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Enhanced electrokinetic remediation of cadmium contaminated soils by chelating agents

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ABSTRACT

Electrokinetic soil remediation by electroosmosis and ionic migration is restricted to soluble substances. At a higher pH, the soil particles sorb more heavy metals than at a lower pH and the precipitation reactions of heavy metals are promoted. Both mechanisms make heavy metals immobile, rendering cleanup more difficult and electrokinetic extraction inefficient.

In this study, the effectiveness of introducing chelating agents to enhance the removal of cadmium from kaolinite in the region of neutral pH by ionic migration is examined. The chelating agents selected were ethylenediaminetetraacetic acid (EDTA) and citric acid. The investigation was carried out in a laboratory-scale column containing kaolinite contaminated with cadmium. Cadmium migrates toward the anode, indicating that cadmium is indeed solubilized by EDTA and citric acid as negatively charged chelates. The dissolved chelates migrate toward the anode by ionic migration and are successfully removed at the anode reservoir. The effectiveness of EDTA and citric acid for removing cadmium was also investigated and it was found that EDTA was more effective than citric acid. © 2005 SDU. All rights reserved.

Keywords: Electrokinetics; Soil remediation; Cadmium; EDTA; Citric acid

1. INTRODUCTION

During the last decade, a great deal of research has been conducted to develop in-situ technologies for treating contaminated soils and ground water. In-situ methods are attractive because of the potential lower cost, less disruption to the environment and reduced worker exposure to the hazardous materials. However, most successful in-situ remediation technologies are restricted to soils with relatively high hydraulic conductivity so that they can not be used for fine-grained deposits. In recent years, there has been considerable interest in the application of electrokinetics as an in-situ method for cleaning up contaminants in fine-grained, low permeability soils (Shapiro *et al.,* 1989; Alshawabkeh and Acar, 1992; Pamukcu and Wittle, 1992; Shapiro and Probstein, 1993; Hicks and Tondorf, 1994; Coletta *et al.,* 1997; Niinae *et al.,* 1998; Niinae *et al.,* 2000; Niinae *et al.,* 2001a,b,c,d). The primary contaminant transport and removal mechanisms are electroosmotic advection and ionic migration. Electroosmosis is the flow of the pore water in the soil under the action of the electric field. The flow rate is proportional to the product of the electric field strength and the zeta potential. Ionic migration is the motion of charged ions in an electric field. The velocity of the ions is proportional to the product of the electric field strength and ion charge and is generally more rapid than electroosmosis. Consequently, heavy metals are typically removed by the migration of their ions, whereas uncharged contaminants, usually organic chemicals, have to be removed by electroosmosis. It is clear that electrokinetic soil remediation by electroosmosis and ionic migration is restricted to soluble substances. Contaminants that are adsorbed on the soil or are present as precipitates can not be effectively removed. In particular, the solubility of most heavy metals may be significantly reduced at elevated pH values. When impurities such as iron oxides are present, electrokinetics alone may not be effective in the extraction of heavy metals due to the higher acid / base buffer capacity (Yeung *et al.,* 1996; Wong *et al.,* 1997). Also, acidification of the medium might cause large weight losses by dissolution of part of the solid matrix (Kedziorek and Bourg, 2000). It would therefore be better if the treatment were performed at neutral pH.

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The solubility of metals can be enhanced by adding reagents that form metal complexes such as chelates. Chelating agents contain two or more ligands that bond with the metal to form stable, ring-like coordination complexes called chelates. Also, extraction with a chelate does not necessarily require very low pH values. Many researchers have shown that ethylenediaminetetraacetic acid (EDTA) and citric acid are excellent solubilizing agents for metals including cadmium from contaminated soils. EDTA is effective at the pH range from 4 to 10 and citric acid is effective at the pH range from 4 to 7 (Chen *et al.*, 1992). EDTA and citric acid are ionic and can, in principle, be introduced into the soil by ionic migration.

In this study, the effect of injecting EDTA and citric acid into the contaminated soil on the efficiency of electrokinetic extraction of cadmium in the region of neutral pH is investigated and the tests conducted for cadmium are provided

2. BACKGROUND

The electrokinetic soil remediation process is governed in part by the electrode reactions which are inherent to the process. These reactions are typically the electrolysis of water at the electrodes which can be described by the following redox reactions:

Anode reaction : $2H_2O - 4e^- = 4H^+ + O_2(g)$ (1)

Cathode reaction: $4H_2O + 4e^- = 4OH^- + 2H_2(g)$ (2)

The hydrogen ions produced at the anode and the hydroxide ions generated at the cathode migrate into the soil under the action of the electric field. When the acid front and the base front meet, the soil between the electrodes is divided into two zones, a low and high pH zone, with a sharp pH jump in between. The location of the pH jump usually locates closer to the cathode, because hydrogen ion has about twice as high ionic mobility as hydroxide ion (Hicks and Tondorf, 1994; Wong *et al.*, 1997). The change in pH may be attenuated by the buffering action of the soil, and may be controlled by washing the electrodes to remove or neutralize the hydrogen or hydroxide ions. For example, neutral or alkaline conditions can be promoted throughout the soil by washing the anode to remove the generated hydrogen ions while allowing the hydroxide ions generated at the cathode to migrate into the soil (Hicks and Tondorf, 1994). However, the high pH environment will favor the sorption of heavy metals by increasing their affinity for the soil surfaces, and favor formation of heavy metal precipitates, thus decreasing the mobility of heavy metals.

