Environmental
Contamination
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In Situ XANES Study of Electrokinetic Remediation of Cadmium-Contaminated Soils

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Cadmium is one of major soil contaminants at numerous industrial sites in Taiwan. The extensive uses of cadmium in electroplating, metallurgy, painting, plastic generation and other industries caused a contamination of soil. Cadmium has been suspected causing symptoms of hypertension, angiopathy, kidney and bone function decay.

Many soil remediation techniques such as chemical stabilized, chemical leaching, electrokinetic's remediation, and bioaccumulation methods have been used on-site (Dickinson 1991; Tsezos and Wang 1991; Acar 1990; Alshawabkeh and Acar 1992). Electrokinetic soil remediation (ESR) is one of the feasible technologies for in-situ soil decontamination (Ottosen et al. 1997).

During the electrokintic soil remediation process, electrolysis of water occurs at the electrodes (Shapiro and Probstein 1993). The H^+ ions generated at the anode and the OH^- ions generated at the cathode will migrate towards the opposite electrode. The extent of migration of H^+ ions and OH^- ions depends upon the buffering capacity of the soil. In soils with a low buffering capacity, a distinct pH gradient ranging from 2 near the anode to 12 near the cathode is generally developed (Acar and Alshawabkeh 1993). pH is one of the major factors which determines the mobility of contaminants in soil. Acidification of the soil increasing the contaminant fractions present in liquid phase and their mobilities, consequently increasing the contaminant transport rate and removal efficiency. The increase in pH at the cathode zone, on the contrary, can immobilize heavy metals as hydroxides (Hicks and Tondorf 1994; Hamed et al. 1991).

X-ray absorption spectroscopy is very useful in identification of elements with a different environment, degree of aggregation or location (Huang and Wang 1999; Huang et al. 1999). Many reactions (ion diffusion, ion exchange, mineral decomposition, precipitation of salts, hydrolysis, oxidation, reduction) in addition to electromigration and electroosmosis occur simultaneously when an electric field is applied on a wet soil. Thus, the main objective of the present work was to study the effect of H^+ in ESR. The ESR process with a cation ion-exchange membrane was studied at constant pH value.

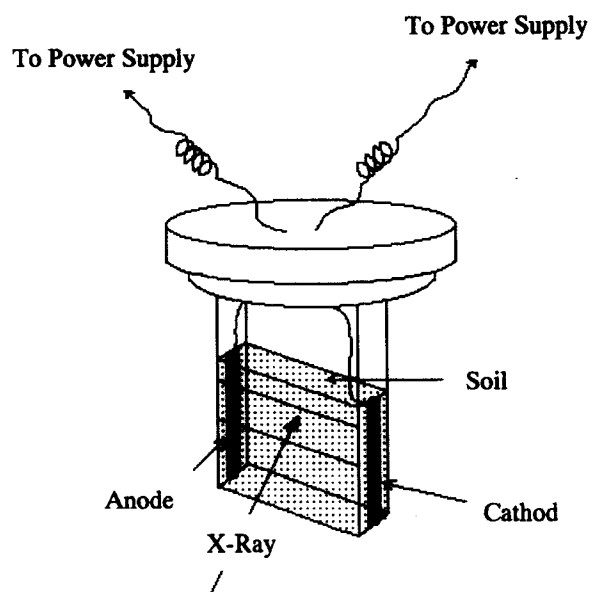*Correspondence to:* Y.-J. Huang

(a)
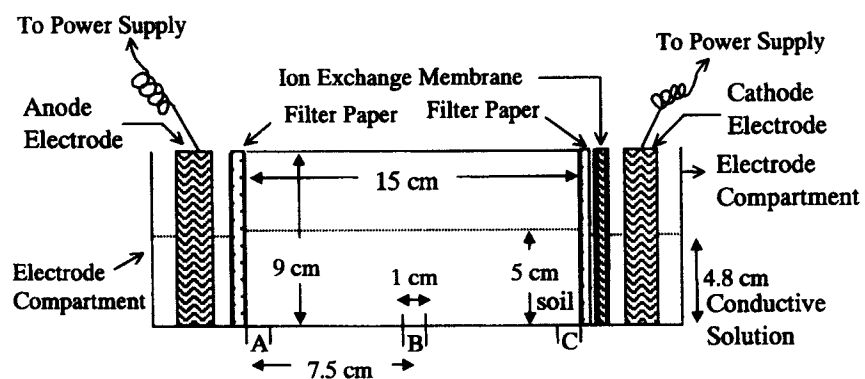
(b)

