Electrokinetic remediation of Zn and Ni-contaminated soil

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ABSTRACT

The feasibility of catholyte conditioning with the acidic solution and pre-treatment of soil with acidic solution was investigated with the electrokinetic remediation of Zn and Ni contaminated field soil. The extraction of Zn and Ni from soil increased with the decrease in pH of the extracting solution and nitric acid was very effective to extract Zn and Ni from the soil. Conventional electrokinetic treatment and acetate buffer circulation method were not effective to remove Zn and Ni from the soil. Pre-treatment of the soil with acidic solution enhanced the desorption of Zn and Ni and catholyte conditioning with this solution was effective in maintaining the overall soil pH within the electrokinetic cell. The catholyte conditioning and pre-treatment method enhanced the removal of Zn and Ni up to 41% and 40% after operation for 4 weeks. More than 96% of Zn and Ni removed by electrokinetic remediation were due to the electromigration. Catholyte conditioning and the pre-treatment method is effective in enhancing metal removal in electrokinetic remediation.

1. Introduction

Recently, heavy metal contamination has caused serious environmental and human health problems in abandoned mine and industrial sites. Soil washing and solidification/stabilization have been used to remediate soil contaminated with heavy metals in Korea [1–3]. Even though soil washing is an effective technology to remove heavy metals from sandy or silt soil, it is not effective for fine-grained soil [1]. Even though stabilization and solidification is the most common choice for treating metal-contaminated soil, these techniques are not applicable to zinc and nickel-contaminated soil because aqua-regia extraction is the Korean standard test method for nickel and zinc. Even though stabilization and solidification method is applied to treat zinc and nickel-contaminated soil, the total mass of the metals is not changed, and most of zinc and nickel are extracted from the treated-soil by the aqua-regia method. Currently, a separation technique needs to be applied to remediate zinc and nickel-contaminated soil in Korea.

Electrokinetic (EK) remediation is one of promising separation technologies and the most effective technique for fine-grained and clayey soil [4,5]. It is effective to remove organic compounds, heavy metals and radionuclides from soil, mine tailings, sludge and sediment [2,5,6]. In electrokinetic remediation, the removal mechanisms are electromigration, electroosmosis and electrophoresis. 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 [2]. The control of soil pH using various methods is a common choice to enhance the removal efficiency of pollutants in the electrokinetic process [2,3,7–11]. However, change in the soil pH influences the zeta potential of the soil surface and the direction of electro-osmotic flow is highly dependent on the zeta potential or surface charge of the soil [2,3]. More negative zeta potential of the soil surface enhanced the more electro-osmotic flow. If the direction of electroosmotic flow is toward the cathode, then the removal of cationic metal might be enhanced, while the removal might decrease in the case of the opposite direction.

This study investigated the feasibility of conditioning the catholyte with an acidic solution and the pre-treatment of soil with an acid on the electrokinetic remediation of Zn and Ni contaminated soil.

2. Materials and methods

2.1. Materials

2.1.1. Soil sample

The soil used in this study was contaminated by soot in power plant stack, which contains a high concentration of Ni and Zn, in a power plant. Initial concentrations of Ni and Zn were 1324 and

* Corresponding author. Tel.: +82 54 478 7635; ax: 82 54 478 7629.
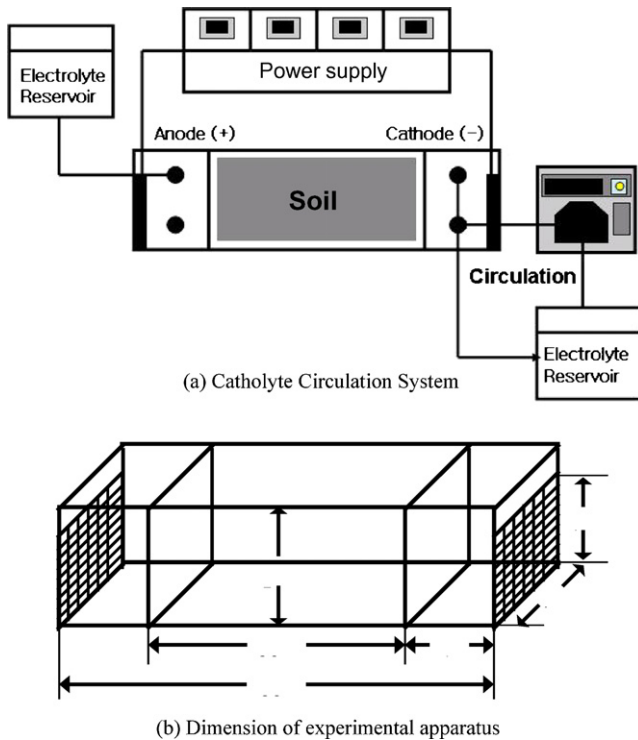E-mail address: kbaek@kumoh.ac.kr (K. Baek).