Of interest here is that reagents such as complexing agents can be added to the electrode rinse or purge streams, and will be introduced into the soil by electroosmosis or, if charged, by ionic migration. For example, EDTA (negatively charged ligand) added to the catholyte solution will be migrated toward the anode by ionic migration and it will enhance the solubility of heavy metal contaminants.

3. EXPERIMENTAL

The soil used in this study was a kaolinite (South Carolina, USA). The soil samples were prepared by mixing 90g of kaolinite (specific surface area = $19.8m^2/g$) with $400cm^3$ of cadmium solution (Cd = $8.9\times10^{-4}mol/dm^3$ (prepared with $Cd(NO_3)_2 \cdot 4H_2O$); $NaNO_3$ = $1.0\times10^{-2}mol/dm^3$). This mixing procedure was conducted while adjusting to around pH 6, periodically adding NaOH solution with a pH-stat. After centrifugation, the saturated soil sample was packed into a polyvinyl chloride column (20cm long, 2cm diameter), which is connected on each end to an electrode reservoir containing a graphite electrode (2cm diameter). A schematic of the experimental apparatus used for this study is shown in Figure 1. The kaolinite is prevented from entering the reservoirs by filter paper supported on a stainless steel screen, which also serves as a reference electrode for measuring the potential across the kaolinite. Voltage probes are embedded along the length of the column to permit measurement of the potential profile. Anolyte solution was $1.0\times10^{-2mol}/dm^3$ $NaNO_3$ and anolyte pH was adjusted to around 7, periodically adding NaOH solution with a pH-stat. EDTA in the di-sodium salt form ($C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$) and tri-sodium salt form ($C_6H_5Na_3O_7 \cdot 2H_2O$) were added to the catholyte solutions ($1.0\times10^{-2}mol/dm^3$ $NaNO_3$). Catholyte pH was adjusted to around 8 by adding NaOH or HNO_3 solution. Anolyte solution was circulated continuously to electrode reservoirs with a micro tubing pump. Meanwhile, fresh catholyte solution from cathode tank was continuously introduced to the cathode reservoir with a micro tubing pump. Pressure-induced flow was prevented by equalizing the water level in the both electrode reservoirs. The applied voltage was 20V DC across the electrodes. The current, applied voltage and local voltage were monitored. During the experiments, samples of solution were taken from the electrode reservoirs for determining cadmium concentration. At the end of the experiments, the kaolinite was sectioned into 10 segments, and each section was analyzed for pH and cadmium concentration. Final soil pH was measured using a pH meter.

After the soil samples of each sections were dried for 24h at 383K, 1.0g of each soil samples were mixed with 50cm^3 of 1.4mol/dm^3 HNO$_3$ before centrifugation for determining the cadmium concentration. The cadmium content was determined using an atomic absorption spectrophotometer. The reagents used were all analytical reagent grade.

4. RESULTS AND DISCUSSION

4.1. Without chelating agents injection

4.1.1. Soil pH and cadmium concentration distributions in kaolinite

The experiment without injecting chelating agents into the soil was performed. Figure 2 shows the measured distribution of pH in kaolinite at 336h. The initial soil pH was 6.20. Anolyte and catholyte pHs were maintained at 7 and 8, respectively. The soil pH at 336h hardly changes as compared to the initial soil pH.

