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Electrokinetic Separation of Heavy Metals from Wastewater Treatment Sludge

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In the study, a preliminary experiment on the removal of heavy metals from industrial wastewater sludge was carried out to evaluate the feasibility of electrokinetic separation. Four different types of processing fluid—tap water, ethylenediaminetetraacetic acid (EDTA), citric acid (CA), and 0.1 M nitric acid—were tested. EDTA was found to be the most effective agent within the set of chemicals tested for removing heavy metals from sludge because of its strong chelating ability with metals. The removal efficiency of Pb and Cu was higher than that of Zn and Ni for all fluids. In tap water, EDTA, and CA, the metals moved toward the anode, implying that they existed as complexes with EDTA and CA or organic matter in the processing fluid. In nitric acid, the metals moved toward the cathode because nitric acid effectively desorbed the metal from the sludge; however, the removal efficiency was very low. The results indicated that electrokinetic technology effectively separated Cu and Pb, but not Zn and Ni.

Keywords chelating ability; electrokinetic separation; processing fluid; sludge

INTRODUCTION

In Korea, part of the sewage wastewater sludge is released into the ocean. Data provided by the Korean government suggested that in 2005, 77% of sewage/industrial sludge was released into the ocean, 1% was dumped in landfills, 11% was incinerated, and 11% was recycled (1). However, ocean dumping was prohibited by the London Convention, and incineration and landfills have been restricted by the "Not In My Back Yard" (NIMBY) phenomenon (2–4). Consequently, the recycling of industrial sludge has become an important environmental issue in Korea (2–4). Sewage sludge is commonly recycled by using it as an agricultural fertilizer or soil conditioner because it contains essential nutrients required for plant growth, such as nitrogen, phosphorus, potassium, calcium, and microelements (5). The main factor hampering the recycling of sludge is its high heavy metal content (2,5–7).

Electrokinetic (EK) technology has been applied to remove or extract various heavy metals from various solid materials including soil, mine tailings, sediment, cement, and sludge (5–13). In EK, a direct current with a density of the order of a few mA/cm^2 is applied to electrodes installed in the contaminated soil or sludge. The following electrolysis reactions occur at electrodes during the electrokinetic process:

$$H_2O \rightarrow 2H^+ + 1/2O_2(g) + 2e^-$$

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2(g)$$

At the anode, hydrogen ions are generated by electrolysis reaction. The hydrogen ions and free cationic species are transported by electromigration toward the cathode. Metals adsorbed onto soil or sludge surfaces are exchanged by hydrogen ions transported by electromigration, and the metal ions desorbed from the surfaces are transported toward the cathode. Electromigration is an important removal mechanism for heavy metals in the EK process. The other mechanism is electroosmosis, in which the soil/sludge moisture moves because of the existence of a space-charge on the solution side of the particle/solution interface. Generally, electroosmosis takes place from anode to cathode because the surface charge of the soil/sludge is negative. Metal ions can be removed in cooperation with electroosmosis.

Sewage sludge has at least 80 wt% of water content and high organic content after the dewatering process. Generally, in the EK process, high water content is advantageous for removing inorganic pollutants. The organic matters such as humic acid and fulvic acid can play a role as complexing agents for heavy metals (14). The phenolic or carboxylic group can serve as an adsorption site for heavy

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metals. In the EK process, the removal of heavy metals from sludge is highly dependent on the extraction of heavy metals from the solid sludge phase to the pore fluid phase. In this study, four different processing fluids were tested to evaluate the extraction efficiency in the EK process.

MATERIALS AND METHODS

Ethylenediaminetetraacetic acid (EDTA) in a two sodium form and citric and nitric acids were purchased from Junsei Chemical (Japan) and used without further purification. The sludge was sampled from the dewatering process at a sewage treatment plant in Ulsan, Korea. Table 1 shows the sludge's water content, initial pH, and heavy metal concentration.

