Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Evaluation on the Feasibility of Microbially Enhanced Electrokinetic Removal of Multiple Heavy Metals from Tailing Soil

Keun-Young Lee[a]; Ki-Rak Kim[a]; Byung-Tae Lee[b]; Ju-Yong Kim[a]; Kyoung-Woong Kim[a]; Soon-Oh Kim[c]
[a] Department of Environmental Science and Engineering, Gwangju Institute of Science and Technology (GIST), Gwangju, Republic of Korea [b] Department of Chemistry & Geochemistry, Colorado School of Mines, Golden, CO, USA [c] Department of Earth and Environmental Sciences and Research Institute of Natural Science, Gyeongsang National University, Jinju, Republic of Korea

To cite this Article Lee, Keun-Young , Kim, Ki-Rak , Lee, Byung-Tae , Kim, Ju-Yong , Kim, Kyoung-Woong and Kim, Soon-Oh(2009) 'Evaluation on the Feasibility of Microbially Enhanced Electrokinetic Removal of Multiple Heavy Metals from Tailing Soil', Separation Science and Technology, 44: 10, 2322 — 2340
To link to this Article: DOI: 10.1080/01496390902983653
URL: http://dx.doi.org/10.1080/01496390902983653

Separation Science and Technology, 44: 2322–2340, 2009
Copyright © Taylor & Francis Group, LLC
ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390902983653

Taylor & Francis
Taylor & Francis Group

Evaluation on the Feasibility of Microbially Enhanced Electrokinetic Removal of Multiple Heavy Metals from Tailing Soil

Keun-Young Lee,[1] Ki-Rak Kim,[1] Byung-Tae Lee,[2] Ju-Yong Kim,[1] Kyoung-Woong Kim,[1] and Soon-Oh Kim[3]
[1]Department of Environmental Science and Engineering, Gwangju Institute of Science and Technology (GIST), Gwangju, Republic of Korea
[2]Department of Chemistry & Geochemistry, Colorado School of Mines, Golden, CO, USA
[3]Department of Earth and Environmental Sciences and Research Institute of Natural Science, Gyeongsang National University, Jinju, Republic of Korea

Abstract: Lab-scale experiments were conducted to evaluate the efficacy of the enhanced electrokinetics combined with anaerobic and aerobic bioleaching processes for remediation of tailing soil. The tailing soil contained multiple heavy metals, such as As, Cd, Co, Cu, Cr, Fe, Mn, Ni, Pb, and Zn. To begin with, the applicability of both anaerobic and aerobic bioleaching was investigated as a pretreatment step to transform them into more mobile forms. In the anaerobic bioleaching, the supply of carbon source into the soil stimulated anaerobic metal reducing bacteria with dissolution of heavy metals, As, Fe, Mn, and Zn. In the aerobic bioleaching, on the other hand, indigenous sulfur oxidizing bacteria oxidized elemental sulfur with acidifying soil and mobilizing heavy metals, such as As, Fe, Mn, Pb, and Zn. To compare the removal efficiencies between individual and combined processes, individual electrokinetics was conducted as a control with only electrolyte conditioning and the tailing soils pretreated by bioleaching were sequentially applied to the electrokinetics to simulate the combined process.

Received 30 August 2008; accepted 12 February 2009.

Address correspondence to Soon-Oh Kim, Department of Earth and Environmental Sciences and Research Institute of Natural Science, Gyeongsang National University, Jinju 660-701, Republic of Korea. Tel.: +82-55-751-6275; Fax: +82-55-757-2015. E-mail: sokim@gnu.ac.kr

Generally speaking, the microbially enhanced electrokinetics showed higher removal efficiencies of almost all the heavy metals tested than the individual electrokinetics, because bioleaching process converted the heavy metals to be labile. One more synergistic effect of the combined processes was that bioleaching enhanced the rate of acidification of tailing soil, which offers a more suitable condition for electrokinetics. The highest removal efficiency of Co, Mn, Ni, and Zn was accomplished in the electrokinetic process combined with anaerobic bioleaching (72.5%, 66.4%, 57.9%, and 76.7%, respectively), whereas that of As, Cd, and Pb was rendered in the process combined with aerobic bioleaching (27.2%, 46.6%, and 25.0%, respectively). The results indicate that the performance of the combination between bioleaching and electrokinetics is significantly dependent on the species of heavy metals to be removed. In addition, this study verifies that the electroosmotical injection of carbon sources is feasible to activate the indigenous microorganisms in the anaerobic bioleaching coupled with the electrokinetics.

Keywords: Bioleaching, combined process, electrokinetics, heavy metal, tailing soil

INTRODUCTION

Soils can be contaminated with multiple heavy metals derived from various sources including abandoned mining wastes, improper control of industrial wastes, leakage from landfill sites, accidental spills and military activities (1). Mine tailing soil, which is largely originated from mining activities, especially contains high concentration of heavy metals such as As, Cd, Cu, Pb, Zn, Cr etc. and it has potential adverse effects on human beings as well as the ecosystem. According to changes in their physicochemical states and the dominant chemical conditions, these heavy metal contaminants migrate and finally threaten human health by affecting surface water, groundwater, and soil. In addition, soil contamination is increasing in sensitive areas, such as paddy fields, residential districts, and reservoirs of drinking water near mining sites (2,3). Recently, technologies for decontaminating these sites are developing variously, and electrokinetic remediation technology is one of the promising methods for simultaneously recovering multiple metal contaminants (4,5). However, from our previous researches (6,7) and others (8,9), the efficiency of the electrokinetics targeting the tailing soils was relatively low, even though the enhanced schemes were applied. It was significantly dependent on the initial concentrations and the partitioning of metals in the tailing soil, and since much amount of heavy metals exists in the immobile and strongly bound forms, in which case the metal removal efficiency is remarkably low. Therefore the electrokinetics overcoming such problems is required. It has been pointed out that the main thrust of future research is to combine electrokinetic remediation with processes like bioremediation (4,10).