The measured distribution of cadmium in the kaolinite at 336h is shown in Figure 3. Cadmium accumulates in the first half of the soil sample (closest to the cathode; cathode section). Cadmium was not detected in the electrode reservoirs. Therefore, it is considered that almost all the cadmium in the kaolinite accumulated as sorbed phase and solid phase (cadmium hydroxide) in this region. The formations of cadmium hydroxide [Cd(OH)$_2$] obtained by using the value of 2.51×10^{-14}mol/dm^3 (Ringbom, 1963) as the solubility product of cadmium hydroxide and the value of 1.0×10^{-3}mol/dm^3 as the total cadmium concentration in the solution are 3.8% at pH 6.5 and 28.5% at pH 7. Therefore, it is considered that the formation of sorbed phase in the soil is predominant compared with the formation of solid phase (cadmium hydroxide) in the region of neutral pH.
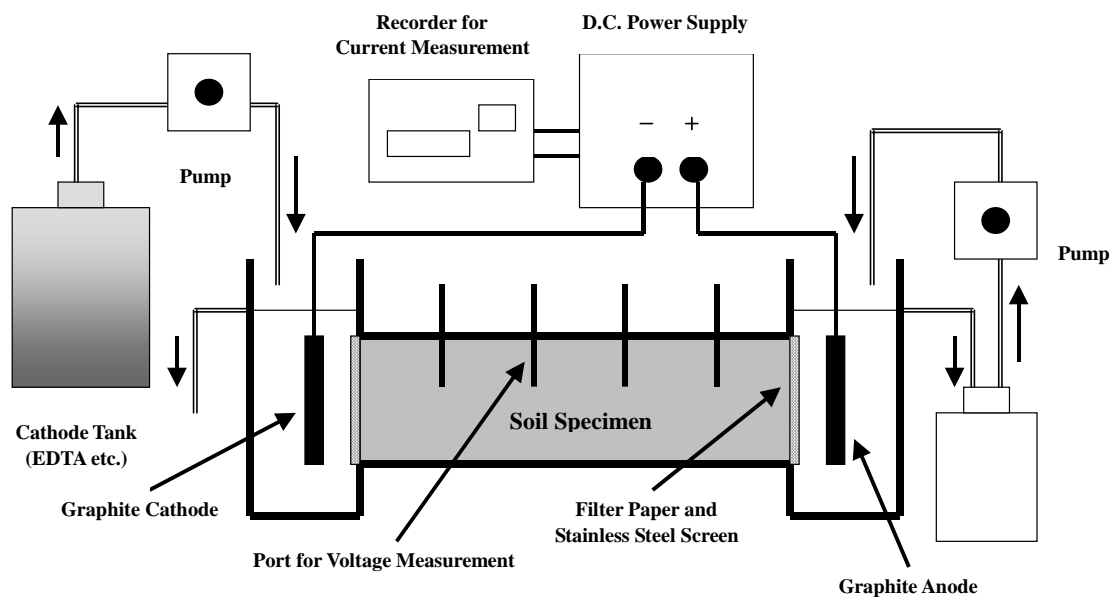

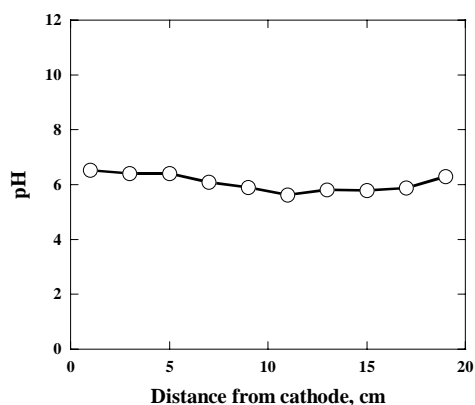Figure 1. Schematic diagram of experimental apparatus

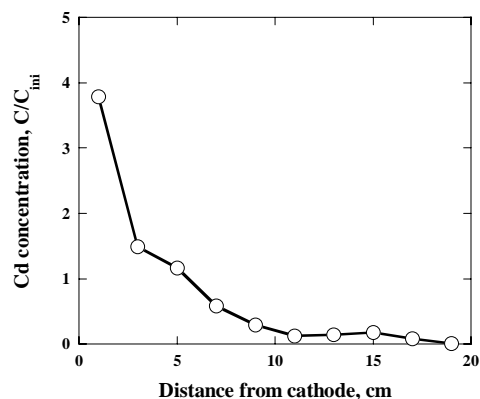Figure 2. Distribution of soil pH at 336h without chelating agents

Figure 3. Distribution of cadmium concentration across soils at 336h without chelating agents (Initial cadmium concentration in soil: 3.09×10^{-6} mol-Cd/g-dry soil)

4.1.2. Electrical potential distribution and current density

Figure 4 shows the measured distributions of electrical potential across the kaolinite. The electrical potential gradients increase in the cathode section. Cadmium forms the sorbed phase and solid phase and the electrical conductivity of the pore solutions in the cathode section decreases. Consequently, the electrical potential gradient increases in the cathode section compared with the anode section (the other half of the soil sample; closest to the anode). The time history of the current density is shown in Figure 5. The current density decreases sharply until 70h and then remains nearly constant.
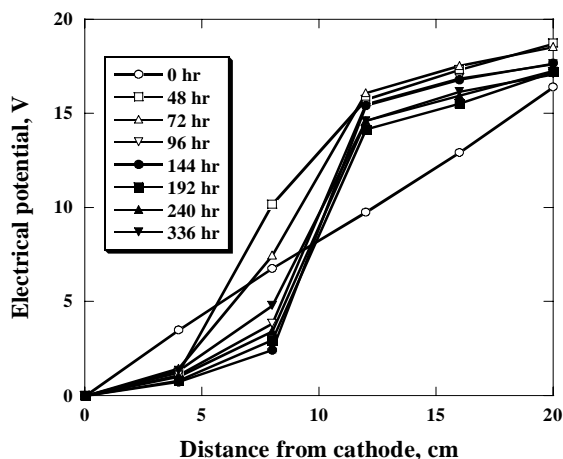

