

Remediation of Electroplating Contaminated Soil by a Field Scale Electrokinetic System with Stainless Steel Electrodes

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ABSTRACT

A 1.5 m (L) × 1.0 m (W) × 1.1 m (H) polypropylene (PP) field scale electrokinetic system coupled with stainless steel electrodes was designed to examine metal removal performance applied 0.2–0.35 V/cm potential gradient and 0.05–0.5 M lactic acid for 20 days. Electroosmosis permeabilities of 2.2×10^{-5} cm²/V-s to 4.8×10^{-5} cm²/V-s were observed and it increased with the potential gradient increased. The reservoir pH controlled at 7.0 ± 1.0 has been effectively diminished the clogging of most metal oxides. The best removal efficiency of Zn, Pb, and Ni was 78.4%, 84.3%, and 40.1%, respectively, in the field scale EK system applied 0.35 V/cm and 0.05 M lactic acid for 20 days. Increasing potential gradient would more effectively enhance metal removal than increasing concentration of processing fluid. The reservoir and soil temperatures were majorly related to potential gradient and power consumption. A 4–16°C above room temperature was observed in the investigated system. It was found that the temperature increase in soil transported the pore water and metals from bottom to the topsoil. This vertical transport phenomenon is critical for the electrokinetic process to remediate in-situ deep pollution.

Keywords : Electrokinetic, Metal, Field scale, Soil remediation, Soil temperature

1. Introduction

The electroplating process is one of the major metal contamination sources among the metal surface treatments. It is resulted from lots of metal solution applied on the cleaning and plating process (Dutra et al., 2008; Panayotova et al., 2007; Jordao et al., 2007). The improper treatment of the metal wastewater has been resulted in serious surface water and sediment contamination (Ouki and Neufeld, 1997; Chang and Kim, 2007). The Yangtze River contamination caused by the electroplating plants has been considered as an environmental issue in China (Hang et al., 2009). The pollution caused by electroplating process depends upon the metal solution used and the key contaminated metals include Zn, Cu, Pb, Cr, and Ni.

Electrokinetic (EK) remediation is a promising in-situ technique for decontamination of media with low hydraulic permeability. Basically, the EK technique relies on the

action of an electric field generated between inserted inert electrodes in the medium by applying a direct current or a constant voltage. The applied potential gradient causes the migration of electrolyte solution and soluble contaminants toward the electrodes via electromigration, electroosmosis, and electrophoresis (Acar and Alshawabkeh 1993). Improving EK performance depends on the interaction between the contaminants and the processing fluid. Additional parameters affecting the EK performance include the potential gradient, processing time, and concentration of processing fluid, which were highly dependent on the characteristics of the soils and contaminants. Since researches on electrokinetic remediation started in 1980, few research groups have tried to apply the technology to real field. Kim et al. (2012) reported a two-dimensional electrode configuration in the field would efficiently transport pore water to the top soil as well as contaminants, which achieved removal efficiency of only 20.7% for As, 12.1% for Cu, and 23.9% for Pb. Lee et

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al. (2012) conducted an EK field test with stainless steel electrode for 100 day and achieved 63.8% removal for Pb and 39.5% removal for Cu. Kim et al. (2013) reported effective circulation might enhance the performance of EK process because of a constant pH within the system. The removal efficiency was 43.2% for As, 17.7% for Cu and 81.2% for Pb with stainless electrode for 28 days. The removal efficiency of metals in field did not as good as expected because many geo-environmental factors should be considered.

Before field test, research data from a scale-up system is much more important to find the optimum in-situ electrokinetic parameters. Additionally, some contaminated sites are limited to in-situ remediation works. In this study, a $1.5\text{ m} \times 1.0\text{ m} \times 1.1\text{ m}$ field scale electrokinetic system was designed to fit the needs, which can also move to the site to remediate the excavated contaminated soil. This study was aimed to examine removal performance of metals by the field scale EK system coupled with stainless steel electrodes applied $0.2\text{--}0.35\text{ V/cm}$ potential gradient and $0.05\text{--}0.5\text{ M}$ lactic acid for 20 day. The electrokinetic behavior and soil/reservoir temperature will be also discussed in this study.