While the approach of bioremediation for organic contaminants was actively studied, there have been few applications of bioremediation for treatment of heavy metal contaminants. It is likely to be caused by the non-degradable property of heavy metals. Bioremediation for separating and transporting metal contaminants from soil and/or water can be summarized as follows; bioleaching, biosorption, biotransformation, and phytoremediation. Anaerobic bioleaching, which has been represented by microbial metal reduction, is a ubiquitous phenomenon occurring in subsurface environments, even in mining-impacted areas (11,12). In our recent research, the dissolution of As, with Fe and Mn, under anaerobic condition was significantly enhanced by activating the indigenous bacteria in several tailing soils collected from different sites (13,14). On the other hand, bioleaching process originated by Fe and/or S oxidizing bacteria in aerobic condition has been put to practical use of the industrial scale (metal extraction from low-grade ores) and environmental scope (removal of metal contaminants from soil and sediment) (12). Microbially-based technologies for removal of heavy metals from soil have become a more fascinating way due to their ecofriendly and cost-effective advantages.

Currently, most of the combination between electrokinetics and bioremediation, so-called bioelectrokinetics, has been used to introduce microorganisms, water, and nutrients into the low-permeable soil by applying electric field in order to enhance the biodegradation of organic pollutants (15,16). The study on the application of vertical electric field to migrate heavy metals towards the active area of phytoremediation is an example of combination of them (17). Microbially enhanced electrokinetic remediation for removal of heavy metal was first reported by Maini et al. (18). In this study, soils artificially contaminated by Cu were treated by aerobic bioleaching and electrokinetics sequentially applied. The pretreatment of soil by amendment with sulfur finally increased the cost-effectiveness of the electrokinetics through reduction of power consumption. Recently, it has been expected by us that the combination of anaerobic bioleaching and electrokinetics might reveal the synergistic effects for removal of As in tailing soil (13,19). These studies prove the enhancement of the electrokinetic process for removal of heavy metal through amendment of the soil using inexpensive bioremediation.

In order to evaluate the feasibility of the electrokinetics combined with bioleaching for removal of multiple heavy metal contaminants from tailing soil, four sets of experiments were carried out. For the anaerobic bioleaching as a pretreatment step, the indigenous metal reducing bacteria were activated by injection of carbon source to the soil. On the other hand, elemental sulfur was put into the soil to stimulate the indigenous sulfur oxidizing bacteria at the aerobic bioleaching. The combined and individual removal processes were conducted in an equivalent condition to compare the major mechanisms and the removal efficiencies.

EXPERIMENTAL SECTION

Soil

The tailing soil used was taken from the Myungbong abandoned gold mine area located in the south-western region of Korean Peninsula. This site has been well known to be seriously contaminated by As and several other heavy metals. The tailing soil samples were carefully collected at a depth of 0–30 cm from the surface of the tailing-dumping area. To maintain the original environment for the survival of indigenous bacteria, the soil sample was stored without drying. The basic physicochemical properties were investigated; such as soil texture (based on particle size distribution), loss on ignition (at 400°C for 24 hr), and soil pH (5 g soil in 50 mL water). To investigate the initial concentrations of 10 heavy metals (As, Cd, Co, Cu, Cr, Fe, Mn, Ni, Pb, and Zn) in tailing soil sample, it was digested with aqua regia, which consisted of concentrated HNO_3 and HCl (1:3), and heated at 70°C on a shaker for 1 hour (20). The heavy metal concentrations in all samples were determined using ICP-OES (ICP-OES, Perkin-Elmer, USA).

Anaerobic Bioleaching Experiment

A diagram showing individual and combined processes is outlined in Fig. 1, and four sets of experimental conditions are summarized in Table 1. Tailing soil sample of 470 ± 5 g was mixed with 1 L of leaching solution, which included 0.1 M of glucose (D-(+)-Glucose, ACS reagent, Sigma, USA) as the carbon source. This mixture was put into a polypropylene bioleaching reactor which has a shape of rectangular parallelepiped and 1.2 L of volume. To maintain the anaerobic experimental condition, all procedures were performed in an artificially made anaerobic-chamber. The anaerobic bioleaching experiment continued at 25°C for 10 days. An aliquot of the leaching solution was collected during the experiment, and the pH, Eh, and heavy metal concentrations of the samples were measured.

Aerobic Bioleaching Experiment

The aerobic bioleaching with elemental sulfur was carried out in the same reactor described previously. Tailing soil sample of 470 ± 5 g was mixed

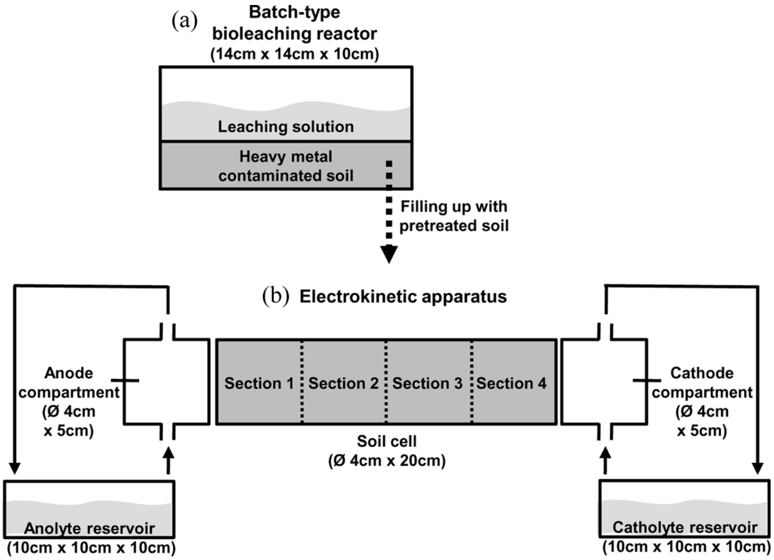

Figure 1. Experimental scheme of the individual and combined processes.

with 25 g of elemental sulfur (5% w/w; Sulfur powder, 99.98%, Aldrich, USA), and 0.5 L of DI water was added. The mixture was incubated at 25°C with shaking (130 rpm) all through the experiment for aeration. Dissolution of heavy metals was also monitored periodically by analyzing the heavy metal concentrations of leaching solution with monitoring of pH and Eh.