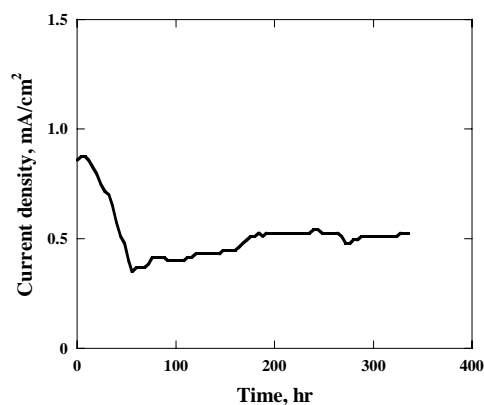Figure 4. Distributions of electrical potential without chelating agents

Figure 5. Time history of current density without chelating agents

4.2. With chelating agents injection

4.2.1. Conditional stability constant of cadmium - EDTA and citric acid complexes

Ethylenediaminetetraacetic acid is a tetraprotic acid abbreviated as H_4Y where Y denotes the ethylenediaminetetraacetate ion $EDTA^{4-}$. It is soluble at pHs above about 3.5 and, in absence of metals, is present in solution as $H_nY^{(4-n)-}$, n = 0 - 4, with the degree of protonation increasing with decreasing pH.

Cadmium is present as the doubly negatively charged chelate (CdY^{2-}) for pH above about 4 (Niinae *et al.*, 1999). The conditional stability constant (K_{CdY}') for cadmium - EDTA complex (CdY^{2-}) (Stability constant of cadmium - EDTA complexes: log K_{CdY} = 16.5, log K_{CdHY} = 2.9; Stability constant of cadmium - hydroxide complexes: log β_1 = 4.3, log β_2 = 7.7, log β_3 = 10.3, log β_4 = 12.0; Acid dissociation constant of EDTA: log K_{HY} = -10.34, log K_{H2Y} = -6.24, log K_{H3Y} = -2.75, log K_{H4Y} = -2.07 (Ringbom, 1963)); Ion product: log K_w = -14.0) are defined as the following equation:

$$K_{CdY}' = (\alpha_{CdY} / \alpha_{Cd}\alpha_Y)K_{CdY} \tag{3}$$

Where K_{CdY} denotes the stability constant of CdY^{2-} and α denotes the side reaction coefficient, and each α is defined as the following equations:

$$\alpha_{CdY} = 1 + K_{CdHY}[H^+] \tag{4}$$

$$\alpha_{Cd} = 1 + \beta_1 K_w / [H^+] + \beta_2 K_w^2 / [H^+]^2 + \beta_3 K_w^3 / [H^+]^3 + \beta_4 K_w^4 / [H^+]^4 \tag{5}$$

$$\alpha_Y = 1 + [H^+] / K_{HY} + [H^+]^2 / K_{HY}K_{H2Y} + [H^+]^3 / K_{HY}K_{H2Y}K_{H3Y} + [H^+]^4 / K_{HY}K_{H2Y}K_{H3Y}K_{H4Y} \tag{6}$$

The relationships between the distributions of cadmium species in the citric acid (H_3L) solution and pH obtained by using the following values of constants, acid dissociation constant of citric acid: log K_{HL} = -5.82, log K_{H2L} = -4.15, log K_{H3L} = -2.85; stability constant of cadmium - citrate complexes: log K_{CdL} = 4.22, log K_{CdHL} = 2.84, log K_{CdH2L} = 2.28 (Perrin, 1999), is shown in Figure 6. Cadmium forms the three kinds of cadmium-citrate complexes (CdL^-, $CdHL$ and CdH_2L^+). However, cadmium is present as the negatively charged chelate (CdL^-) for pH above 6. The conditional stability constant (K_{CdL}') for cadmium - citrate complex (CdL^-) are defined as the following equation:

$$K_{CdL}' = (\alpha_{CdL} / \alpha_{Cd}\alpha_L)K_{CdL} \tag{7}$$

$$\alpha_{CdL} = 1 + (K_{CdHL} / K_{HL}K_{CdL})[H^+] + (K_{CdH2L} / K_{HL}K_{CdL})[H^+]^2 \tag{8}$$

$$\alpha_L = 1 + [H^+] / K_{HL} + [H^+]^2 / K_{HL}K_{H2L} + [H^+]^3 / K_{HL}K_{H2L}K_{H3L} \tag{9}$$

Figure 7 shows the dependence of the conditional stability constants of CdY^{2-} and CdL^- on pH obtained from equations (3) - (9). The larger the conditional stability constant, the more stable the complex. As shown in Figure 7, the relatively high values of the conditional stability constants of CdY^{2-} in the region of neutral pH signify the stability of this water soluble complex and indicate the high potential of EDTA in enhancing the removal of cadmium from contaminated soils compared with citric acid.

4.2.2. Soil pH and cadmium concentration distributions in kaolinite with EDTA injection

The experiments with injecting 0.01mol/dm^3 EDTA into the soil were performed using different durations of treatment (336h, 504h and 840h). Anolyte and catholyte pHs were maintained at 7 and 8, respectively. Figure 8 shows the distributions of pH in the kaolinite at 336h, 504h and 840h, respectively. The initial soil pHs of each experiment were 6.52 for 336h, 6.38 for 504h and 6.21 for 804h. The soil pHs at the end of each experiment ranged between 6 and 7 and do not change significantly as compared to the initial soil pHs.