Figure 1. Schematic diagram of (a) electrokinetic test cell and (b) cell for in situ X-ray absorption spectroscopic study of electrokinetic soil remediation.

MATERIALS AND METHODS

The soil sample was obtained from the Lu-zhu village located at Taoyuan, Taiwan. The contaminated soil was air-dried, coarsely ground and sieved (20 mesh). The equipment arrangement used in the experiments is schematically shown in Figure 1 (a). A DC voltage of 50 volts is constantly applied to the electrodes. The conductive solution is 0.01 N potassium nitrate solution. Each electrokinetic experiment was conducted for a duration of five days. The condition of the working electrodes was measured two times each day. The soil specimen was sectioned into 0-1 cm (A), 7-8 cm (B) and 14-15 cm (C) slices starting from the anode (see Figure 1 (a)).

An ORP meter was used to measure the oxidation-reduction potential. A pH meter was used to measure the pH value of soil. The pH value of the conductive solution (potassium nitrate) was adjusted to 5 by addition of a 1N KCH₃COO and CH₃COOH buffer solution. A cation ion-exchange membrane was installed in the electrode compartments to reduce the migration of OH⁻ ions to soil. Inductively coupled plasma-mass spectroscopy (PE, Elan 6100 Drc) was used to measure the concentrations of metals. Chemical structures of Cd on soil were studied by X-ray absorption spectroscopy (XAS). Electrokinetic reactions were also carried out in the homemade in-situ XAS cell (Figure 1(b)). The absorption edge was determined at the half-high (precisely determined by the derivative) of the XANES (X-ray absorption near edge structural) spectrum after preedge baseline subtraction and normalization to the maximum post edge intensity.
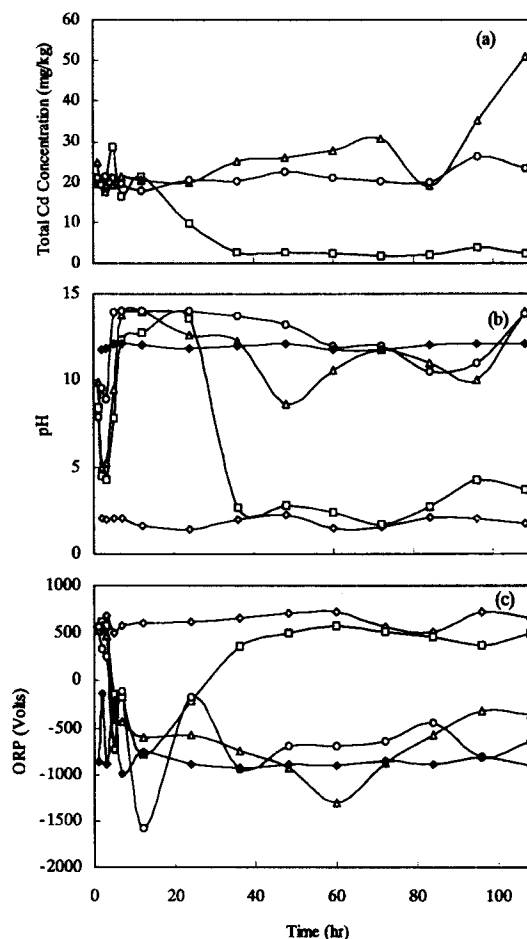

Figure 2. (a) Total Cd concentration, (b) pH and (c) ORP profiles as function of time in ES at (□) slice A, (△) slice B, (○) slice C, (◇) anode and (◆) cathode.