Electrokinetic Experiments

One single (experiment 1) and three combined (experiments 2, 3, and 4) electrokinetic processes were tested with an equivalent duration (10 days). Experiment 1 was conducted by only electrokinetics without the pretreatment of bioleaching. The tailing soil pretreated by batch-type anaerobic and aerobic bioleaching was moved into the electrokinetic soil cell in experiment 2 and 3, respectively (see Table 1 and Fig. 1). Apart from these, all the other conditions of the three experiments on electrokinetics (experiments 1, 2, and 3) were identical. Cylindrical type of electrokinetic soil cell (20 cm in length, 4 cm in diameter) was used. Cathodes were of stainless steel, and titanium-coated stainless steel was used for anodes. In addition, mesh type electrodes bordered by a filter paper to allow ions and water to pass were located between soil cell and electrode

Table 1. Summary of experimental program for individual and combined processes

	Bioleaching		Electrokinetics				
				Electrolyte			
Experiment	Type	Duration (days)	Voltage (V)	Anode	Cathode	Duration (days)	Comments
1			20	Tap water	0.5 M H_2SO_4	10	Individual process
2[a]	Anaerobic	10	20	Tap water	0.5 M H_2SO_4	10	2 step-combination
3[b]	Aerobic	10	20	Tap water	0.5 M H_2SO_4	10	2 step-combination
4			20	0.1 M glucose	0.5 M H_2SO_4	10	1 step-combination

[a] Tailing soils pretreated by glucose in the anaerobic bioleaching were subsequently transferred to the electrokinetic cell.

[b] Tailing soils pretreated by elemental S in the aerobic bioleaching were subsequently transferred to the electrokinetic cell.

compartments. Both electrode compartments were connected to each electrolyte reservoir of a sufficient volume, and the electrolyte solutions were circulated regularly. In experiments 1, 2, and 3, tap water was used as anolytes. Catholyte solutions were 0.5 M H_2SO_4 to neutralize the hydroxide ions generated by cathodic water electrolysis and to prevent alkaline conditions from developing within the soil bed. It is a conventional electrolyte conditioning to decrease soil pH and increase heavy metal mobility. On the other hand, tap water in anode compartment was changed by 0.1 M glucose solution in experiment 4. This modification was designed to investigate the applicability of simultaneous (1-step) implementation of the electrokinetics and bioleaching through the injection of glucose by electroosmotic water flow. Because glucose ($C_6H_{12}O_6$) is fully dissolved into solution and it shows zero charge in the solution, this compound cannot be transported by electromigration but by electroosmosis. When the sufficient amount of carbon source was injected to the electrokinetic soil cell, anaerobic bioleaching and electrokinetics may occur simultaneously.

The variations of soil pH were monitored by daily measurement of pH during electrokinetic experiment. A voltage gradient of 1 V/cm was applied at a constant voltage, 20 V, with measuring the overall current density of the soil cell. Electroosmotic flow was observed by transported water volume. After electrokinetic process, soil samples were obtained directly from the four sections of soil bed to determine the residual concentrations of heavy metals and final soil pHs. To investigate the residual concentrations of 10 heavy metals, collected soil samples were digested and analyzed by same methods as mentioned previously.

RESULTS AND DISCUSSION

Characteristics of Tailing Soil Used

The tailing soil was predominantly sandy loam (soil texture according to USDA) with loss on ignition of 0.55%, and pH 7.8. In our preliminary study, the minerals containing S and Fe in the tailing soil were determined as primary sulfides, e.g., pyrite (FeS_2), and the Fe oxides as secondary minerals formed as a result of weathering and alteration of primary minerals (14). Such a result suggests that this tailing soil contains the minerals which can be microbially affected in anaerobic and aerobic bioleaching system. Heavy metals may coexist with these minerals as adsorbed, co-precipitated, or mineralized forms in the tailing soil. Table 2 represents the initial concentrations of heavy metals in tailing soil. The chemical analysis revealed that the tailing soil was contaminated

Table 2. Initial concentrations of heavy metals in tailing soil (unit: mg/kg)

	As	Cd	Co	Cu	Cr	Fe	Mn	Ni	Pb	Zn
Natural conc.[a]	7.2 (0.1∼97)[b]	0.35 (0.01∼2)	9.1 (3∼70)	25 (1∼700)	54 (1∼2000)	26000 (100∼100000)	550 (2∼7000)	19 (5∼700)	19 (10∼700)	60 (5∼2900)
Tailing soil	4075.7	22.5	3.5	39.0	5.5	17846	158.6	9.9	658.1	389.2

[a] Natural concentration of each species in soils suggested in U.S. Geological Survey Professional Paper 1270 (1984) (21).

[b] Median (range).

with several heavy metals such as As, Cd, Pb, and Zn in comparison with natural concentrations presented by USGS (21).