The measured distributions of cadmium in the kaolinite at 336h, 504h and 840h are shown in Figure 9. Cadmium migrates toward the anode with increase in duration of treatment. Figure 10 shows the cadmium concentration at the anode reservoir for 504h experiment. Cadmium is not detected until 250h at the anode reservoir and cadmium concentration at the anode reservoir increases thereafter. EDTA (negatively charged ligands) migrates toward the anode through the kaolinite by ionic migration and forms negatively charged cadmium - EDTA complex (CdY^{2-}). The dissolved chelate then migrates toward the anode by ionic migration.
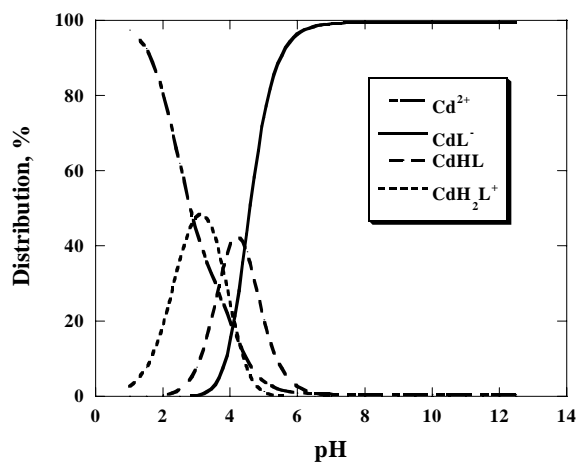
Figure 6. Distributions of ionic species of cadmium in citric acid (H_3L) solution as a function of pH (cadmium concentration: $0.01mol/dm^3$, citric acid concentration: $0.01mol/dm^3$)
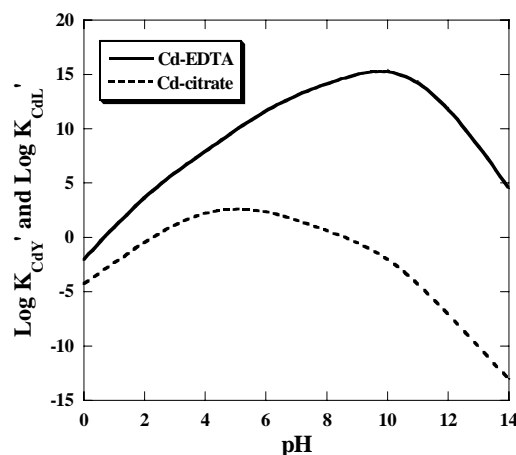
Figure 7. Relationships between pH and conditional stability constants of cadmium - EDTA complex (CdY^{2-}) and cadmium - citrate complex (CdL^-)

4.2.3. Electrical potential distribution and current density with EDTA injection

Figure 11 shows the measured distributions of electrical potential across the kaolinite for 840h experiment. Measurements show a linear increase in the potential values across the kaolinite from the cathode to the anode. This linear increase in electrical potential is considered to be due to the nonformation of sorbed phase and solid phase (cadmium hydroxide) in the soil.

The time histories of current density are shown in Figure 12. The current density decreases sharply until 70h and increases thereafter. The increase in current density is considered to be due to the increase in concentration of EDTA ligands in the soil.
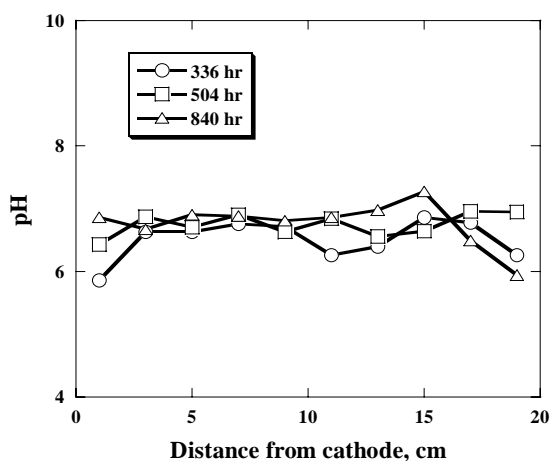

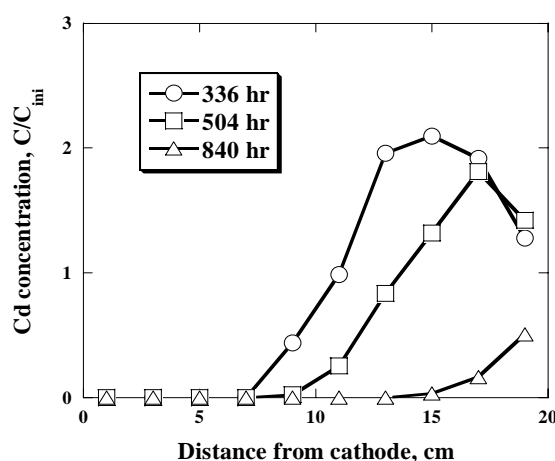Figure 8. Distributions of soil pH with $0.01mol/dm^3$ EDTA