2. Materials and Methods

2.1. Soil and processing fluid

Tested soils were sampled from a wasted electroplating factory in southern Taiwan. The texture of the soil sample

was classified as loamy sand (85.2% sand, 7.8% silt and 7.0% clay) by particle size analysis. A soil organic matter content of 3.1% was determined by the combustion method (Matamoros et al. 2009). A soil pH of 8.2 was measured in water suspensions with a 1 : 1 volume ratio of soil to solution, and a soil pH_{ZPC} of 2.7 was determined using a zeta potential instrument (Pen Kem-Laser Zee 3.0, USA). A soil solid density of 2.41 g/cm^3 was determined according to the method of ASTM D854-92 method. The hydraulic conductivity of the soil sample was $7.5 \times 10^{-5}\text{ cm/}$ measured by a falling-head permeameter.

After removing debris and plants from soil, the soil sample was microwave-digested with mixed acid solution ($\text{HF}:\text{HBO}_3:\text{HCl}=1:4:1$) and quantified by ICP (Perkin Elmer Optima 2000DV, USA). A biodegradable lactic acid was selected as processing fluid because of (1) preventing from second pollution of soil matrix; and (2) keeping the soil/reservoir pH less than 8.0 to hinder the clogging of most metal oxides (Zhou et al., 2006).

2.2. The field scale EK system

A polypropylene (PP) field scale electrokinetic system with $1.5\text{ m (L)} \times 1.0\text{ m (W)} \times 1.1\text{ m (H)}$ was designed to conduct EK experiments, as shown in Fig. 1. The field scale EK system includes three units: anode reservoir ($L \times W \times H = 1.0\text{ m} \times 0.25\text{ m} \times 1.1\text{ m}$), cathode reservoir ($L \times W \times H = 1.0\text{ m} \times 0.25\text{ m} \times 1.1\text{ m}$), and soil chamber ($L \times W \times H = 1.0\text{ m} \times 1.0\text{ m} \times 0.9\text{ m}$). Two hundred and fifty liter process-

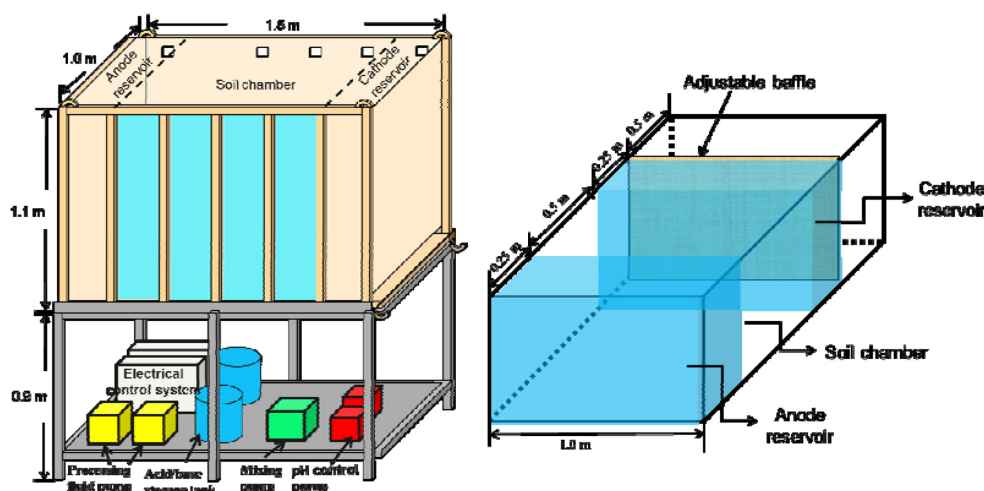


Fig. 1. (a) The front view of field scale electrokinetic system; (b) side view of soil chamber.