Anaerobic and Aerobic Bioleaching Experiments

In anaerobic bioleaching as a pretreatment step, the indigenous metal reducing bacteria were activated by mixing glucose to the soil under anaerobic condition. A significant amount of As, Fe, Mn, and Zn was continuously leached from soil to solution with decreases in pH and Eh (Figs. 2(a) and (b)). In the case of anaerobic bioleaching process, generally, indigenous Fe and Mn reducing bacteria utilize carbon source artificially injected as an electron donor and Fe and Mn oxides as electron acceptors. It is speculated that oxidized form of heavy metals, Fe(III) and Mn(VI), existing in the oxides were reduced to soluble Fe(II) and Mn(II) by this mechanism, and then the coexisting heavy metals appeared to be dissolved into the aqueous system. The abundance of reduced form of heavy metals in solution was supported by the decrease in Eh. The biological production of carbon dioxide or organic acids could be sufficient to lower the pH and indirectly accelerate the dissolution of heavy metals (22,23). In particular, the previous research has reported that organic acid can be produced by bacteria in nutrient-limited and carbon substrate-sufficient condition (24), which is very similar with

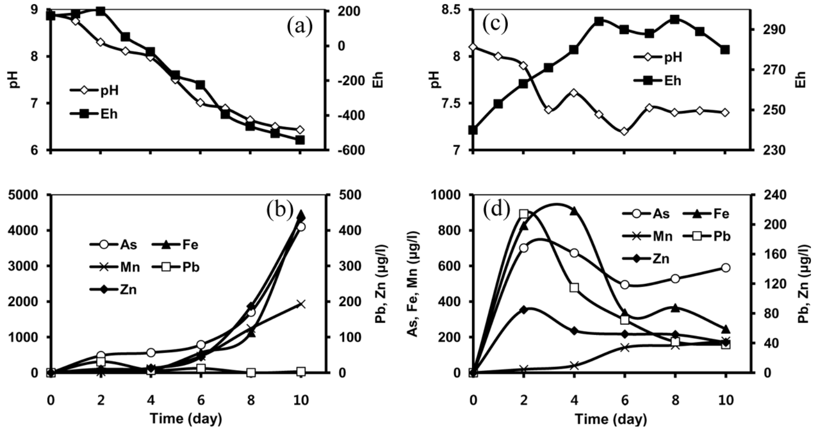

Figure 2. Results of bioleaching experiments: (a) Variation in pH and Eh, (b) heavy metal concentrations in leaching solution of anaerobic bioleaching, (c) variation in pH and Eh, and (d) heavy metal concentrations in leaching solution of aerobic bioleaching.

our experiment. Organic acids can be also produced by fermentative bacteria as the final metabolic byproducts including acetic acid, lactic acid, butyric acid etc.

On the other hand, elemental sulfur was put into the soil to activate the indigenous sulfur oxidizing bacteria in the aerobic condition. Sulfur oxidizing bacteria involved in aerobic bioleaching are able to oxidize metal sulfides to sulfates, thereby transforming them from insoluble to soluble form. Sulfide minerals initially existing in soil and/or elemental sulfur artificially injected can be electron donors in this process, and finally the electrons are transported to oxygen. The final product of this process is H_2SO_4 which also increase the metal mobility by decreasing soil pH. The pH decrease indicates that such a mechanism was occurred in this experiment (Fig. 2(c)). Heavy metals (As, Fe, Mn, Pb, and Zn) significantly dissolved into the leaching solution might be oxidized forms, which derived the increase of solution Eh (Figs. 2(c) and (d)). Much amount of heavy metals was dissolved within 2 days, and then the concentrations in the leaching solution decreased and the Eh of the solution did not increase any more after 5 days, which were caused by the stop of S oxidation and re-adsorption and/or precipitation of mobilized heavy metals. The reasons not to continue for this reaction, even though the sufficient amount of elemental sulfur was supplied, can be suggested by:

1. Insufficient oxygen supply to the soil and solution system
2. Inhibition of bacterial metabolism by mobilized toxic metals (e.g., As, Pb and Zn in this experiment) (18,25).

Dissolved oxygen level in the solution was not measured, but the stop of Eh increase indicates indirectly the possibility of depletion of oxygen. Hence, the S oxidation might be improved in aerobic experiment if sufficient oxygen is supplied to the system.

Although the tailing soil contains various heavy metals, only the heavy metals showing high initial concentration (more than 100 mg/kg), such as As, Fe, Mn, Pb, and Zn, were detected in bioleaching experiments. In the cases of As and Fe, the amount dissolved in the anaerobic bioleaching was observed to be 5 times as much as that in the aerobic bioleaching. In anaerobic bioleaching, in particular, a significant dissolution of Zn occurred, while that of Pb was negligible. On the other hand, the dissolution degree of Pb was almost 3 times higher than that of Zn in the aerobic bioleaching. These differences can be contributed to the physicochemical and geochemical features of heavy metal species in the tailing soil, which supports that the most suitable microbial mechanism to mobilize each species of heavy metal contaminants should be taken into great account before application of these technologies.

Individual and Combined Electrokinetic Experiments

One conventional electrokinetics (experiment 1), two 2 step-combination (experiments 2 and 3) and one 1 step-combination processes were tested, as summarized in Table 1. The current density measured was gradually increased in all the experiments, and it reached to $0.8 \sim 1.3\,\mathrm{mA/cm^2}$ after 10 days. Transported water volume in the cathode compartment increased during these experiments, which means the normal electroosmosis was dominant in all cases (Fig. 3). The rate of electroosmotic water flow was estimated $7 \sim 10\,\mathrm{ml/day}$. This result guarantees that the glucose supplied to the anode compartment was electroosmotically injected into the soil bed in the experiment 4.

Figure 4 represents the variation of pH at each section during electrokinetic experiments. All electrokinetic processes generated H^+ at the anode and OH^- at the cathode. While H^+ entered the soil bed and migrated toward the cathode by electromigration, OH^- was neutralized at the cathode with H_2SO_4 to render a slight decrease of the soil pH in this compartment. The individual electrokinetics made the soil rapidly acidified to around pH 2 near the anode and pH 6 near the cathode, and this decrease in soil pH was more rapidly advanced in the electrokinetic process combined with bioleaching. The acidifying rates were observed in the following order: $\text{exp.}\,3 > \text{exp.}\,2 > \text{exp.}\,4 \approx \text{exp.}\,1$ Soil pH profiles after bioleaching and electrokinetic experiments are separately presented in Fig. 5. These results also support that both anaerobic and aerobic bioleaching processes enhanced the acidification of soil, as shown in the experiments 2 and 3. Even though the decrease in soil pH