Figure 9. Distributions of cadmium concentration across soils with $0.01mol/dm^3$ EDTA (Initial cadmium concentration in soil: 336h (3.37×10^{-6} mol-Cd/g-dry soil); 504h (3.19×10^{-6} mol Cd/g-dry soil); 840h (3.17×10^{-6} mol-Cd/g-dry soil))
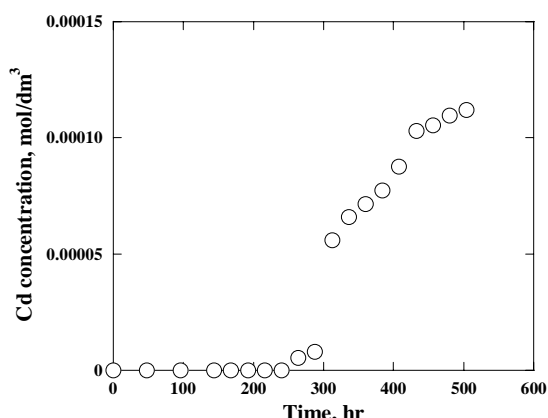
Figure 10. Distributions of cadmium concentration at anode reservoir with $0.01 mol/dm^3$ EDTA (504h)
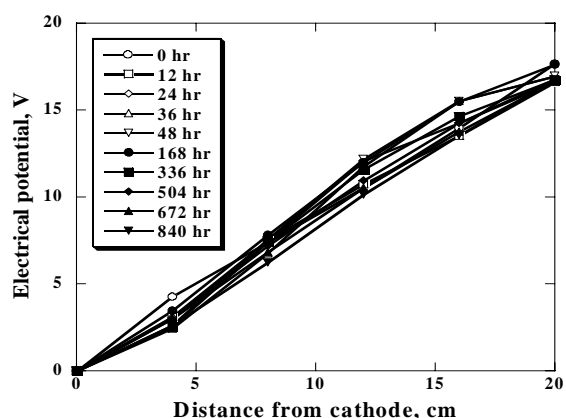

Figure 11. Distributions of electrical potential with $0.01 mol/dm^3$ EDTA
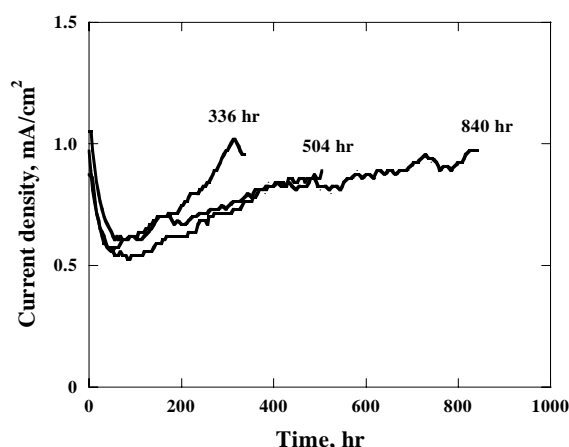

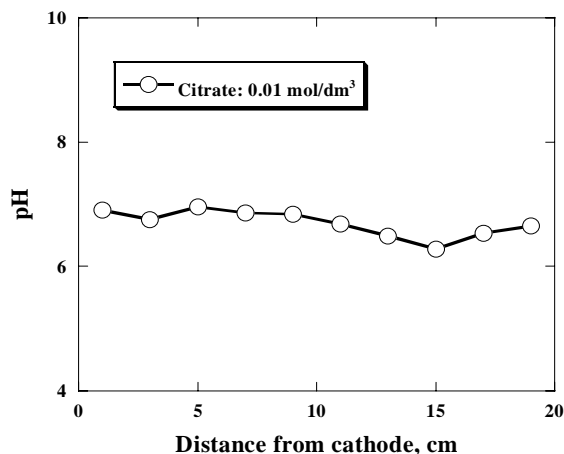Figure 12. Time histories of current density with $0.01 mol/dm^3$ EDTA

Figure 13. Distribution of soil pH at 336h with $0.01 mol/dm^3$ citrate

4.2.4. Soil pH and cadmium concentration distributions in kaolinite with citric acid injection

The experiment with injecting $0.01 mol/dm^3$ citric acid into the soil was performed. Anolyte and catholyte pHs were maintained at 7 and 8, respectively. Figure 13 shows the distribution of pH in the kaolinite at 336h. The initial soil pH was 6.59. The soil pH at the end of experiment ranged between 6 and 7 and does not change significantly as compared to the initial soil pH.