Figure 1 shows a schematic of the electrokinetic experimental system. The apparatus consisted of four parts: the anolyte tank ($4 \times 4 \times 4\,\mathrm{cm}^3$), cell ($4 \times 4 \times 20\,\mathrm{cm}^3$), catholyte tank ($4 \times 4 \times 4\,\mathrm{cm}^3$), and power supply (60 V, 1.5 A). Pt-coated titanium was used as a mesh-type anode and graphite carbon, as a cathode. The catholyte tank was connected to a 1-L catholyte reservoir containing the processing fluids, and these fluids were continuously circulated in the reservoir using a peristaltic pump (ColeParmer, USA) at a flow rate of 2 mL/min. The processing fluids were 0.1 M EDTA, 0.1 M citric acid, and 0.1 M HNO_3, and these were replaced every 2 days with fresh processing solution. Anolyte and tap water was circulated in the anolyte tank using a pump, and the old tap water was replaced every 2 days. To pour sludge in the electrokinetic cell, 800 g of air-dried sludge during 5 days was packed into the cell without any treatment. Then, a constant voltage gradient of 1 V/cm was supplied using a power supply. The experiments were carried out for 2 weeks, and the system current was monitored during the experiment. The electroosmotic flow was calculated by measuring the change in catholyte volume every day. After electrokinetic treatment, the sludge in the cell was equally divided into 5 sections and dried in a drying oven at 105°C. The water content, pH, and metal concentration were analyzed in each section. To evaluate the pseudo-total extraction efficiency of metals content in sludge by Korean Standard Test (KST) methods with some modification, aqua regia extraction was performed. Briefly, 7.0 ml of aqua regia (HNO_3:HCl = 1:3) was inserted into a test tube containing 1.0 g of sludge. The solution was kept in a hood for 16 h to oxidize the organic matter at room temperature and heated at 70°C for 2 h in a heating block. Deionized water was injected to make 10 ml, followed by cooling. After vortex mixing and filtering, the metal concentration in the extractant was analyzed by ICP-MS. (ICP-MS, Agilent 7500CX, USA).

TABLE 1
Chemical composition of sludge used in this study

Properties	Contents
Initial pH	6.0
Water content (%)	80.3
Initial Metal concentration (mg/kg) as a dried basis	
Cu	380.65
Pb	79.3
Zn	702.0
Ni	87.4

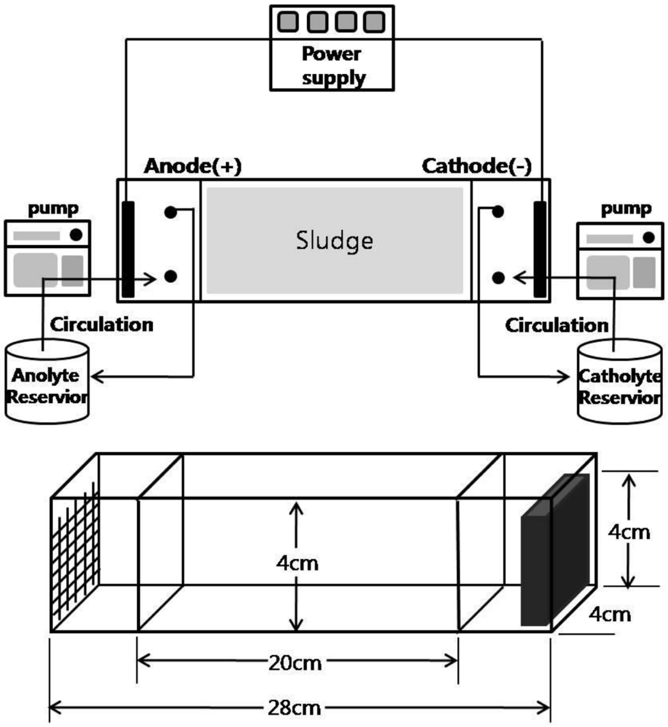


FIG. 1. Schematics of electrokinetic experimental apparatus.