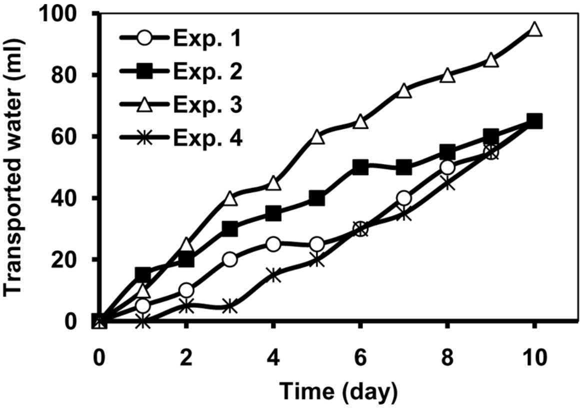

Figure 3. Transported water volume measured in the cathode compartment during electrokinetic experiments.

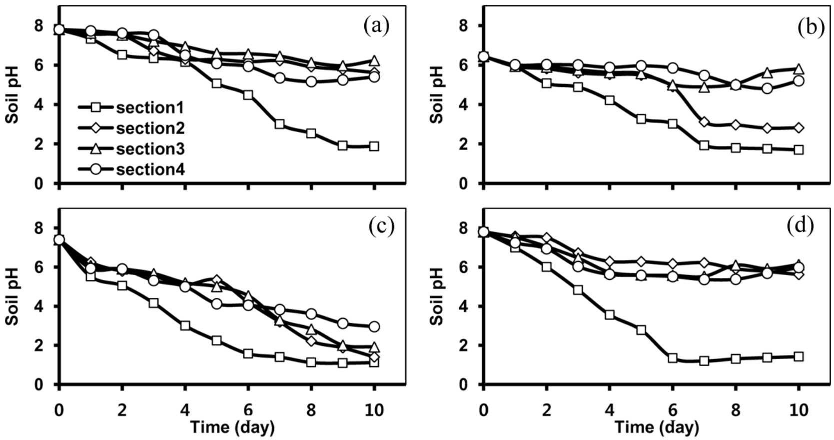

Figure 4. Variation of pH at each section during electrokinetic experiments: (a) experiment 1, (b) experiment 2, (c) experiment 3, and (d) experiment 4.

was observed larger after the anaerobic bioleaching than the aerobic bioleaching (Figs. 5(b) and (c)), the final soil pH was much more decreased in the electrokinetic process combined with the aerobic

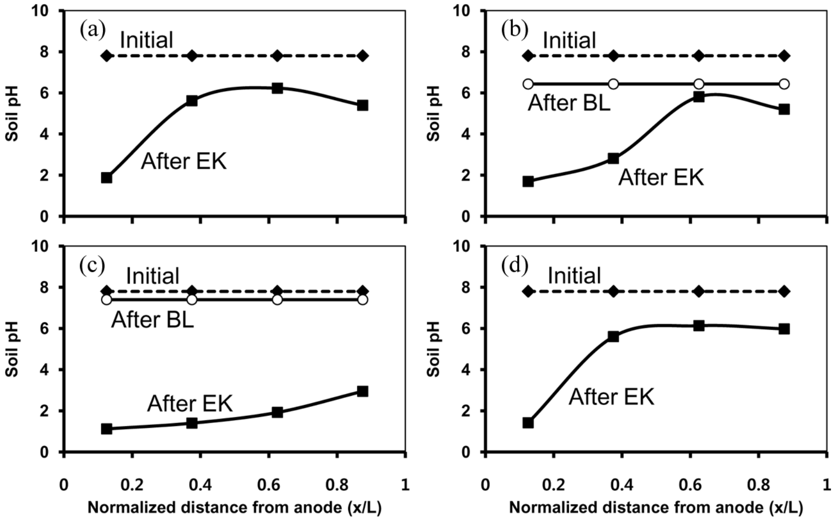

Figure 5. Soil pH profiles after bioleaching (BL) and electrokinetic (EK) experiments: (a) experiment 1, (b) experiment 2, (c) experiment 3, and (d) experiment 4 (x = distance from anode, L = length of soil bed).

bioleaching rather than with the anaerobic bioleaching. As already mentioned by Maini et al. (18), this result suggests that the residual elemental sulfur remaining due to incomplete oxidation in the aerobic bioleaching step was oxidized microbially in the electrokinetic step subsequently applied. In this point of view, the electrokinetic process overcomes the limitations of the aerobic bioleaching owing to:

1. Plenty of oxygen can be generated at the anode and oxygenated water transports into the soil
2. Inhibitory toxic metal species can be removed by the electric current supplied, which resulting in a sufficient stimulation of sulfur oxidizers.

Acidifying rate in experiment 4 was somewhat faster than that in experiment 1, which indicates that the soil pH was decreased by the anaerobic bioleaching as well as electrokinetics, simultaneously (Figs. 4(d) and 5(d)).

Figures 6, 7, and 8 show the distribution of residual heavy metal concentrations within the soil bed after experiments. Heavy metals were classified into three groups according to the removal trend. The first group of heavy metals (Co, Mn, Ni, and Zn) shown in Fig. 6 revealed a relatively higher removal only near the anode, and they were accumulated at the middle and/or near the cathode instead of moving into the catholyte compartment. The electrokinetics combined with the anaerobic bioleaching (experiment 2) seemed to be successful, particularly at sections 1 and 2. The electrokinetics with glucose injection (experiment 4) showed relatively low residual concentrations compared to experiment 1 and 3, which supports that the enhancement in consideration attained. Significantly enhanced mobilization of Mn and Zn in the anaerobic bioleaching was reflected to the final removal efficiency of the combined process (See Fig. 2(b)). Although the dissolution of Co and Ni was not detected in the bioleaching step due to their low initial concentrations, they showed similar removal trend with Mn and Zn, which supports that they were also affected mainly by the combination with the anaerobic bioleaching.