Detailed analyses of experimental data were conducted to reveal the local environment of Cd in these complex solids.

RESULTS AND DISCUSSION

Three different condition of the electrokinetic soil remediation (ESR) were studied. ES denotes the electrokinetic soil remediation experiment that was conducted at a constant voltage gradient across electrodes. ESI and ES5 denotes the ES experiments conducted with cation ion exchanged membrane and the pH=5 of the conductive solution, respectively. The time dependences for total Cd concentration, pH or oxidation-reduction potential (ORP) in the ESR are given in Figures 2-4. Figures 2(a), 3(a), and 4(a) show that Cd might migrate toward the cathode. After 30 hr of ESR, concentration of Cd in some soil portions were below 3 mg Cu/kg dry soil. Figure 5 shows that the in-situ XANES (X-ray absorption near edge structural) spectra of electrokinetic remediation in the portion B. The faster migration rate of Cd under electric field caused the accumulation of Cd in the cathode. Figure 2(a) also shows that the Cd was accumulated in the median of slices.

Figure 3. (a) Total Cd concentration, (b) pH and (c) ORP profiles as function of time in ESI at (□) slice A, (△) slice B, (○) slice C, (◇) anode and (◆) cathode.

This zone of accumulated ion can be correlated to soil pH. Figure 2(b) shows that pH values were approximately 12 near the cathode and approximately 2 near the anode. The pH variations in soil have profound effects on the mobility of Cd ions and, consequently, on the electrokinetics removal efficiency. The acidification occured on the anion (due to water dissociation) and then the acidic front moved toward the cathode. In ES experiment, the pH values of the soil in portion A decreased from 8-9 to 2-3 after 36 hr of current. The Cd concentration (Figure 2(a)) also decreased significantly from 20 to 2 mg/kg.
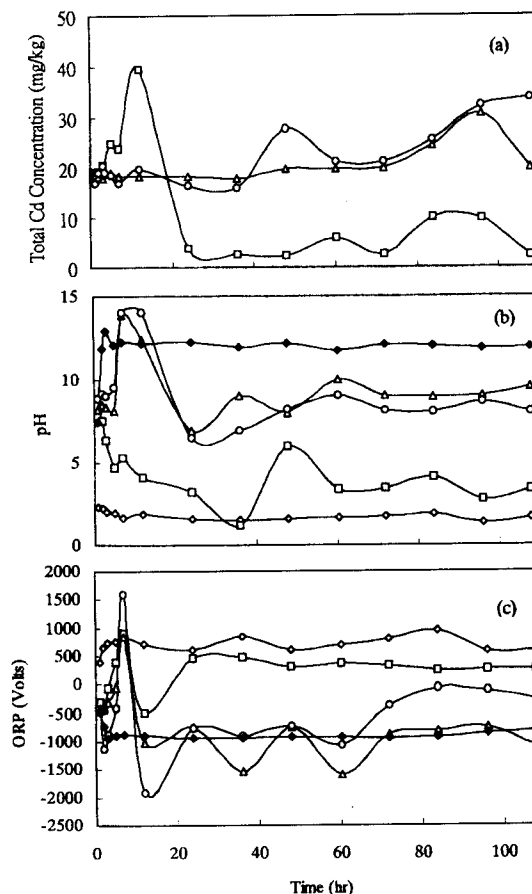
However, pH of soil in portion B and C increased from 8-9 to 11-12 after 5 hr of current. Accumulated of Cd was, therefore, observed in portion B and C. Figures 2(b) and (c) also show that at low pH values, Cd was in high oxidation states (ORP >0).

Figure 3(a) shows the total Cd concentration of soil in the ESI was relatively high near the anode. Interestingly, the pH value at B is higher than that at C after 24 hr of ESI (Figure 3(b)). The increase in pH value might be due to the existence of alkaline media in soil that migrated from C to B. The pH value is decreased at C because of the migration of H^+ from the anode (to C). Figure 3(c) also shows that the reduction potential is relatively greater at B after 24 hr of ESI. The decrease in the reduction potential at C might cause the migration of Cd ion to cathod.

