

Concentration of copper and a copper–EDTA complex at the pH junction formed in soil by an electrokinetic remediation process

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Abstract

The formation and stability of a pH junction was investigated, and the precipitation and accumulation of a metal hydroxide at the pH junction was confirmed. Moreover, the possibility that metal ions could be accumulated as a Me–EDTA complex at the pH junction was demonstrated. As a result, the pH junction where the acidic and alkali fronts of soil meet and the pH of soil changes rapidly, appeared at the 0.6 position in the EK process for 6–12 h. Copper ions accumulated in the form of copper hydroxide. EDTA was also concentrated in the position, in general agreement with the position of the pH junction. In addition to copper hydroxide, a copper–EDTA complex was concentrated at the 0.6 position from the anode after EK treatment for 12 h. The copper–EDTA complex was retained in 0.7 position from the anode after 12 h and, after 24 h, the position shifted to 0.8–0.9 from the anode. The possibility of accumulating metal ions within a narrow area, such as a pH junction was demonstrated.

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1. Introduction

Electrokinetic (EK) remediation is a promising in situ technology for removing pollutants from clayey soils on the basis of electrokinetic phenomena [1–4]. The EK process is suitable for treating various contaminants (e.g. heavy metals, organic pollutants and radionuclides) in many kinds of soils [5–10]. This method can be performed under a low-level voltage or a current between electrodes, inserted in the vicinity of the contaminated sites. Charged species can be removed by electromigration and the electrically neutral species by electroosmotic flow (EOF) if they are soluble in water. Various attempts have been made to enhance the effectiveness of removing metal ions, including the addition of chelating agents to remove metal ions, such as Me–EDTA complexes [11–17]. Reddy et al. discussed some factors on electrokinetic remediation enhanced by EDTA [18]. On the other hand, Probst et al. investigated the accumulation of heavy metal ions at the “pH jump”, where the acid and base fronts of water meet in soil during electrolysis [1]. The technique is based on the isoelectric focusing, which is often used in electrophoretic separation. We refer to it as the “pH junction” in this paper. The precipitation of a metal hydroxide at the pH junction

generally leads to a decrease in the efficiency of the removal of metals from soil. However, as Probst et al. described, the storage and accumulation of metals in the relative narrow area is clearly remediation, because the accumulated metals can be subsequently removed by the excavation of a relative small amount of soil. Although they showed visual examples of the formation and motion of a pH junction in a migrating chamber using two different pH indicators, the process involved in the formation and the stability of the pH junction have not been investigated in detail.

The purpose of this study was: (1) to investigate the formation and stability of the pH junction, (2) to confirm the precipitation and accumulation of a metal hydroxide at the pH junction and (3) to demonstrate that metal ions as a Me–EDTA complex can be accumulated at the pH junction. If a metal complex could be accumulated at the pH junction, the selective accumulation of metals using the EK process could be achieved using an adequate chelating agent in the future.

2. Material and methods

2.1. Soil for this experiment

Commercial kaolin, which mainly consists of kaolinite, was obtained from the Wako Pure Chemical Co. (Tokyo, Japan), and was used as a model of soil. Since this kaolin contains traces of

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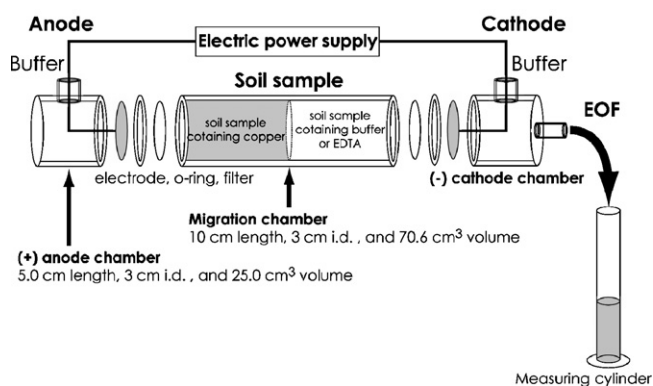


Fig. 1. Schematic diagram of the electroremediation apparatus.

iron, it was removed by shaking with 0.1 M HCl (w/w = 1:4) for 24 h. The pH of the model soil was adjusted to 7 by the addition of aqueous 0.1 M NaOH and the kaolin was then dried for 24 h. The water content of the model soil was adjusted to 30% using a buffer solution (pH 7, 0.1 M $\text{NaH}_2\text{PO}_4/\text{NaOH}$ buffer). The transmission coefficient of the kaolin after acid treatment was $1.0 \times 10^{-8} \text{ cm s}^{-1}$ and the particle size by the soil classification method was a silt (0.02 mm to $2 \mu\text{m}$) content of 18% and a clay ($>2 \mu\text{m}$) content of 82%.