Another group (As, Cd, and Pb) showed no significant difference in residual concentrations between sections, and the apparent accumulation was not observed, contrary to the first group (Fig. 7). In addition, the process integrating the aerobic bioleaching and electrokinetics resulted in the most efficient removal of these heavy metals. These results can be attributed to the increase in the mobilities of the heavy metal species categorized into the second group in the aerobic bioleaching (See Pb in Fig. 2(d)). Also, Cd is likely to be mainly affected by the aerobic bioleaching, while it was not detected in the bioleaching step due to its low initial concentration. Although the mobility of As in the anaerobic bioleaching seemed to be enhanced almost 5 times higher than that in the aerobic bioleaching

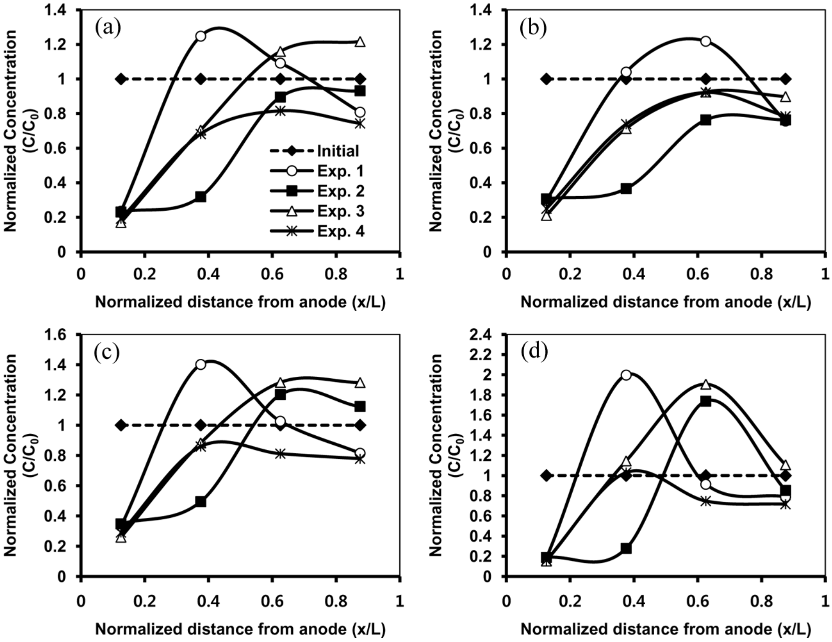

Figure 6. Distribution of residual concentrations of heavy metals classified into group 1 within the soil bed after experiments: (a) Co, (b) Mn, (c) Ni, and (d) Zn (C_0 = initial concentration, C = final concentration, x = distance from anode, L = length of soil bed).

(See Figs. 2(b) and (d)), experiment 3 could be considered as the most successful combination due to a significant removal of As. Such an unexpected result was caused by the chemical properties which discriminate As from the other heavy metals targeted. In a high oxidative condition simulated by the aerobic bioleaching, the predominant form of As species dissolved from soil is likely to be As(V) (26), while it has been confirmed in our previous research that the dominant species dissolved in the anaerobic bioleaching is up to 90% of As(III) from the identical tailing soil (14). In the solution of $pH < 9$, As(V) is negatively charged such as $HAsO_4^{2-}$ or $H_2AsO_4^-$, and As(III) is neutral such as $H_3AsO_3^0$, in general. Therefore, As(V) in experiment 3 is removed towards the anode by electromigration, which has at least one order of magnitude higher rate than electroosmotic flow in the opposite direction (towards cathode), whereas As(III) in experiment 2 is transported only by electroosmosis. It has been proven that the alkaline condition is proper for the removal of As in the electrokinetic process (19), and therefore the acidification method for the removal of multiple heavy metals does not seem to be an efficient technology for As.

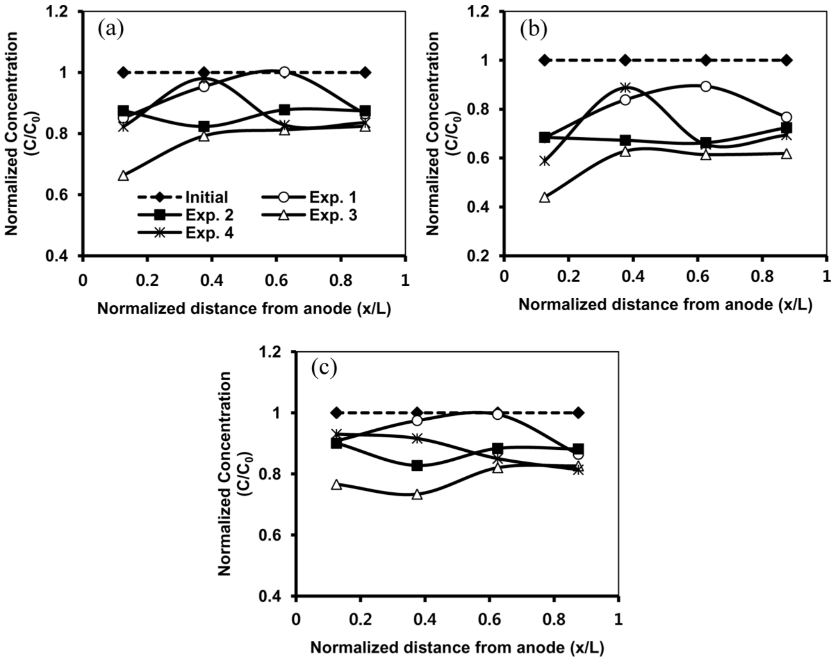

Figure 7. Distribution of residual concentrations of heavy metals classified into group 2 within the soil bed after experiments: (a) As, (b) Cd, and (c) Pb (C_0 = initial concentration, C = final concentration, x = distance from anode, L = length of soil bed).