RESULTS AND DISCUSSIONS

Current Density during Treatment

Figure 2 shows the time course of current density under a constant voltage gradient of 1 V/cm. When tap water was used as an anolyte, the current was maintained at very low levels for 120 h, after which it gradually increased. Generally, when the current is under a constant voltage, it is proportional to the amount of ions in the pore fluid. The low level of current implies a high electrical resistance arising from the low ionic concentration of the sludge. The gradual increase in current is related to the pH change due to the migration of hydrogen ions generated by the electrolysis reaction at the anode. At a low pH, the solubility of metals

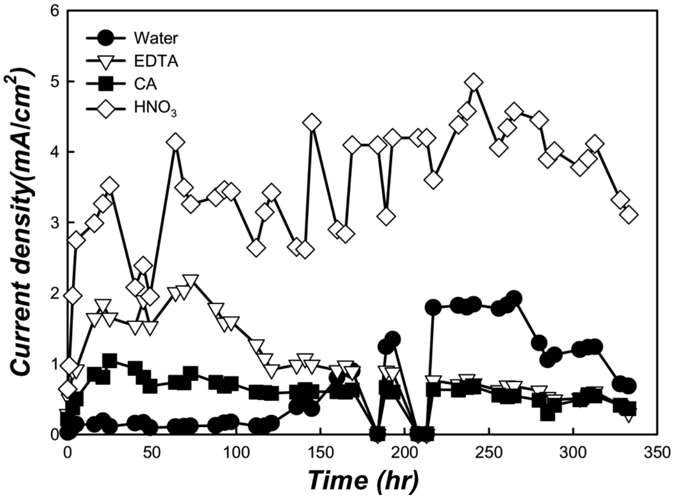


FIG. 2. Time course of current density under 1 V/cm of constant voltage gradient.

or inorganic materials increased; this led to a decrease in electrical resistance and an increase in current. In the case of citric acid, the current increased sharply initially, and then the value plateaued. Citric acid was supplied to the catholyte tank, where it dissociated into citrate and hydrogen ions. Meanwhile, hydroxide ions were produced by the electrolysis reaction at the cathode. The citrate was transported toward the anode, thus supplying additional ions to the system. However, citrate could form complexes with several cations. A pseudo-constant value of current density implies that most of the citrate supplied by the catholyte circulation formed citrate-cation complexes in the system. In the case of EDTA, the current gradually increased and then gradually decreased. The increase was due to the supply of ions such as ethylenediaminetetraacetate and sodium from the catholyte circulation. The decrease might be attributable to the formation of EDTA cations. In the case of nitric acid, the pattern of current density was quite different from those of other processing fluids. The current density increased gradually with operation time. Sufficient hydrogen and nitrate ions were supplied by catholyte circulation using the nitric acid in the system; the excess hydrogen acidified the sludge, and the acidification of the sludge increased the overall concentration of ions in the pore fluid. Nitrate ions, counter ions of hydrogen ions in nitric acid, were supplied and moved toward the anode, implying that nitrate ions entered the sludge pore fluid. Nitrate is relatively stable as compared to EDTA and CA; it forms complexes with other cationic compounds and exists in the ionic form in pores. These contributed to the increase in current density. However, the high current density entails high electrical energy consumption, in turn increasing the treatment cost of sludge.

pH Distribution

pH is a very important parameter influencing the behavior of heavy metals. To remove heavy metals from sludge, the pH should be acidic because most metals exist as cations below a pH of 4.0 (10). In addition, the sludge has a high content of organic matter, and the organic matter strongly influences the behavior of metals. The organic matter has various functional groups that bind with heavy metals, and the organic-metal complex is very stable over a broad pH range (14). Figure 3 shows the pH distribution of sludge after electrokinetic treatment. In the case of tap water, EDTA and citric acid increased slightly as compared to the initial pH value except in the anode region. It appears that carbonate materials or the alkalinity in the sludge consumed the hydrogen ions in the pore fluids. However, when using nitric acid as a processing fluid, the pH reduced to less than 4 and ranged between 2 and 4. Continuous circulation of the catholyte using nitric acid provided sufficient hydrogen ions, which consumed the hydroxide ions generated at the cathodes and reduced the overall pH of the sludge. The low final pH of nitric acid could be expected to result in the higher removal of heavy metals because the acidic condition promoted the desorption of heavy metals from the sludge.