2.2. Simulator for this study

In order to investigate the behavior of the pH junction, copper ions and copper–EDTA in soil by the EK technology, an apparatus having a small migration chamber (3.0 cm in diameter and 10 cm length) and two electrode chambers (3.0 cm in diameter and 5.0 cm length) was prepared (Fig. 1). To prevent the soil in the migration chamber from leaking into the buffer solution of the electrode chambers, each chamber was connected using 5B filter paper (Advantec, Japan) and an O-ring (Kokudo Co., Japan). A meshed Pt coated Ti electrode was inserted into each electrode chamber, and the anodic and cathodic chambers were filled with a buffer solution.

A dc power supply AE-8270 (Atto Co., Japan) or MP-7612D (System Instruments Co., Ltd., Japan) was used to provide a constant voltage across the anode and cathode during the experiment. The voltage during the EK process was measured using this power supply as a function of time. The effluent by EOF was collected in a measuring cylinder and stored for analysis. A constant dc current of 50 mA was applied through the soil for 1–24 h.

Contaminated soil was prepared by adding a copper ion solution, prepared with $\text{Cu}(\text{SO}_4)$, to the treated kaolin and mixing them well. The concentration of the copper was 250 mg/kg, two times the environmental quality standard value for copper in soil in Japan and the water content in the soils was adjusted at 30% using a buffer solution (pH 7.0, 0.1 M $\text{NaH}_2\text{PO}_4/0.1 \text{ M NaOH}$ buffer). The contaminated soil was placed in half of the anode side of the migration chamber. The remaining area, from the center in the migration chamber to the cathodic chamber, was packed with soil containing only buffer solution. The total amount of copper in the migration chamber was 14.75 mg. The

Table 1
Conditions in all tests in the EK treatment

Test	Applied current (mA)	Applied time (h)	Migration chamber	Result
1	50	24	Indicator	Fig. 2
2	50	24	Buffer soil	Fig. 3
3	50	6	Copper soil + buffer soil	Fig. 4
4	50	9	Copper soil + buffer soil	Fig. 4
5	50	12	Copper soil + buffer soil	Fig. 4
6	50	24	Copper soil + buffer soil	Fig. 4
7	50	9	EDTA soil	Fig. 6
8	50	6	Copper soil + EDTA soil	Fig. 7
9	50	9	Copper soil + EDTA soil	Fig. 7
10	50	12	Copper soil + EDTA soil	Fig. 7
11	50	24	Copper soil + EDTA soil	Fig. 7

total weight of soil in the migration chamber was 120.0 g in all runs. The anode and cathode chambers were filled with the buffer solution.

In the case of the experiment using EDTA, kaolin containing EDTA was placed in half of the migration chamber on the cathode side. Soil containing EDTA was prepared by adding 39 ml of a 0.01 M EDTA buffer solution (w/w = 7:3) to 91 g of the pH-adjusted soil. The concentration of EDTA in the soil was 1000 mg/kg. The conditions for all tests are summarized in Table 1.

2.3. Analytical method

After the EK experiment, the soil sample was removed from the migration chamber and sliced into several sections. The water content, pH and the concentration of copper and EDTA was determined in each section. The solutions in the two electrode chambers and in the measuring cylinder were also analyzed by the same method.

To measure the pH of the soil after the EK treatment, 2.5 ml distilled water was added to 1.0 g of soil in each section (w/w = 1:2.5) and the mixture was shaken at 1500 rpm at room temperature for 1 h. The pH of the water extracted from the soil by centrifugation was measured using a Horiba digital pH meter (pH Meter M-13, Horiba Co.) and a glass electrode.

After the EK remediation treatment, the amounts of copper in the soil, two electrode chambers and the overflow by EOF were measured. The copper ions in 3.0 g of soil of each section were extracted by adding 30 ml of 1 M HCl (w/w = 1:10), followed by shaking at 1500 rpm for 6 h. After shaking, suspension of soil and hydrochloric acid was centrifuged at 4000 rpm for 15 min using a centrifugal separator 2410 (Kubota Co., Japan). The concentration of total copper ion in the supernatant was determined using an atomic absorption spectrophotometer (AAS), A-2000 (Hitachi Co., Japan). The analytical method for copper ion was that approved for use by the Japanese Industrial Standard (JIS) K 0102. The mass balance for copper in the EK system was within the range of $\pm 10\%$.