(a) Catholyte Circulation System

(b) Dimension of experimental apparatus

Fig. 1. Schematic diagram and dimensions of experimental apparatus (a) catholyte circulation system and (b) dimensions of experimental apparatus.

1632 mg/kg, respectively. The soil was sampled in the field and sieved using mesh 10 and soil of <2 mm was used in electrokinetic experiments. The soil was silty loam and the organic content was 10.3%. The initial pH and water content of the soil were 6.8% and 20%.

2.1.2. Experimental apparatus

Fig. 1 shows a diagram of EK experimental apparatus. The apparatus consisted of four major compartments; a soil compartment (4 cm × 4 cm × 20 cm), electrode compartments (4 cm × 4 cm × 1 cm), electrolyte solution reservoirs (4 cm × 4 cm × 4 cm), and a D.C. power supply (0–300 V, 0–1 A). A mesh type electrode of Ti coated with Pt (4 cm × 4 cm × 0.2 cm) was used as an anode and plate type electrode of graphite (4 cm × 4 cm × 0.8 cm) was used as a cathode. The electrolyte solution reservoir was circulated with an purging solution in anode and cathode compartment. Both ends of the soil compartment and two sheets of filter paper (Advantec 5B, Japan) were inserted to prevent soil particles from penetrating into the electrolyte solution reservoirs.

2.2. Methods

2.2.1. Basic extraction experiment

Basic extraction experiments were carried out to investigate the effect of pH on the extraction of Zn and Ni from soil. A 3 g soil sample was mixed with 30 ml of nitric acid solution at various pH levels; the mixtures were agitated by an over-end shaker for 24 h and centrifuged. The supernatant was analyzed using atomic adsorption spectrometry (Shimadzu 6701F, Japan).

2.2.2. EK experiment

A soil samples of 800 g and 200 ml de-ionized water (initial water content 20 ± 0.5%) was mixed and compacted into an elec-

Table 1
Experimental condition of electrokinetic process.

Exp. no.	Anolyte purging solution	Catholyte purging solution	Pre-treatment of soil
Exp. 1	MgSO$_4$ (0.05 M)	–	–
Exp. 2	MgSO$_4$ (0.05 M)	Acetic acid (0.1 M) + sodium acetate (0.1 M) at pH 4.0	–
Exp. 3	MgSO$_4$ (0.1 M)	HNO$_3$ (0.1 M)	–
Exp. 4	MgSO$_4$ (0.1 M)	HNO$_3$ (0.1 M)	HNO$_3$ (0.1 M)
Exp. 5	MgSO$_4$ (0.1 M)	HNO$_3$ (0.1 M)	HNO$_3$ (0.5 M)
Exp. 6	MgSO$_4$ (0.1 M)	HNO$_3$ (0.1 M)	HNO$_3$ (1.0 M)

trokinetic cell. A constant voltage was applied to the system and the electrical voltage gradient was 2 V/cm. Experimental conditions are summarized in Table 1. Exp. 1 is a conventional electrokinetic experiment, and Exp. 2 used an acetate buffer solution to control the catholyte pH 4.0. In Exp. 4–Exp. 6, the contaminated soil was mixed with various concentrations of HNO$_3$ (0.1–1.0 M) instead of de-ionized water to control the pH of soil as acidic condition, which enhance the desorption of Zn and Ni from soil. The catholyte solution was circulated with 0.1 M HNO$_3$ to maintain a low pH for the catholyte using a peristaltic pump (Cole-Parmar, Masterflex, USA) at the flow rate of 2 ml/min in Exp. 3–Exp. 6. The purging solution was changed with fresh nitric acid solution everyday. After 4 weeks, the soil was sliced into five sections. Nickel and zinc from each slice of soil sample were extracted by the aqua-regia, and the extractants were analyzed using atomic absorption spectrometry (Shimadzu 7601F, Japan).