Electro-Osmotic Flow

Generally, cationic heavy metals in normal soil can be removed by both electromigration and electroosmosis toward cathode. The total accumulated electroosmotic flow(EOF) during 336 hours was 83, 41, 87, and 47 ml for tap water, EDTA, citric acid, and nitric acid, respectively (Fig. 4). Accumulated EOF is highly related to the solution pH and zeta potential, as the pH is decreased, the zeta potential becomes less negative until the point of zero

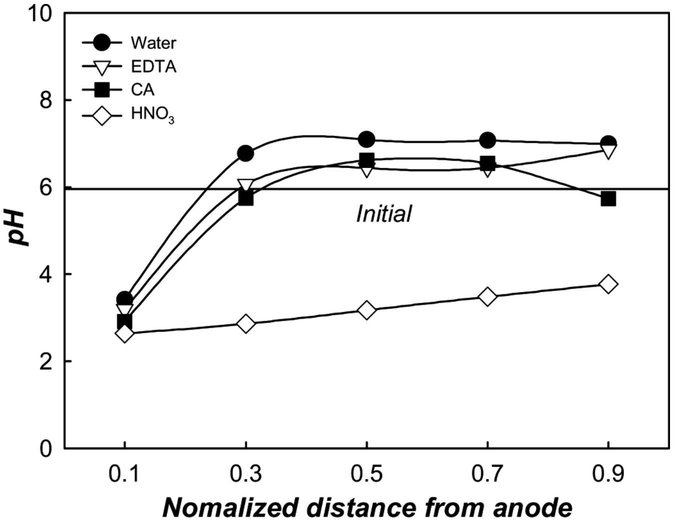


FIG. 3. pH distribution in sludge after electrokinetic treatment.