During the ESR, parallel experiments were also conducted at pH=5.0. Figure 4(a) shows that the
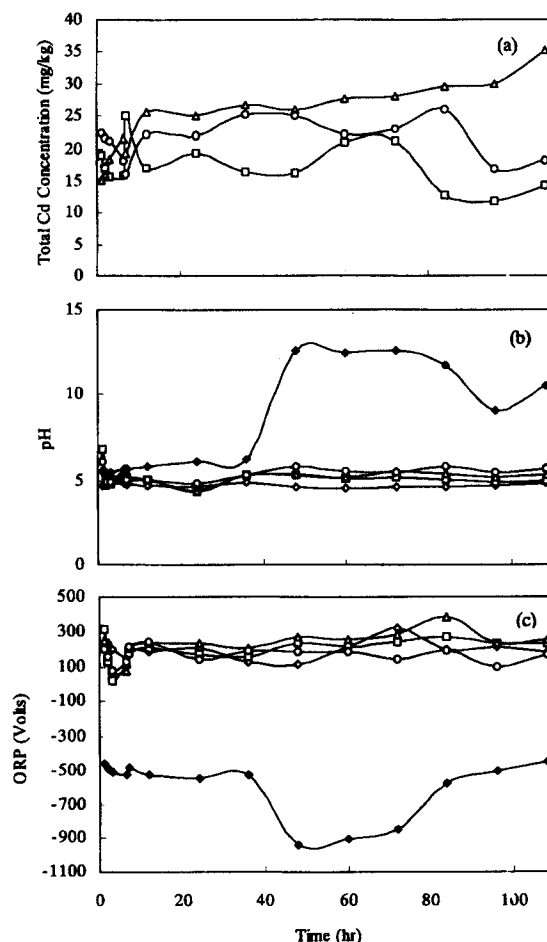

Figure 4. (a) Total Cd concentration, (b) pH and (c) ORP profiles as function of time in ES5 at (□) slice A, (△) slice B, (○) slice C, (◇) anode and (◆) cathode.
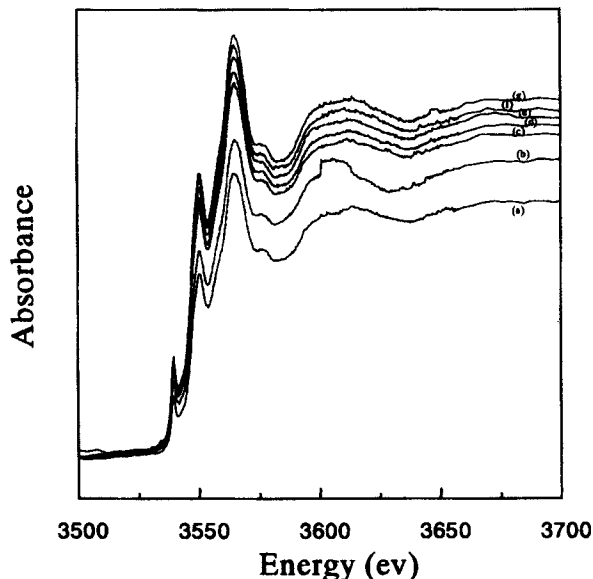
total Cd concentration of soil at A is about 10-15 mg/kg after 108 hr of ES5. Efficiency of Cd contaminated soil in ES5 was not better than in ES or ESI. Compared with pure potassium nitrate solution, the conductive solution (potassium nitrate adjusted to pH=5.0 by using buffer solution) has a higher conductivity. That caused a higher ratio of current passing through the conductive solution, and led to a lower electrokinetic remedial efficiency.

Figure 5. In-situ XANES spectra of electrokinetic soil remediation after (a) 1, (b) 2, (c) 3, (d) 4, (e) 5, (f) 6 and (g) 7 hr of current.

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