3. Results and discussion

3.1. Basic extraction experiment

Fig. 2 shows the extraction efficiency of Zn and Ni by nitric acid and equilibrium pH after washing. The extraction efficiency of Zn and Ni from soil increased sharply as the pH of acidic washing solution decreased from 4 to 1. As the initial pH of the extracting solution decreased from 2 to 1, the extraction efficiency increased dramatically from 0.2% to 39.7% for Zn and from 0.7% to 16.8% for Ni. Except pH 1.0, the extraction of nickel and zinc from soil was negligible and the equilibrium pH was greater than pH 4.0 due to the soil buffering capacity. This result shows that the extraction of Zn and Ni from soil increases as the pH of extracting solution is low and HNO$_3$ is very effective to extract Zn and Ni from soil.
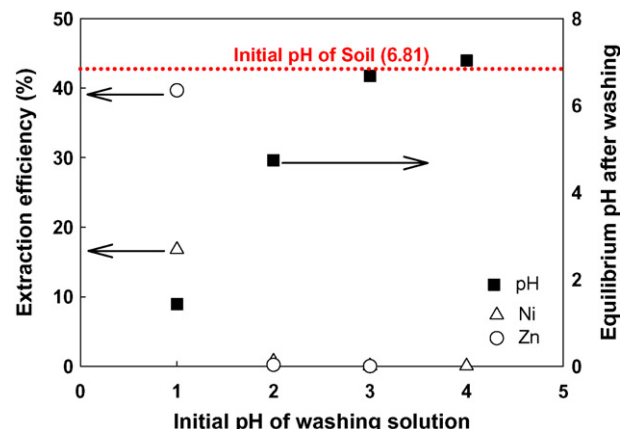

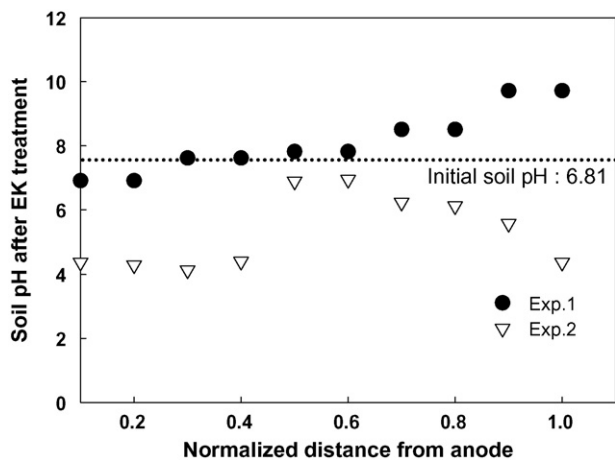**Fig. 2.** Simple extraction of Zn and Ni by acidic solution.

Fig. 3. pH distribution in soil compartment after application of experiment.

Fig. 5. Time course of current density during enhanced-electrokinetic remediation.

3.2. Normal electrokinetic experiment

Fig. 3 shows the pH distribution of Exp. 1 and Exp. 2 after application of EK process. In Exp. 1, the pH shows a general trend in EK experiment. In Exp. 2, the pH was lowered compared to the initial soil pH, because of consumption of hydroxyl ion by the acetate buffer in catholyte.

Fig. 4 shows the distribution of Zn and Ni in Exp. 1 and Exp. 2. Even though an electrokinetic process was applied to the soil for 4 weeks, the removal or transport of Zn and Ni was negligible. This result shows that conventional EK and acetate buffer circulation are not effective to remove Zn and Ni from the soil.

3.3. Acid-enhanced EK

3.3.1. Current density and pH distribution in the soil section

Fig. 5 shows the time course of current density during an electrokinetic experiment. Initial current density was 1.1, 2.9, 6.7 and 10.0 mA/cm^2 for Exp. 3, Exp. 4, Exp. 5 and Exp. 6, respectively. This result means that the conductivity of soil increased dramatically by the pre-treatment of soil using a HNO$_3$ solution. The acidic solution enhanced desorption of ions from the surface of the soil into pore water, and higher concentration of ions in pore water increased the current density under a constant voltage condition. However, higher current density caused to higher power consumption.
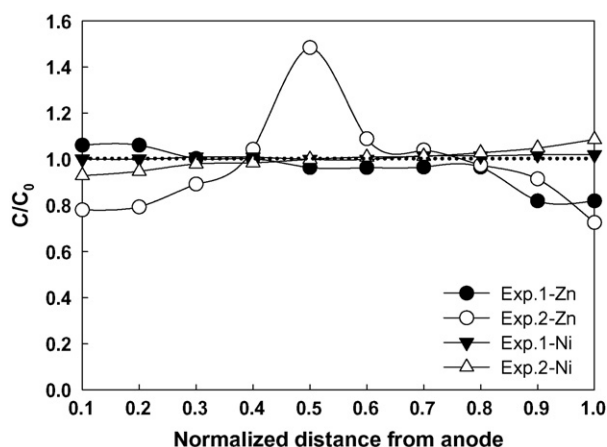
Fig. 6 shows pH distribution of soil sections after EK experiments. The Initial pH of soil was 6.8, but the pH of the soil samples after the application of EK was ranged between 3.0 and 4.0. As shown in the basic extraction (Fig. 2), the extraction of Zn and Ni was effective from soil at the condition below pH 4.0. The effect of pre-treatment with nitric acid on final soil pH was negligible and the lower pH of soil comes from the circulation of nitric acid in catholyte reservoir.