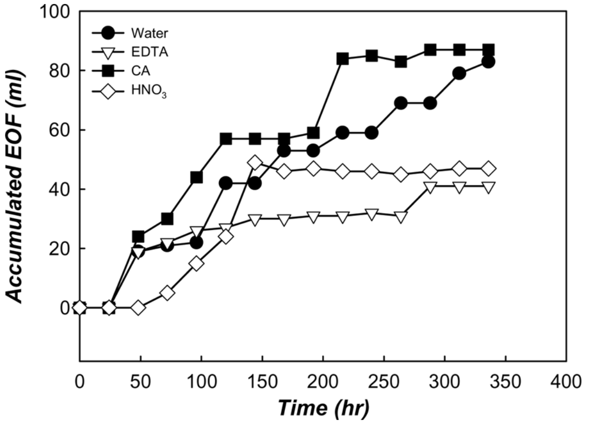
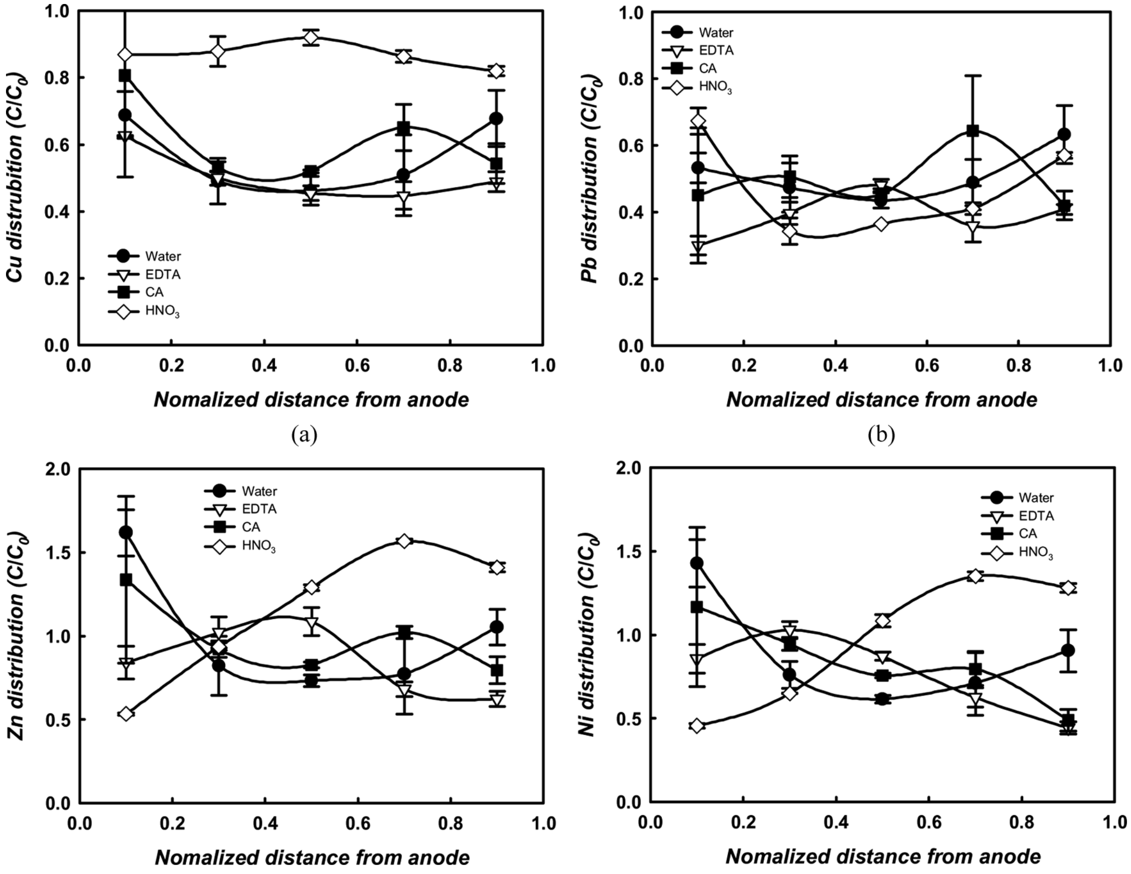


FIG. 4. Accumulated electro-osmotic flow during electrokinetic treatment.

charge is reached and then becomes positive (5). In case of nitric acid, the acidification of sludge decreased zeta potential, which causes to reduce the flow. In case of tap water, the overall pH was neutral or slightly alkaline, and the increase in pH played a role on the continuous flow (11). The overall charge of EDTA is −4 and still shows negative charge when it forms a complex with metals. The EDTA and EDTA-metal complexes were transported toward the anode under direct current. This is a reason for the less amount of EOF for EDTA even though the pH was neutral. In addition, the reduced polarization of pH in citric acid as compared to tap water enhanced the EOF.

Removal of Heavy Metals

Figure 5(a) shows the final distribution of copper in sludge after treatment. The removal of metal was calculated as follows; (Initial concentration of metal – Average residual concentration of metal after treatment)/Initial concentration of metals $\times$ 100%. The average removal of copper for tap water, EDTA, citric acid, and nitric acid was 43.5, 49.7, 38.9, and 13.0%, respectively. The EDTA-Cu complex is a negatively charged species, and the movement was toward the anode. This explains the higher average concentration of copper in the anode region. However, copper removal in nitric acid was not significant, possibly because the speciation of copper in sludge was not strongly influenced by pH.



(a) (b)

(c) (d)

FIG. 5. Distribution of heavy metals in sludge after electrokinetic treatment; (a) Cu, (b) Pb, (c) Zn, and (d) Ni.