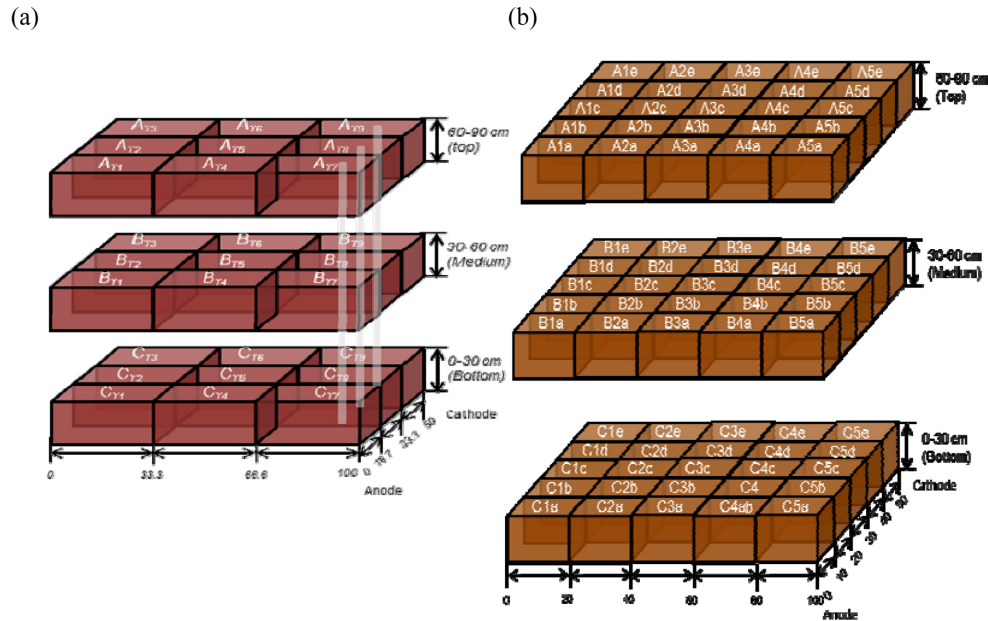


Fig. 2. Sample collection for (a) soil current and soil temperature; (b) residue metal in soils.

ing fluid could be contained in the reservoir. The reservoir pH and temperature were real-time monitored and the digital data were collected by the monitoring system. The reservoir pH was maintained at $\text{pH } 7.0 \pm 1.0$ preventing from clogging of most metal oxides. During the experiments, the electroosmotic flow (Q_e) was collected from both the anode and cathode reservoirs; hence, the average permeability was investigated throughout the field scale EK system. The soil temperature and the current across the soil chamber were manually measured at the 10th day and the 20th day. Owing to the heterogeneity of soil, the soil was horizontally sectioned to three layers, 30 cm height per layer, and nine evenly divided per sectional layer, as shown in Fig. 2a. Total 27 samples were collected per sampling time. Similarly, the sample collection for the metal residue in soil was similar as that for soil current and soil temperature, except 25 evenly divided per sectional layer, as shown in Fig. 2b. Totally, 75 soil samples were collected for metal residual quantification per sampling time and the concentration contour plotted using SURFER software would be shown in this study.

Three electrickinetic experiments were conducted in the above-mentioned field scale EK system coupled with 24 stainless steel electrodes (3 cm (Φ) \times 120 cm (L)) to examine metal removal performance applied 0.2-0.35 V/cm

potential gradient and 0.05-0.5 M lactic acid for 20 day, as summarized in Table 1. The amount of soil treated per batch test was around 700-780 kg and the major pollutant was Zn, Pb, and Ni, as shown in Table 1.

3. Results and Discussion

3.1. Electrokinetic behavior

In electrokinetic processes, the movement of an electrolyte solution driven by an electrical field, which carries the soluble pollutants toward the electrodes, is considered to be one of the treatment mechanisms. The movement of the electrolyte solution, i.e., electroosmotic flow, Q_e (cm^3/s), for a soil chamber is directly proportional to the applied electric potential gradient, i_e (V/cm):

$$Q_e = k_e \times i_e \times A \quad (1)$$

where A (cm^2) is the cross-section area of the soil chamber and k_e ($\text{cm}^2/\text{V-s}$) is the average electroosmosis permeability. The results, shown in Table 2, indicated that $2.4 \times 10^{-2} - 7.5 \times 10^{-2} \text{ cm}^3/\text{s}$ of electroosmosis flow were collected for Tests 1-3. The k_e value of Test 2 was $4.8 \times 10^{-5} \text{ cm}^2/\text{V-s}$, which was greater than that of Test 1. It might because a higher potential gradient of 0.35 V/cm applied in Test 2 and resulted in vigorous electrolysis reaction. As increased con-