The amounts of EDTA in the soil, the electrode chamber and the overflow by EOF were measured by the following method. EDTA was extracted from 3.0 g of soil in each section by adding

30 ml of Milli-Q water (Millipore Co.) and shaking at 1000 rpm at room temperature for 1 h. After shaking, the soil sample was centrifuged for 15 min. The supernatant was filtered through a Millex[®]-LH (0.45 μm , filter size, Millipore Co.), to separate the solution from the soil. The analysis of EDTA was carried out using an HPLC system; L-6000 Pump and L-4200 UV-VIS Detector (210 nm, UV wavelength, Hitachi Co.) with RSpak DE-413 column (4.6 mm in diameter and 150 mm length, Shodex Co.) and a RSpak DE-G guard column (4.6 mm in diameter, Shodex Co.). 10 mM phosphoric acid was used as the eluent and the flow rate was 1.0 ml min⁻¹.

3. Results and discussion

3.1. Generation of "pH junction"

As is known well, the pH of the solution in the anode chamber would decrease to around 2–3 and the pH of the solution in the cathode chamber would increase to around 11 by the electrolysis of water. Since proton and hydroxide ions move by electromigration to soil in the migrating chamber, the acidification and alkalization of soil would soon be evident. The change in soil pH of the migrating chamber during the EK process was measured by two methods. One is the visual observation of the pH of the soil with pH indicators, a mixture of methyl yellow and thymolphthalein, mixed in the soil. This soil containing two indicators shows red at pH < 4 (red zone), yellow at pH 4–9.3 (yellow zone) and blue at pH > 9.3 (blue zone).

Fig. 2 shows the change in the pH of the soil in the migrating chamber, as determined by the color of the indicators as a function of time. The horizontal axis of this figure shows the position of the soil in the migration chamber. That is, the 0 of the axis means the edge of the anodic chamber and 1.0 corresponds to the edge of the cathodic chamber. In this figure, the acid area of soil is shown as a 'red zone', the neutral area is a 'yellow zone' and the alkali area is a 'blue zone'. Initially, all of the soil was neutral. However, as soon as the voltage was applied, the acidification and alkalization began in the soil close to the cathode and anode. After 6–12 h, the acidic front and alkali front of soil meet and the pH junction, where pH of soil jumps abruptly, appeared

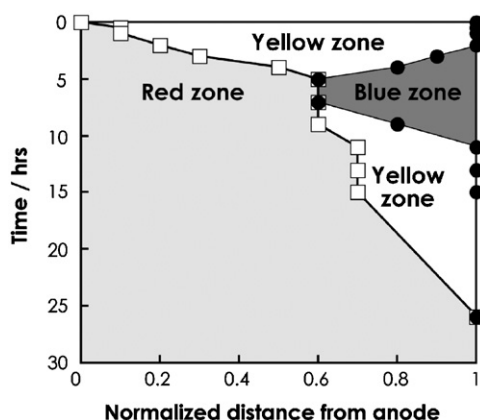


Fig. 2. pH change evaluated by the color of an indicator in soil as a function of time. Applied constant current = 50 mA; applied time = 48 h.

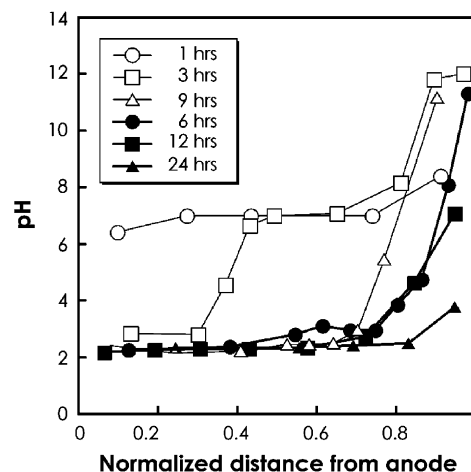


Fig. 3. Distribution of the pH of the soil in the migration chamber after the EK process. Applied constant current = 50 mA; applied time = 48 h.

at the 0.6 position in Fig. 2. The pH junction can be stable for several hours, but, after a longer period, it began to shift to the cathodic side and became wider, finally forming a yellow zone and all of the soil in the migrating chamber then become acidic. Another method is based on the pH measurement of a solution extracted from the soil in the migration chamber.

Fig. 3 shows the pH distribution of the soil in the migration chamber after the EK process for different periods of time. The results are consistent with that in Fig. 2. Protons, produced at the anode and hydroxide ions, produced of the cathode can be carried to the migration chamber by electromigration. However, the pH change of the soil was barely detectable after the EK process for 1 h because of the presence of the buffer solution in the soil. After 3 h, the soil begins to be acidified from the soil close to the anode chamber and alkalinity develops from soil close to the cathode chamber. A pH junction where the pH jumps appeared after about 6–9 h. After about 24 h, the entire soil sample in the migration chamber became completely acidified.