The measured distribution of cadmium in the kaolinite at 336h is shown in Figure 14. Cadmium accumulates in the cathode section. Also, cadmium was not detected in the electrode reservoirs. This result is similar to that without injecting chelating agents. Therefore, it is considered that almost all the cadmium in the kaolinite accumulated as sorbed phase and solid phase in this region, because $0.01 mol/dm^3$ citric acid is insufficient to form cadmium - citrate complex.

4.2.5. Effect of EDTA and citric acid concentrations

The experiments with injecting $0.05 mol/dm^3$ EDTA and $0.1 mol/dm^3$ citric acid were performed. Anolyte and catholyte pHs were maintained at 7 and 8, respectively. Figure 15 shows the distributions of pH in the kaolinite at 336h. The initial soil pHs of each experiment were 6.19 for EDTA and 6.48 for citric acid. The soil pHs at the end of each experiment ranged between 6 and 7 and do not change significantly as compared to the initial soil pHs.
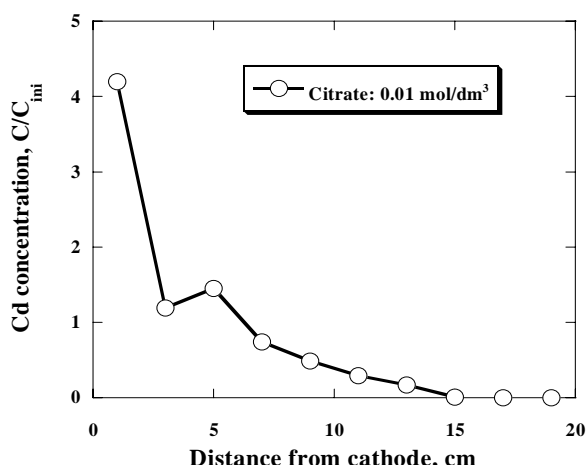
Figure 14. Distribution of cadmium concentration across soil at 336h with 0.01mol/dm³ citrate (Initial cadmium concentration in soil: 3.24×10^{-6}mol-Cd/g-dry soil)
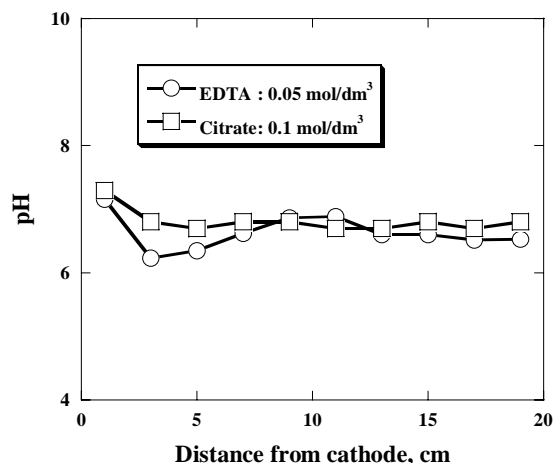
Figure 15. Distributions of soil pH at 336h with 0.05mol/dm³ EDTA and 0.1mol/dm³ citrate

Figure 16 shows the distributions of cadmium in the kaolinite at 336h. With injecting 0.05mol/dm³ EDTA into the soil, cadmium migrates significantly toward the anode as compared to 0.01mol/dm³ EDTA. The movement of cadmium toward the anode at 336h with 0.05mol/dm³ EDTA is comparable to that at 840h with 0.01mol/dm³ EDTA as shown in Figure 9. Cadmium concentrations at the anode reservoir for each experiment are shown in Figure 17. Cadmium is not detected until 150h at the anode reservoir and cadmium concentration at the anode reservoir for EDTA increases thereafter. With injecting 0.01mol/dm³ EDTA into the soil, cadmium concentration at the anode reservoir increased after 250h. Removal of cadmium can be enhanced by increasing EDTA concentration.

Meanwhile, with injecting 0.1mol/dm³ citric acid into the soil, cadmium is uniformly removed from soil. Cadmium was also detected at the anode reservoir. Citric acid (negatively charged ligands) migrates toward the anode through the kaolinite by ionic migration and forms negatively charged cadmium – citrate complex (CdL⁻). The dissolved chelate then migrates toward the anode by ionic migration.
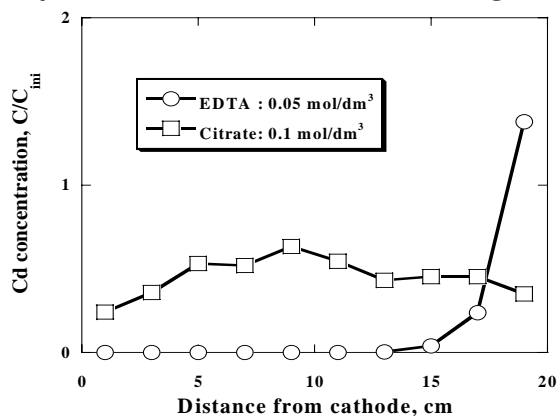