Table 1. Experimental design for the field scale electrokinetic system

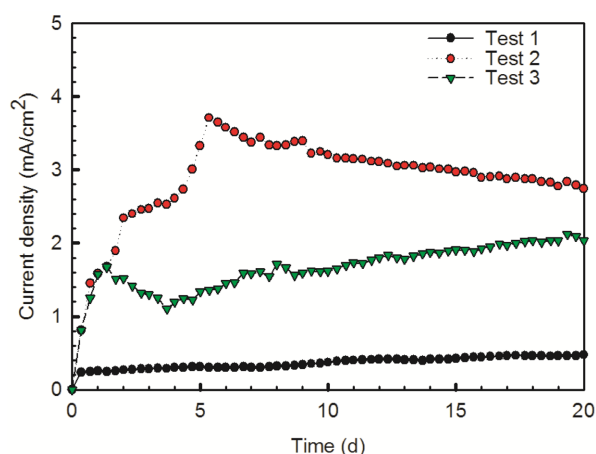
Variables		Test 1	Test 2	Test 3
Experimental parameters	Electrode	Hollow stainless steel rods	Hollow stainless steel rods	Hollow stainless steel rods
	Duration (d)	20	20	20
	Soil treated (kg)	780	700	755
	Porosity (%)	29	36	31
	Processing fluid	0.05 M Lactic acid	0.05 M Lactic acid	0.5 M Lactic acid
Experimental parameters	Potential gradient (V/cm)	0.2	0.35	0.35
	Electrode distance (cm)	70	70	70
	Electrode area (m ²)	3.768	3.768	3.768
Metals	Zn (mg/kg)	425 ± 14	436 ± 33	198 ± 22
	Pb (mg/kg)	219 ± 13	1,322 ± 63	105 ± 5
	Ni (mg/kg)	393 ± 10	766 ± 38	779 ± 35

Table 2. Summary results of the field scale electrokinetic experiments

Test No.	Electrode	Potential gradient (V/cm)	Lactic acid (M)	Electrode area (m ²)	Q_e (cm ³ /s)	k_e (cm ² /V-s)	Power consumption (kwh/m ³)	Residue in soil		Removal efficiency (%)	Mass balance (%)
								Metal	%		
1	Stainless steel (SUS 316)	0.2	0.05	3.768	2.4×10^{-2}	2.6×10^{-5}	9.8	Zn	58.2	39.1	97.3
								Pb	67.2	28.3	95.5
								Ni	64.4	32.7	97.1
2	Stainless steel (SUS 316)	0.35	0.05	3.768	7.5×10^{-2}	4.8×10^{-5}	74.5	Zn	17.6	78.4	96.0
								Pb	9.8	84.3	94.1
								Ni	55.1	40.1	95.2
3	Stainless steel (SUS 316)	0.35	0.5	3.768	3.5×10^{-2}	2.2×10^{-5}	44.4	Zn	38.4	57.5	95.9
								Pb	64.4	31.0	95.4
								Ni	56.4	41.0	97.4

centration of lactic acid to 0.5 M, the color of concentrated lactic acid became much milky white and the fluidity was quite different from the diluted solution. Further, the higher concentration of lactic acid should decrease the soil pH, then the acidification decrease EOF. As a consequence, lower k_e was found (2.2×10^{-5} cm²/V-s) for Test 3.

A smooth electric current transfer through the soil chamber represents no clogging occurred inside and pollutants would successfully migrate with electroosmosis flow to cathode reservoir. The electric current was monitored during the experiment period and the result of current density was shown in Fig. 3. For Test 1, the current density increased with time and kept at 0.45-0.46 mA/cm² after the 5th day. As increased potential gradient to 0.35 V/cm (Test 2), the current density significantly increased to 3.7 mA/cm² at Day 5 and then gradually decreased to 2.8 mA/cm². As increased

**Fig. 3.** The current density vs. time in the field scale EK system.

lactic acid concentration to 0.5 M (Test 3), the current density did not increase as expected. It was found that 0.5 M lactic acid turned to milky white color and was very vis-