3.2. Accumulation of copper ions as metal hydroxide at pH junction

As Probst et al. reported, copper ions can be accumulated at a pH junction. Fig. 4 shows the distribution of copper in the migration chamber after EK treatment for 6, 9, 12 and 24 h. The initial concentration of copper before EK treatment is shown as a square gray zone in this figure. When a voltage is applied, copper ions in the soil moved in the direction of the cathode by electromigration and electroosmotic flow. However, when the copper ions enter the alkali zone, they are converted to copper hydroxide and lose their electrical, becoming concentrated at the 0.6 position from the anode, i.e., the pH junction. The concentration of copper at the pH junction was observed as a pale-blue, thin line of copper hydroxide in the soil. Therefore, copper ions were accumulated within a very narrow area of the pH junction. After 12 h, the color of copper hydroxide line, was at 0.7 position from the anode, and copper in the soil is barely moved, even after more 12 h. As shown in Fig. 6, the distribution of copper, based

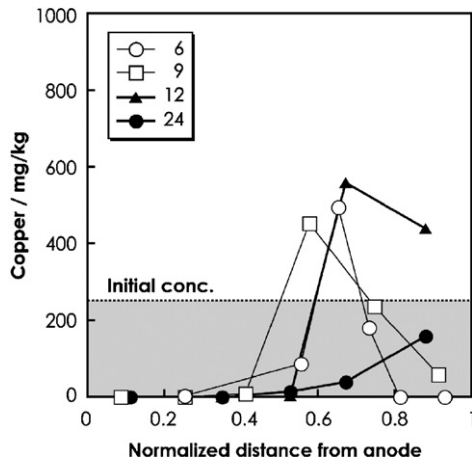


Fig. 4. Distribution of the copper in the migration chamber after EK treatment. Applied constant current = 50 mA; applied time = 6, 9, 12 and 24 h.

on the determination of copper in slices soil was not as sharp as be expected because the width of sliced soil was relatively thick. After 24 h, since the entire soil sample in the migration chamber was acidified completely, most of the copper in the soil moved out to the cathodic chamber.

3.3. Accumulation of EDTA at pH junction

EDTA is a multidentate ligand and is present as a negatively charged compound in alkaline solution due to the acidic dissociation equilibrium of its carboxyl groups. Therefore, this anionic species attempts to move in the direction of the anode by electromigration under acidic conditions. When EDTA enters the acidic zone, it loses its electric charges by association with protons and then moves back in the direction of the cathode by EOF, i.e., into alkali conditions. In alkaline conditions, EDTA becomes an anionic species again by acid dissociation. Therefore, EDTA will exist only at the pH junction.

Fig. 5 shows the distribution of EDTA after an EK treatment of 9 h. The soil containing EDTA of 1000 mg/kg was used to fill the entire migration chamber, and the initial concentration of

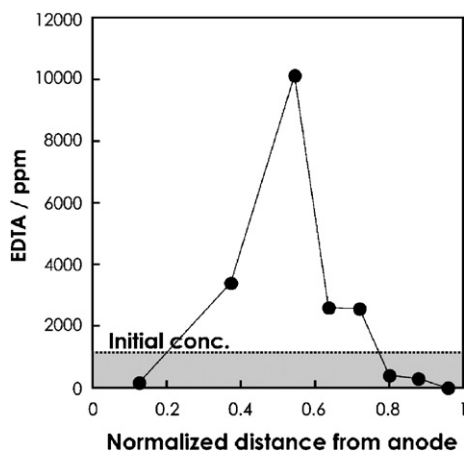


Fig. 5. Distribution of the EDTA in the migration chamber after EK treatment. Applied constant current = 50 mA; applied time = 9 h.

EDTA before EK treatment is shown by the square gray zone in the figure. EDTA was concentrated at the 0.5 position from the anode by the EK treatment. This position is in general agreement with the position of the pH junction. EDTA was not detected in solutions of the anode and cathode chambers and the overflow by EOF.

3.4. Accumulation of copper–EDTA complex at pH junction

Copper ion, complexed with EDTA, would also be expected to be concentrated at the pH junction. Because when copper ions are carried by electromigration to the pH junction, they form Cu–EDTA complexes, which are delivered by electromigration to the anode side because the complexes have negative charges (Scheme 2, Fig. 6). However, when Cu–EDTA complexes enter the acidic media, the Cu–EDTA complexes dissociate into copper ions and EDTA and the copper cations move to the pH junction, and these processes are repeated. Consequently, metal ions cannot be present at any position except the pH junction (Scheme 3, Fig. 6).