TABLE 2
Summary of electrokinetics treatment of sludge

Processing fluids	Metals	Removal efficiency (%)	Removal amount (mg)	Energy expenditure (kWh/ton)	Effective removal (mg/Wh)
Tap water	Cu	43.5	132.5	107.8	1.99
	Pb	48.8	31.0		
	Zn	0.0	0.0		
	Ni	11.6	8.1		
EDTA	Cu	49.7	151.3	140.8	2.58
	Pb	61.2	38.8		
	Zn	14.9	83.7		
	Ni	23.5	16.4		
Citric acid	Cu	38.9	118.5	84.2	2.57
	Pb	50.6	32.1		
	Zn	1.9	10.7		
	Ni	17.0	11.9		
Nitric acid	Cu	13.0	39.6	471.3	0.20
	Pb	52.8	33.5		
	Zn	0.0	0.0		
	Ni	3.6	2.5		

Figure 5(b) shows the removal of Pb after electrokinetic treatment. The order of removal of Pb was as follows: EDTA (61.2%) > nitric acid (52.8%) > citric acid (50.6%) > tap water (48.8%). EDTA exhibited the highest average removal and the other processing fluids exhibited similar Pb removal results. The middle part of the sludge had the highest residual Pb because the transport direction of the EDTA complex by electromigration was opposite to the direction of EOF. The Pb distribution in the sludge did not exhibit any special pattern, and the Pb was removed partially in the entire region.

The distribution of Zn is shown in Fig. 5(c). The movement of Zn toward the cathode was clearly observed when nitric acid was used as a processing fluid. The low pH contributed to the desorption of Zn, and the desorbed Zn was transported by electromigration. However, the Zn was not removed, but only transported toward the cathode by nitric acid circulation in the catholyte tank. For EDTA, the highest average residual concentration of Zn remained in the middle region as Pb because of the opposing directions of the electromigration and the electroosmotic flow. Even though EDTA exhibited the highest average removal as compared to other fluids, the removal efficiency was just 14.9%. The distribution of Ni was very similar to that of Zn (Fig. 5(d)); however, the removal efficiency was slightly higher than that of Zn in all processing fluids. On the other hand, the average water content of sludge after the experiments ranged between 79.8–81.7 wt%, and it was similar to the initial value (80.3 wt%).

On the basis of the voltage (V) and current (I) values, the energy expenditure (E) was calculated using the following equation: $E = \int VIdt$. The energy expenditure is summarized in Table 2. The energy expenditure was directly proportional to the time course of the current. To consider the removal efficiency and energy simultaneously, a new parameter, effective removal, was introduced (8,9). Effective removal (unit: mg/Wh) was calculated by dividing the removed amount of heavy metals (Cu + Pb + Zn + Ni) by the energy expenditure. This indicator reflects the energy consumed with respect to the unit removal of target metals by electrokinetic treatment. The order of this indicator was EDTA (2.58) > citric acid (2.57) > tap water (1.99) > nitric acid (0.20). As a result, nitric acid was not considered to be a suitable processing fluid for removing metals from sludge, whereas EDTA was considered to be the most suitable processing fluid.

CONCLUSIONS

To promote the recycling of sludge from sewage treatment plants, an electrokinetic technique for the removal of heavy metals from sludge was investigated using four different processing fluids: tap water as an anolyte and EDTA, citric acid, and nitric acid as a catholyte. The current density was closely related to the solution pH change, and the solution pH change influenced the electroosmotic flow. The residual distribution of metals was significantly affected by the direction of electromigration and electroosmotic flow. As compared to other metals, Pb and Cu was effectively removed by the electrokinetic process. Considering the removal efficiency and the energy consumption simultaneously, EDTA was found to be the most suitable processing fluid, whereas nitric acid was ineffective. However, the overall removal efficiency was too low, and techniques to further improve the efficiency should be investigated, including longer operations and a pulsed power supply.

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