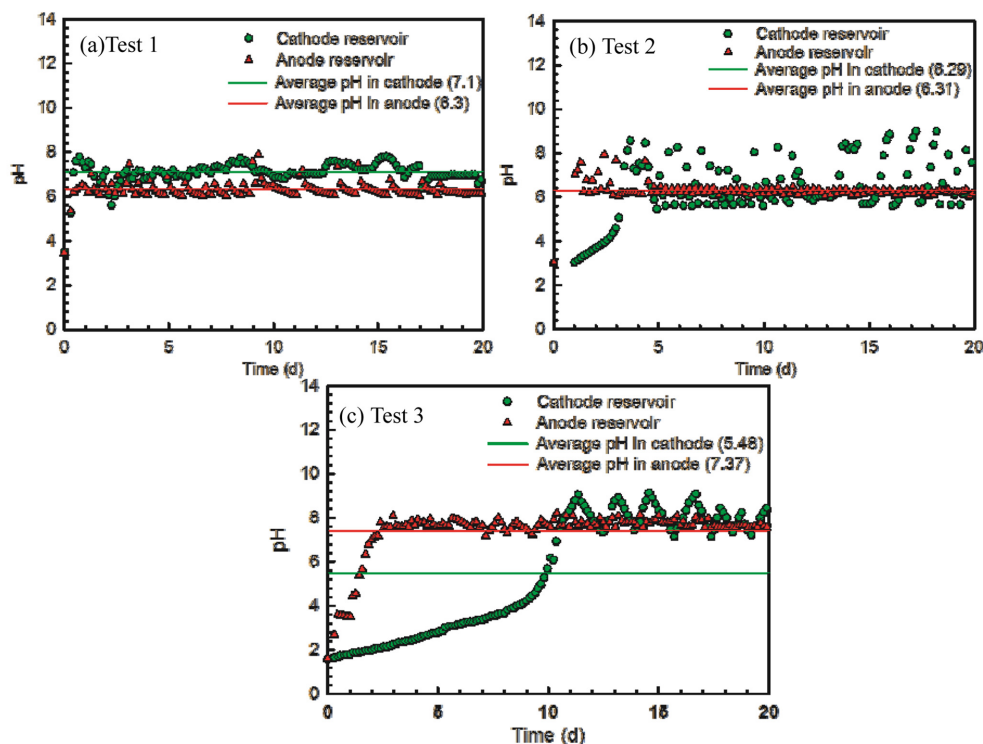


Fig. 4. The reservoir pH vs. time in the field scale EK system.

cous. The higher viscosity of lactic acid would hinder the migration of electroosmosis flow.

3.2. The variation of reservoir pH

As applied direct current on EK systems, the H^+ and OH^- was produced at the anode and cathode, respectively, due to water electrolysis reaction. The metal oxides will form as the case of higher pH near the cathode. Therefore, control mild reservoir pH is very important to keep migration of electroosmosis flow. The variation of reservoir pH in investigated systems was shown in Fig. 4. Results showed that the anode and cathode reservoir pH were kept at the range of 6.30–7.37 and 5.48–7.10, respectively, which was met the target range of 7.0 ± 1.0 . As increased potential gradient and lactic acid concentration (Test 2 and Test 3), the fluctuation of pH became more significant. It might reasonably due to (1) vigorous electrolysis reaction caused by higher potential gradient and resulted in more H^+ and OH^- released; (2) the higher viscosity of concentrated lactic acid resulted in difficult to control reservoir pH. The fluctuation of reservoir pH could abate by using more delicate pH controller.

3.3. The variation of temperature in reservoirs and soils

The temperature increase in EK system is highly related to the total energy consumption as well as the safety of human and building. The variation of reservoir temperature was shown in Fig. 5. The initial reservoir temperature was set at 31.5°C . Results showed that the average reservoir temperature in the cathode and in the anode was 40.8 – 47.8°C and 41.6 – 49.2°C for Tests 1–2, respectively, which was higher than that for Test 3. It might largely because both Test 1 and Test 2 were operated in summer and Test 3 was operated in winter. Owing to higher potential gradient applied, a highest reservoir temperature was found for Test 2, which was agreed with the highest power consumption shown in Table 2. No significant variation of temperature between anode and cathode reservoirs was found.

The soil temperature profile along the field scale EK system was showed in Fig. 6. The average soil temperatures were $39.0 \pm 0.4^\circ\text{C}$, $44.5 \pm 0.4^\circ\text{C}$, and $38.8 \pm 1.7^\circ\text{C}$ for Test 1, Test 2, and Test 3, respectively, which resulted in 4 – 16°C higher than room temperature. It found that the higher