3.3.2. Accumulated electro-osmotic flow

Fig. 7 shows the accumulated EOF during EK experiments. The accumulative volume of water transported by electro-osmosis was measured in the cathode reservoir during electrokinetic remediation. In Exp. 4–Exp. 6, the volume of circulating solution decreased in the cathode region, which means that the direction of electro-osmotic flow was from the cathode to the anode. At a lower pH of soil, the net surface charge of soil was changed from negative to positive, due to the sorption of the hydrogen ion onto the soil surface. The change in net surface charge caused a change in the direction of EOF [2,3]. In the soil with a positive surface charge, the direction of electro-osmotic flow changed from the cathode to the anode. The lower pH of the soil enhanced desorption of zinc and nickel from the soil to pore fluid. However the overall removal of metal ions was not enhanced significantly, because the direction of electromigration was opposite to that of the electro-osmotic flow. Thevanayagam and Rishindran reported that the reverse EOF
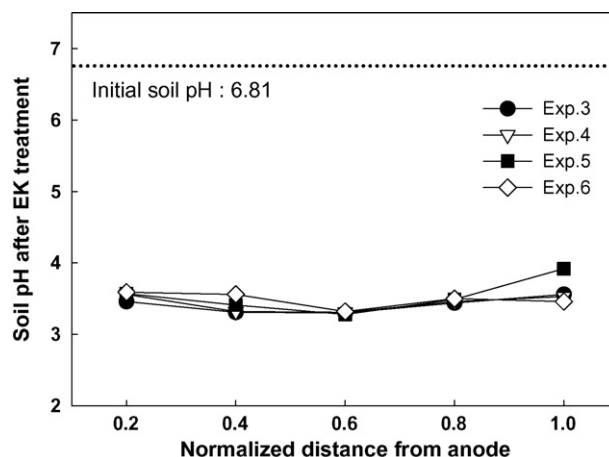

Fig. 4. Distribution of Zn and Ni after electrokinetic treatment.

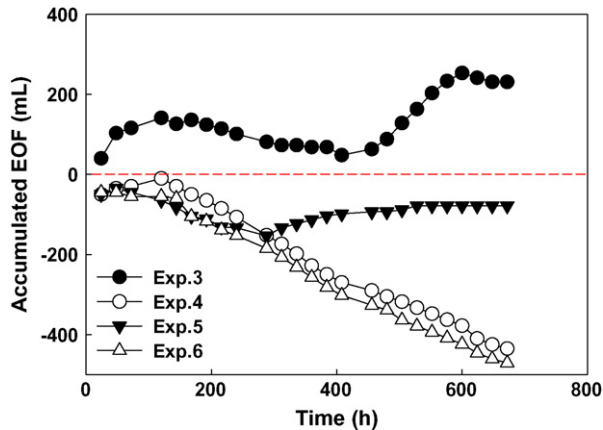Fig. 6. pH of soil treated by enhanced-electrokinetic process.

Fig. 7. Accumulated EOF during enhanced-electrokinetic remediation.

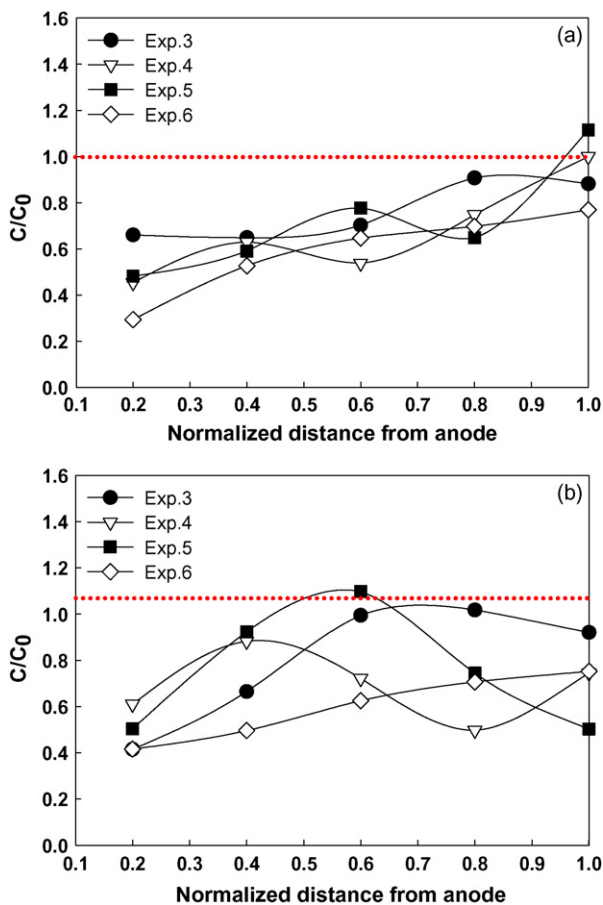**Fig. 8.** Zinc and nickel distribution after enhanced-electrokinetic remediation. (a) Zn and (b) Ni.