Figure 16. Distributions of cadmium concentration across soils at 336h with 0.05mol/dm³ EDTA and 0.1mol/dm³ citrate (Initial cadmium concentration in soil: EDTA (3.52×10^{-6}mol-Cd/g-dry soil); Citrate (3.61×10^{-6}mol-Cd/g-dry soil))
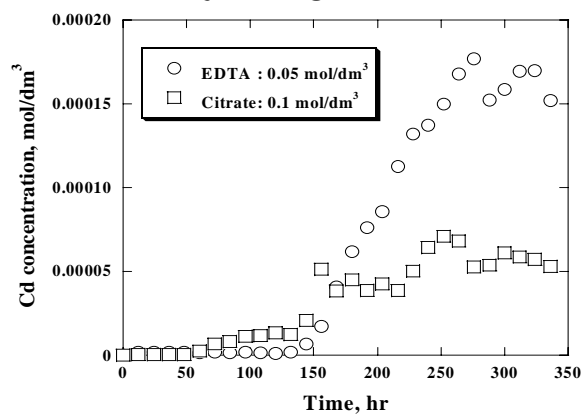
Figure 17. Distributions of cadmium concentration at anode reservoir (Initial cadmium concentration in soil: EDTA (3.52×10^{-6}mol-Cd/g-dry soil); Citrate (3.61×10^{-6}mol-Cd/g-dry soil))

Figure 18 shows the measured distributions of electrical potential across the kaolinite for 0.01mol/dm³ and 0.1mol/dm³ citric acid. With injecting 0.01mol/dm³ citric acid into the soil, the electrical potential gradients increase in the cathode section. Cadmium forms the sorbed phase and solid phase and the

electrical conductivity of the pore solutions in the cathode section decreases. Consequently, the electrical potential gradient increases in the cathode section compared with the anode section.

Meanwhile, with injecting $0.1 mol/dm^3$ citric acid into the soil, measurements show the linear increase in the potential values across the kaolinite from the cathode to the anode. This linear increase in electrical potential is considered that cadmium migrates toward the anode without accumulation of cadmium as sorbed phase and solid phase. However, as shown in Figures 16 and 17, it is found that EDTA is more effective than citric acid for removing cadmium from the soil
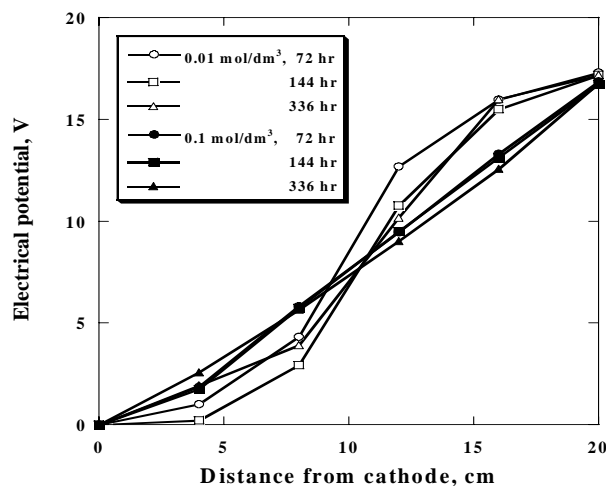

Figure 18. Distributions of electrical potential with citrate

5. CONCLUSIONS

Effectiveness of introducing EDTA and citric acid as chelating agents to enhance the removal of cadmium from kaolinite in the region of neutral pH by ionic migration was examined. Without injecting the chelating agents into the soil, cadmium accumulated in the cathode section. Cadmium was not detected in the electrode reservoirs. Therefore, it is considered that almost all the cadmium in the soil accumulated as sorbed phase and solid phase (cadmium hydroxide) in this region. Meanwhile, with injecting EDTA and citric acid into the soil, cadmium migrated toward the anode, indicating that cadmium was indeed solubilized by EDTA and citric acid as negatively charged chelates and the dissolved chelates migrated toward the anode by ionic migration. Removal efficiency of cadmium from the soil increased with increase in the concentrations of EDTA and citric acid. Also, it was found that EDTA was more effective than citric acid for removing cadmium from the soil.

ACKNOWLEDGEMENT

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NOMENCLATURE

$O_2(g)$	: Oxygen gas
$H_2(g)$	: Hydrogen gas
H_4Y	: Ethylenediaminetetraacetic acid (EDTA)
Y	: Ethylenediaminetetraacetate ion ($EDTA^{4-}$)
K_{CdY}'	: Conditional stability constant for cadmium – EDTA complex (CdY^{2-})
K_{CdY}, K_{CdHY}	: Stability constant of cadmium-EDTA complexes
β_n (n = 1 – 4)	: Stability constant of cadmium – hydroxide complexes
K_{HnY} (n = 1 – 4)	: Acid dissociation constant of EDTA
K_w	: Ion product
α	: Side reaction coefficient
H_3L	: Citric acid
L	: Citrate ion
K_{HnL} (n = 1 – 4)	: Acid dissociation constant of citric acid
K_{CdL}, K_{CdHL}, K_{CdH2L}	: Stability constant of cadmium – citrate complexes
K_{CdL}'	: Conditional stability constant for cadmium – citrate complex (CdL^-)