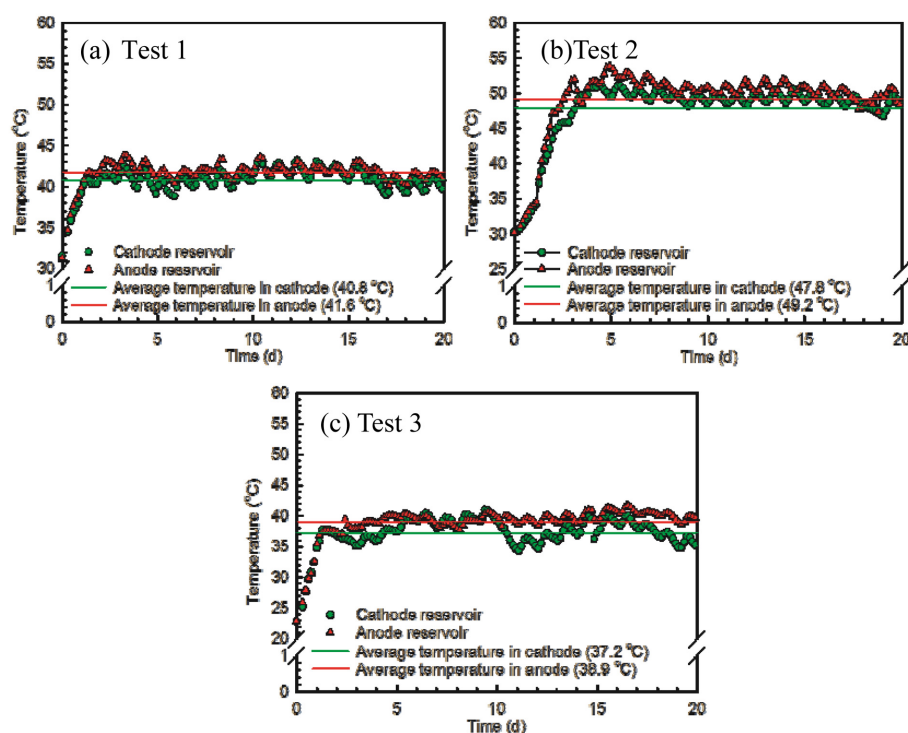


Fig. 5. The reservoir temperature vs. time in the field scale EK system.

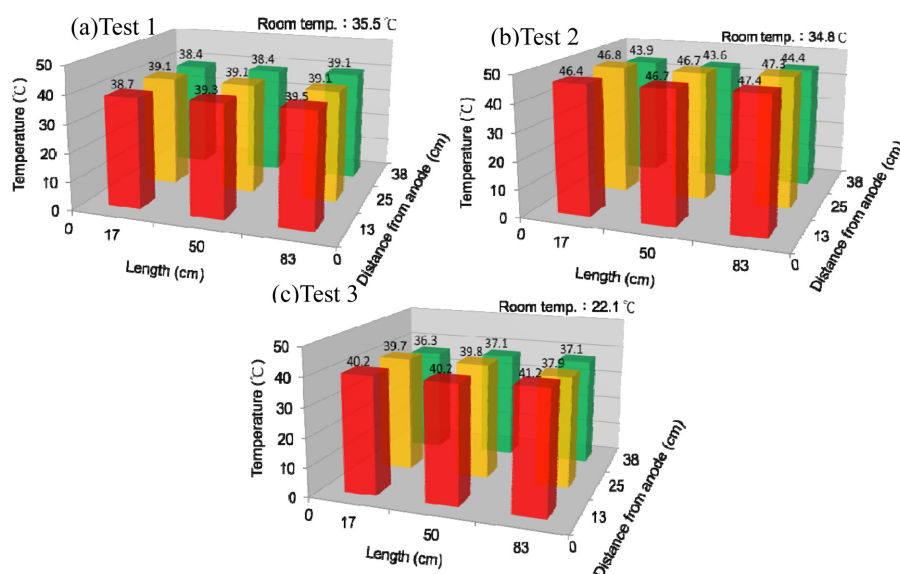


Fig. 6. The soil temperature profile in the field scale EK system.

potential gradient applied, the greater different between soil temperature and room temperature. It might result from vigorous electrolysis reaction. It was also found that the sectional soil temperature decreased from anode to cathode. To conquer high soil temperature, extending remediation peri-

ods or using variable-frequency drive power supply might be a solution way. How to compensate soil temperature and removal efficiency will become a potential issue as applied EK process in the fields to keep the safety of human activities and building.