Finally, Cu, Cr, and Fe show behaviors different to the heavy metals assigned to the other two groups, and there was no significant improvement between the experiments (Fig. 8). In the combined processes, a relatively larger amount of Cu and Cr still remained in the soil bed after treatment, which indicates that their mobilization was not sufficiently improved by the bioleaching processes. The residual Fe concentration in experiment 2 showed even a slight removal over the soil bed, which reflects the influential dissolution of Fe in the anaerobic bioleaching.

Evaluation

Table 3 represents the average removal efficiencies of whole soil cell and near anode area (section 1 and 2) after each treatment. Because the tailing soil targeted, generally, contained the heavy metals existing as relatively strongly bound chemical forms, compared to the soil contaminated with those of weakly bound ones, the individual electrokinetic process resulted

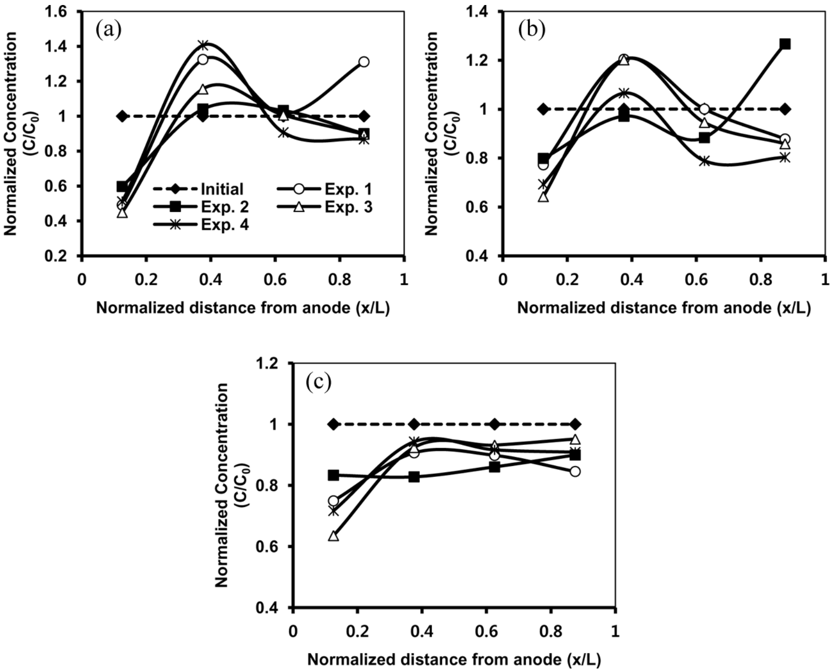

Figure 8. Distribution of residual concentrations of heavy metals classified into group 3 within the soil bed after experiments: (a) Cu, (b) Cr, and (c) Fe (C_0 = initial concentration, C = final concentration, x = distance from anode, L = length of soil bed).

in a poor removal (6). However, the overall removal efficiencies of almost all the heavy metals considered appeared to be relatively higher in the microbially enhanced electrokinetics than in the individual electrokinetics using only electrolyte conditioning. The removal efficiencies calculated for section 1 and 2 make clear in grouping the heavy metals. The highest removal efficiency of Co, Mn, Ni, and Zn was observed in experiment 2 (72.5%, 66.4%, 57.9%, and 76.7%, respectively), whereas that of As, Cd, and Pb was measured in experiment 3 (27.2%, 46.6%, and 25.0%, respectively). Due to the relatively small duration of experiments, the heavy metals mobilized by the pretreatment of bioleaching did not seem to be completely transported into the electrolyte compartment. However, this research proves that the efficacy of the combination between electrokinetics and bioleaching absolutely depends on the species of heavy metals. Additionally, the result supports that the simultaneous (1-step) application of the anaerobic bioleaching and electrokinetics is possible through the injection of carbon sources, such as glucose, using electroosmosis.

Table 3. Average removal efficiencies of heavy metals after processes

	Removal efficiency (%)[a]									
	As	Cd	Co	Cu	Cr	Fe	Mn	Ni	Pb	Zn
Exp. 1	8.2 (9.7)[b]	20.5 (23.9)	15.5 (25.9)	–[c] (9.3)	3.6 (1.2)	15.0 (17.2)	17.2 (33.1)	10.6 (13.3)	6.5 (5.9)	2.9 (–)
Exp. 2	13.8 (15.1)	31.4 (32.2)	40.6 (72.5)	10.8 (18.1)	2.0 (11.5)	14.5 (16.9)	45.0 (66.4)	20.8 (57.9)	12.7 (13.6)	23.6 (76.7)
Exp. 3	22.7 (27.2)	42.5 (46.6)	18.7 (56.3)	12.3 (19.8)	8.8 (7.8)	14.0 (22.1)	31.3 (53.8)	7.4 (42.9)	21.3 (25.0)	– (35.1)
Exp. 4	13.3 (9.9)	29.4 (26.2)	39.6 (56.3)	7.8 (4.2)	16.2 (12.1)	12.9 (17.0)	32.7 (50.6)	31.5 (42.6)	12.3 (7.7)	33.6 (40.5)

[a] The ratio of the initial concentration to the removed concentration after treatment.

[b] Values in parentheses designate the removal efficiencies at section 1 & 2.

[c] Less than zero percent; no significant difference between before and after experiment.

Further research will be required to confirm and prevent the precipitation of heavy metals derived by the microbial effects and to monitor and quantify the biomass during the biostimulation processes. Besides, the more efforts to find the optimal conditions should be emphasized to achieve the successful implementation of the combined process to remove multiple heavy metals from soils.

ACKNOWLEDGMENT

This work was supported by Korea Ministry of Environment as "The GAIA Project". We are deeply grateful to Dr. Rainer U. Meckenstock and Dr. Julian Bosch supporting this work in Helmholtz Center Munich (Germany).