Table 2
Mass balance of Zn and Ni.

EK exp.	Amount of removal (mg)	Amount removed by EOF (mg)	Residual amount in catholyte (mg)	Mass balance (%)
Zn				
Exp. 3	293.2	321.4	1.34	110.08
Exp. 4	399.5	381.8	3.38	96.42
Exp. 5	339.2	335.6	2.0	99.53
Exp. 6	505.4	510.6	1.68	101.36
Ni				
Exp. 3	195.9	188.0	0.8	96.38
Exp. 4	307.0	302.0	2.5	99.19
Exp. 5	244.1	242.8	1.4	100.04
Exp. 6	398.1	391.0	1.3	98.54

Exp. 3 increased up to about 20% compared to Exp. 1 and Exp. 2. This result means that the catholyte conditioning with acidic solution enhanced the removal of nickel and zinc. Generally, the higher concentration of acid for circulating catholyte makes the soil more acidic and the acidic condition enhances the extraction of nickel and zinc. Acar and Alshawabkeh reported that the major removal of heavy metals from soil is electromigration and electrokinetic [4]. The removal of nickel and zinc in Exp. 6 was two times higher than Exp. 3, which shows that pre-treatment of soil with an acidic solution dramatically enhanced the removal of nickel and zinc. In general, the removal efficiency of Zn and Ni from soil increased with the increase in concentration of HNO_3 for pre-treatment of soil. As a result, the acidic pre-treatment of soil and catholyte conditioning with an acidic solution enhanced the performance of the electrokinetic remediation of nickel and zinc.

3.3.4. Mass balance (residual Zn and Ni concentration)

On the basis of EK experimental results, the mass balance of Zn and Ni was calculated (Table 2). Mass balance (%) was calculated as following:

Mass balance = {amounts removed by EOF + residual amount in catholyte}/{initial amount of metal in soil – residual amount of metals in soil after treatment} × 100 The amount of metals in the anolyte reservoir was negligible. The mass balance of Zn and Ni were 110.1%, 96.4%, 99.5% and 101.4% in Zn and 96.4%, 99.2%, 100.0% and 98.5% in Ni for Exp. 3, Exp. 4, Exp. 5, Exp. 6, respectively. This result shows that the major removal mechanism for Zn and Ni is electromigration and more than 96% of metal was removed by migration in this study even though the direction of the electro-osmotic flow was opposite to that of electromigration.

4. Conclusions

In this study, the feasibility of catholyte conditioning and pre-treatment of soil with an acidic solution for an electrokinetic experiment was investigated in a laboratory study. Zn and Ni were not extracted by the nitric acid solution of less than 0.1 M. Conventional electrokinetic and acetate buffer circulation was not effective to remove Zn and Ni from the contaminated soil. Catholyte conditioning played a major role in maintaining the soil pH as acidic, which enhanced the overall removal of Zn and Ni. Pre-treatment of soil with an acidic solution increased desorption of Zn and Ni, then the removal efficiency of Zn and Ni increased with the concentration of pre-treatment solution. The removal efficiency of Zn was <1.0% for conventional EK, 20% for catholyte conditioning, and 41% for pre-treatment and catholyte conditioning. Pre-treatment and catholyte conditioning is good enhancement method in the electrokinetic remediation of metals.

resulted in the retardation of the movement of Pb^{2+} ions [12]. In this study, the reverse EOF inhibited slightly the removal of Zn and Ni in electrokinetic remediation.

3.3.3. Removal efficiency (residual Zn and Ni concentration)

Fig. 8 shows the distribution of Zn and Ni in the soil section after electrokinetic remediation. The overall removal efficiency of Zn was 23%, 33%, 28%, and 41% for Exp. 3, Exp. 4, Exp. 5, and Exp. 6, respectively. For Ni, removal efficiencies were 20%, 31%, 24%, and 40% for Exp. 3, Exp. 4, Exp. 5, and Exp. 6. The removal of nickel and zinc in

Acknowledgement

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