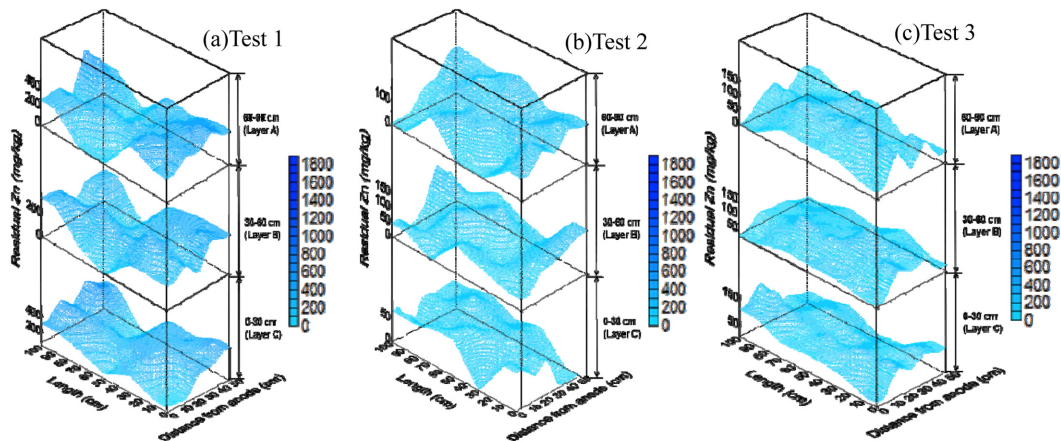


Fig. 7. The residual concentration profile of Zn.

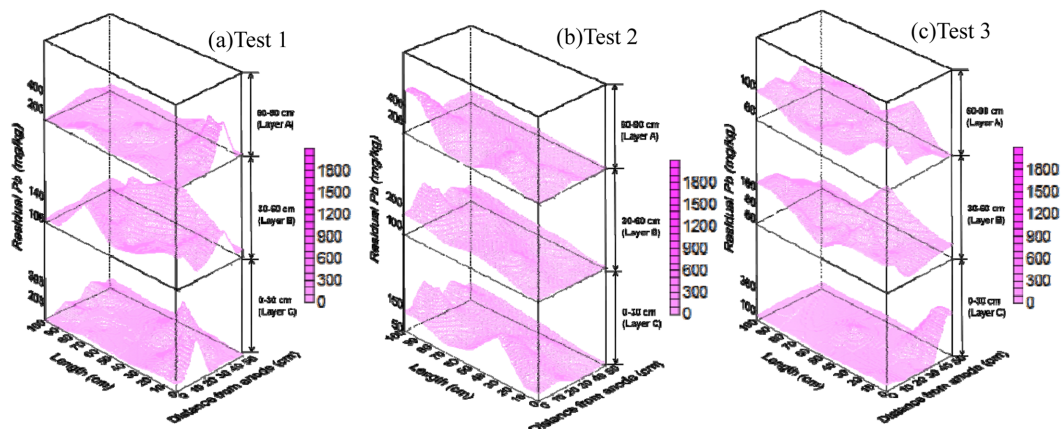


Fig. 8. The residual concentration profile of Pb.

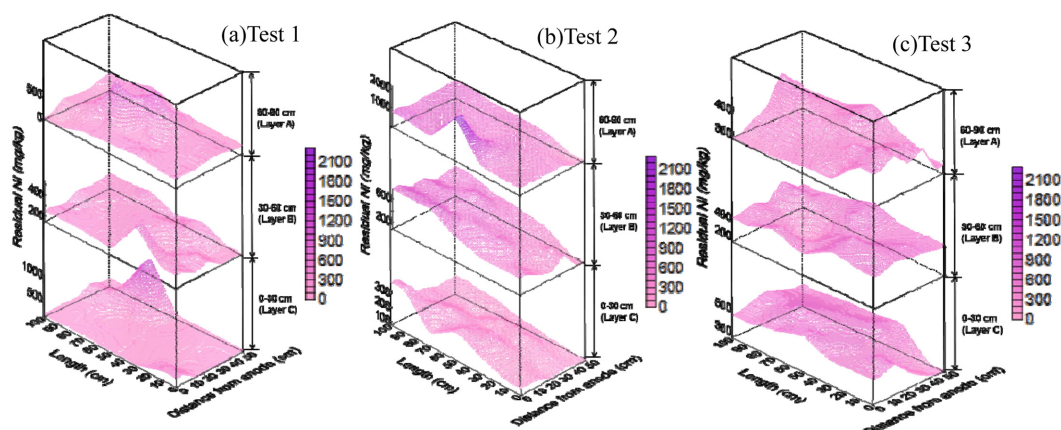


Fig. 9. The residual concentration profile of Ni.

3.4. Removal performance of metals

The residue concentration profiles of Zn, Pb, and Ni for EK remediation of 20 days were shown in Figs. 7-9, respec-

tively. The horizontal and vertical migrations of the three metals along the field scale EK system were clearly indicated in the concentration contours.