Fig. 7 shows the distribution of copper ions with EDTA after EK treatments for 6, 9, 12 and 24 h. In this experiment, the soil contaminated with copper at a level of 250 mg/kg was placed in half of the migration chamber of the anode side. In the other half of the chamber, soil-containing EDTA of 1000 mg/kg was added. The initial concentration of copper before EK treatment

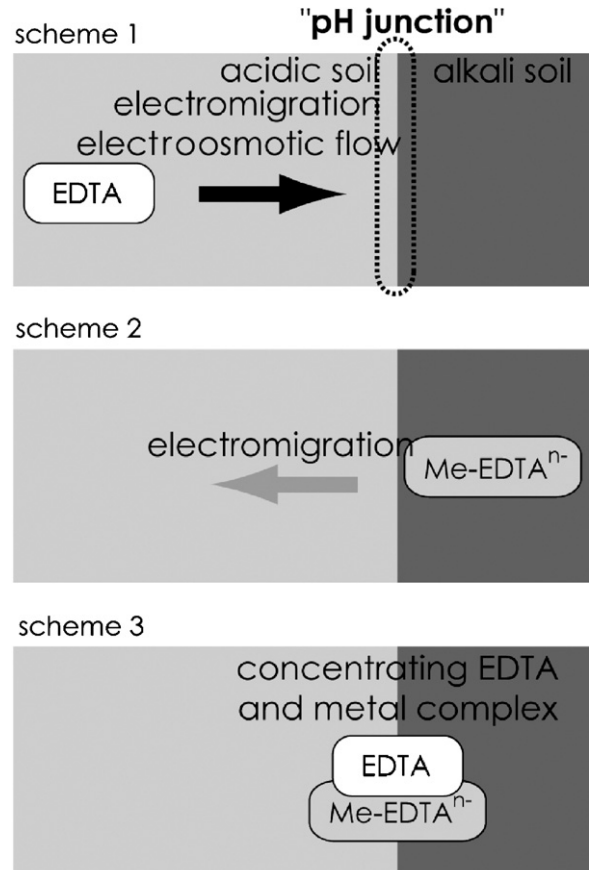


Fig. 6. Mechanism of concentrating Me–EDTA at the pH junction.

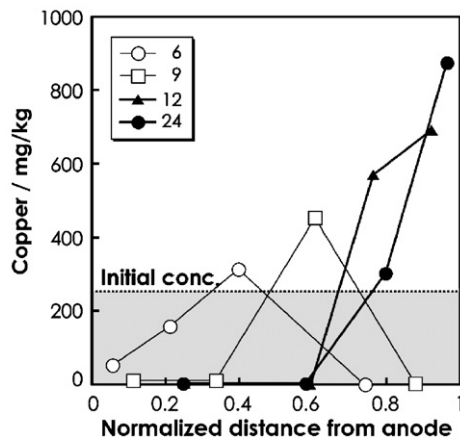


Fig. 7. Distribution of copper with EDTA in the migration chamber after EK treatment. Applied constant current = 50 mA; applied time = 6, 9, 12 and 24 h.

is shown as a square gray zone in this figure. The same as the copper hydroxide, the copper–EDTA complex was concentrated at the 0.6 position from the anode after EK treatment for 12 h, i.e., at the pH junction. The copper–EDTA complex was retained at the 0.7 position from the anode after 12 h and, after 24 h, the position was of 0.8–0.9 from the anode. This difference in the time where the pH junction was formed was weakened to the point for a concentrated copper containing EDTA compared with not using EDTA. These results show the concentration of copper as an EDTA complex in the pH junction.

4. Conclusions

The formation of a pH junction by electrokinetic remediation process in soil and the accumulation of copper ions and a copper–EDTA complex were confirmed. The accumulation of copper–EDTA at the pH junction was due to the isoelectric focusing of EDTA and Me–EDTA on the basis of acid dissociation between the acidic and alkaline zones. The concentration of a metal as a metal–EDTA complex at the pH junction has some advantages, for example, (1) it permits heavy metals to

be collected in a specific narrow zone (pH junction), then (2) it confirms that pollutants can be retained in soil, and that such a treatment might be feasible.

If various metal ions can be accumulated with various chelating agents at a pH junction, the selective accumulation of metals in the soil using the EK process will be expected by selecting an adequate chelating agent in the future.

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