particle. Using 0.1 N nitric acid as a purging solution, it seems that after initial 10 d of treatment cobalt and lead accumulated in the middle of the cell. As a result of the low pH close to the anode, lead and cobalt existed as Pb^{2+} and Co^{2+}, and migrated towards the cathode (Hamed et al., 1991; Virkutyte et al., 2002). By the end of the experiment, 62.88% of lead had been removed from the soil close the anode. According to Puppala et al. (1997), soil pH should be kept below 6 to hinder these precipitation reactions. Virkutyte et al. (2002) report that these reactions occur at their lowest level when pH is between 4 and 4.5.

Cobalt seems to follow the almost same route as lead. An amount of cobalt dissolved close to the anode accumulated in the middle of the cell. Presence of peak concentrations of cobalt in the middle of column, suggests that while Co is transported from anode to cathode by electromigration. By the end of the experiment, about 73.83% of cobalt had been removed from the soil close the anode. As expected, the increase in remediation time from 5 to 20 days increases the removal efficiency of cobalt 7% to 42.58%, respectively (Exp. 2).

From the analysis of the results for different remediation time, it can be concluded that 9.38% to 38.14% of the total lead removed from soil at 5 to 20 days, respectively. Higher remediation times would increase the cobalt and lead removal at the soil section close to the anode. The results suggest that longer treatment periods will results in further transport of cobalt and lead in the soil.

3.4. Comparison of residual concentration of cobalt and lead after electrokinetic treatment in two different depths

Fig. 4 illustrates the results of the remaining concentration cobalt after the experiment was completed in two different depths. As it can be seen, more than 70% of the initial Co and more than 60% of the initial Pb were removed from the soil with the application of electric field in areas close to the anode (0-5cm). After 20 days of Exp. 1, the residual concentration of cobalt in the soil sections after the electrokinetic treatment decreased and removal efficiency of cobalt was in two depths almost similar. In the lower 5 cm, cobalt removal is less than in the upper 5 cm as shown in Fig. 4.

Compared with the control, lead concentration extracted by HNO$_3$ clearly decreased in the sections near the anode, which is in good agreement with the fact that Pb^{2+} migrates from anode toward cathode. As seen from Figs. 4 and 5, the difference of between removal efficiency of lower and upper 5 cm was not significant for Exp. 1, while for Exp. 2 in upper 5 cm, the removal efficiency was higher than in lower 5 cm in the same locations particularly for cobalt. The general trend of decrease in the removal efficiency as distance from the anode increases is also seen in these electrokinetic experiments. The removal efficiency drops below 25% for all soil sections, and for both cobalt and lead in lower 5 cm in the Exp. 1.

The highest removal efficiency comes from the section closest to anode, as expected. When the soil at the section closest to anode were analyzed, the results are comparable with the findings in various studies in which the same conditioning solution was treated (Kim et al., 2009, 2011; Ryu et al., 2011). In the Exp. 2, when the soil at the lower 5 cm were analyzed, it can be seen that the removal efficiency for cobalt and lead is lower than 30% except for Pb in area close to the anode (0-5cm), which is 60% (Fig. 5).

4. Conclusions

The present study has demonstrated the possibility to remove the cobalt and lead in soil when submitted to an electric field concurrently, as well as the applicability of the electrokinetic (EK) process to remove them from two different depths.
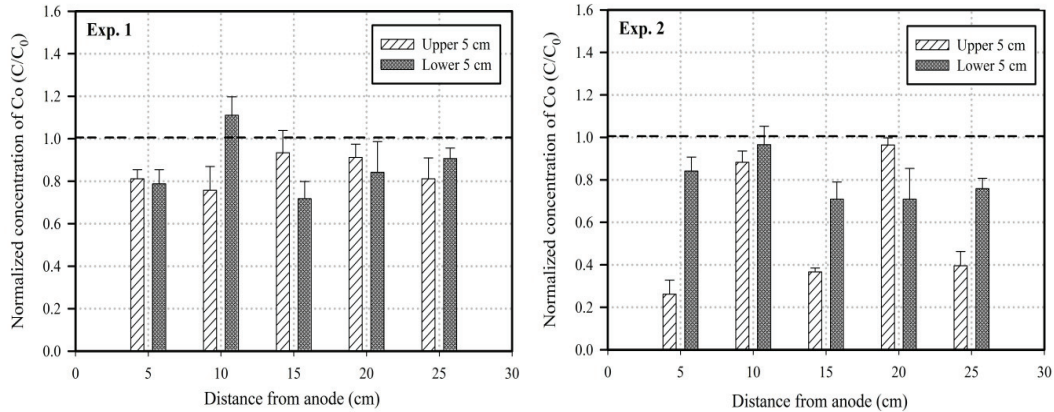
Fig. 4. Comparison of residual concentration of Co after electrokinetic remediation in upper and lower 5 cm, Error bars represent ± one standard error (n = 3)
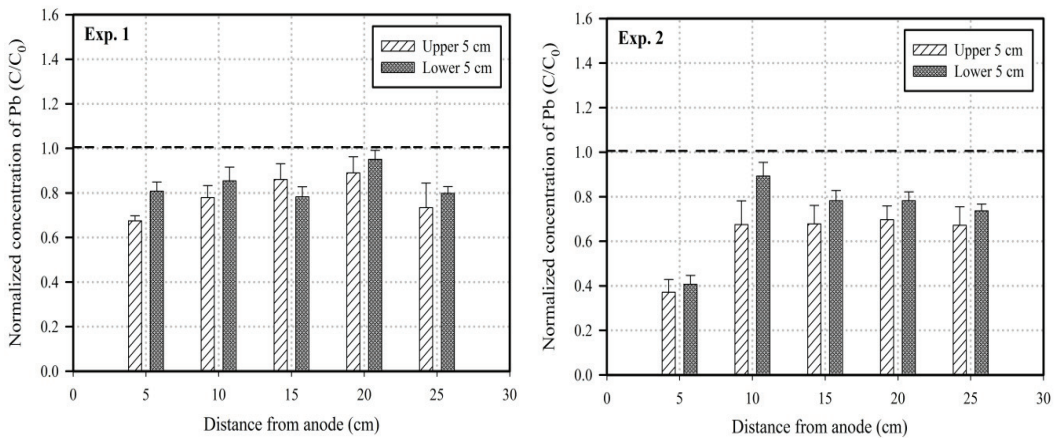

Fig. 5. Comparison of residual concentration of Pb after electrokinetic remediation in upper and lower 5 cm, Error bars represent ± one standard error (n = 3)

The results indicated that with application of electric field in soil, acidic conditions dominated in the soil cell, and the highest quantities of cobalt and lead moved towards the catholyte, particularly at upper 5 cm. Also, this shows that catholyte conditioning (0.1N nitric acid) is a very effective enhancement method to remove cobalt and lead from polluted soil in electrokinetic remediation.

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