3.4.1. Zn

At natural pH, $\text{Zn}(\text{OH})_2$ precipitate would form, which might hinder the migration of Zn along the field scale EK system. In Fig. 3, no sharp variance of current density was found, which indicated the clogging by $\text{Zn}(\text{OH})_2$ precipitate was insignificant. As applied 0.2 V/cm (Test 1), Zn migrated from anode to cathode horizontally but insignificant in vertically. The removal efficiency of Zn was only 40.4%, 42.7%, and 24.3% in the layers A, B, and C, respectively, which resulted in total removal of 39.1%. The low removal efficiency could be enhanced by higher potential gradient. Applied potential gradient of 0.35 V/cm (Test 2), the total removal efficiency increased to 78.4% and the removal efficiency of Zn in the top layer (layer A) was greater than that in the layer B and C. It indicated that the vertical migration of Zn became more significant (Fig. 7). The reason might be temperature increase in soil (Fig. 6) transported pore water from bottom to top layer, which co-transported Zn to the topsoil. This result was agreed with Alshawabkeh et al. (2005) and Kim et al. (2012). The total removal efficiency decreased to 57.5% as applied a concentrated lactic acid in EK system (Test 3). It was inferred that the low electroosmosis permeability might result from the high viscosity and low pH (Fig. 4c) of the concentrated processing fluid.

3.4.2. Pb

The hydroxide precipitate of Pb would form at pH greater than 11 and, at the natural pH, complex of $\text{Pb}(\text{OH})^+$ would form instead of Pb^{2+} . Applied 0.2 V/cm (Test 1), the total removal efficiency of Pb was 28.3% and the highest removal of 36.6% was found in the layer B, which was lower than that of Zn. The horizontal migration was more significant than vertical migration (Fig. 8). Applied potential gradient of 0.35 V/cm (Test 2), the total removal efficiency of Pb largely increased to 84.3%. The vertical migration of Pb in Test 2 was more significant than that on Test 1, which was similar as that of Zn. Applied concentrated lactic acid in EK system (Test 3), the total removal efficiency of Pb was largely decreased to 31.0%. That indicated the effect of low fluidity of processing fluid on Pb removal was more significant than on Zn removal.

3.4.3. Ni

The hydroxide precipitate of Ni would form at pH greater than 11 and, at the natural pH, only Nickel hydroxide complex would form. Applied 0.2 V/cm (Test 1), the total removal efficiency of Ni was 32.7% and the highest removal of 39.6% was found in the top layer (Layer A). The vertical migration of Ni was similar as Zn and Pb. Some soils with high concentrated Ni were found in Layer B and C, which might result from the slowest migration velocity of Ni (0.09–0.18 m/s) in soil compared with other metals. The horizontal migration was also more significant than vertical migration. Applied higher potential gradient of 0.35 V/cm (Test 2), the total removal efficiency of Ni increased to 40.1% only. The highest removal efficiency of Ni of 76.5% was found in the top layer (layer A), which meant the vertical migration of Ni was more significant than that of Zn and Pb. Applied concentrated lactic acid in EK system (Test 3), the total removal efficiency of Ni was 41.0%, which was similar as Test 2. That indicated the concentrated lactic acid would largely hinder the migration of Ni.

4. Conclusion

A field scale electrokinetic system with 1.5 m (L) \times 1.0 m (W) \times 1.1 m (H) was successfully designed and conducted EK experiments. The important conclusions can be drawn from this study as follows:

1. The reservoir pH controlled at 7.0 ± 1.0 has been effectively avoided the extreme high soil pH near the cathode. It diminished the metal oxide clogging and resulted in a better migration of pollutants.
2. The reservoir and soil temperatures were majorly related to potential gradient and room temperature. A 4–16°C above room temperature was found in the investigated system. How to compensate soil temperature and removal efficiency will become a potential issue as applied EK process in the fields to keep the safety of human activities and building.
3. The best removal efficiency of Zn, Pb, and Ni was 78.4%, 84.3%, and 40.1% in the EK system applied 0.35 V/cm and 0.05 M lactic acid for 20 days. Increasing potential gradient would more effectively enhance metal removal than increasing concentration of processing fluid.

4. A significant vertical migration was found for metals along the field scale electrokinetic system, which is very helpful for the remediation of deep polluted site. It confirmed that the electro current applied push the metals from the bottom to the top soil and, then, deep excavation might be no more needed.

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