REFERENCES

1. Anderson, R.J.; Davies, B.E. (1986) Dental caries prevalence and trace elements in soil with special reference to lead. *J. Geol. Soc. Lond.*, *137*: 547–559.
2. Kim, K.W.; Lee, H.K.; Yoo, B.C. (1998) The environmental impact of gold mines in the Yugu-Kwangcheon Au-Ag metallogenic province, Republic of Korea. *Environ. Technol.*, *19* (3): 291–298.
3. Kim, J.Y.; Davis, A.P.; Kim, K.W. (2003) Stabilization of available arsenic in highly contaminated mine tailings using iron. *Environ. Sci. Technol.*, *37*: 189–195.
4. Lageman, R.; Clarke, R.L.; Pool, W. (2005) Electro-reclamation, a versatile soil remediation solution. *Eng. Geol.*, *77*: 191–201.
5. Virkutyte, J.; Sillanpaa, M.; Latostenmaa, P. (2002) Electrokinetic soil remediation – critical overview. *Sci. Total Environ.*, *289*: 97–121.
6. Kim, S.O.; Kim, K.W.; Stűben, D. (2002) Evaluation of electrokinetic removal of heavy metals from tailing soils. *J. Environ. Eng.*, *128* (8): 705–715.
7. Kim, S.O.; Kim, K.W. (2001) Monitoring of electrokinetic removal of heavy metals in tailing-soils using sequential extraction analysis. *J. Haz. Mat. B 85* (5): 195–211.
8. Hansen, H.K.; Rojo, A.; Ottosen, L.M. (2007) Electrokinetic remediation of copper mine tailings implementing bipolar electrodes. *Electrochim. Acta*, *52*: 3355–3359.
9. Zhou, D.M.; Deng, C.F.; Alshawabkeh, A.N.; Cang, L. (2005) Effects of catholyte conditioning on electrokinetic extraction of copper from mine tailings. *Environ. Int.*, *31*: 885–890.
10. Page, M.M.; Page, C.L. (2002) Electroremediation of contaminated soils. *J. Environ. Eng.*, *128* (3): 208–219.
11. Cummings, D.E.; March, A.W.; Bostick, B.; Spring, S.; Caccavo, F.; Fendorf, S.; Rosenzweig, R.F. (2000) Evidence for microbial Fe(III) reduction in anoxic, mining-impacted lake sediments (Lake Coeur d'Alene, Idaho). *Appl. Environ. Microbiol.*, *66*: 154–162.

12. Chatain, V.; Bayard, R.; Sanchez, F.; Moxzkowicz, P.; Gourdon, R. (2005) Effect of indigenous bacterial activity on arsenic mobilization under anaerobic conditions. *Environ. Int.*, *31*: 221–226.
13. Lee, J.U.; Lee, S.W.; Kim, K.W.; Yoon, C.H. (2005) The effects of different carbon sources on microbial mediation of arsenic in arsenic-contaminated sediment. *Environ. Geochem. Hlth.*, *27*: 159–168.
14. Ko, I.; Ahn, J.S.; Park, Y.S.; Kim, K.W. (2003) Arsenic contamination of soils and sediments from tailings in the vicinity of Myungbong Au mine, Korea. *Chem. Speciation Bioavail.*, *15*: 67–74.
15. Marks, R.E.; Acar, Y.B.; Gale, R.J. (1994) In situ remediation of contaminated soils containing hazardous mixed wastes by bioelectrokinetic remediation and other competitive technologies. In: *Remediation of Hazardous Waste Contaminated Soils*, Wise, D.L.; Trantolo, D.J., Ed.; Marcel Dekker: New York, pp. 405–436.
16. Wick, L.Y.; Shi, L.; Harms, H. (2007) Electro-bioremediation of hydrophobic organic soil-contaminants: A review of fundamental interactions. *Electrochim. Acta*, *52*: 3441–3448.
17. Zhou, D.M.; Chen, H.F.; Cang, L.; Wang, W.J. (2007) Ryegrass uptake of soil Cu/Zn by EDTA/EDDS together with a vertical direct-current electrical field. *Chemosphere*, *67*: 1671–1676.
18. Maini, G.; Sharman, A.K.; Sunderland, G.; Knowles, C.J.; Jackman, S.A. (2000) An integrated method incorporating sulfur-oxidizing bacteria and electrokinetics to enhance removal of copper from contaminated soil. *Environ. Sci. Technol.*, *34*: 1081–1087.
19. Kim, S.O.; Kim, W.S.; Kim, K.W. (2005) Evaluation of electrokinetic remediation of arsenic-contaminated soils. *Environ. Geochem. Health*, *27*: 443–453.
20. Ure, A.M. (1995) *Heavy metals in Soils*; Alloway, B.J., Ed.; Chapman & Hall: Glasgow, pp. 55–68.
21. U.S. Geological Survey (1984) *Element concentrations in soils and other surficial materials of the conterminous United States*. U.S. Geological Survey Professional Paper 1270, 4pp.
22. Grantham, M.C.; Dove, P.M.; DiChristina, T.J. (1997) Microbially catalyzed dissolution of iron and aluminum oxyhydroxide mineral surface coatings. *Geochim. Cosmochim. Acta*, *61*: 4467–4477.
23. Liermann, L.J.; Kalinowski, B.E.; Brantley, S.L.; Ferry, J.G. (2000) Role of bacterial siderophores in dissolution of hornblende. *Geochim. Cosmochim. Acta*, *64*: 587–602.
24. Ullman, W.J.; Dirchman, D.L.; Welch, S.A.; Vandevivere, P. (1996) Laboratory evidence for microbially mediated silicate mineral dissolution in nature. *Chem. Geol.*, *132*: 11–17.
25. Collins, Y.E.; Stotzky, G. (1989) *Metal ions and bacteria*; Beverigde, T.J.; Doyle, R.J., Eds.; John Wiley & Sons: New York, pp. 31–90.
26. Bayard, R.; Chatain, V.; Gachet, C.; Troadec, A.; Gourdon, R. (2006) Mobilisation of arsenic from a mining soil in batch slurry experiments under bio-oxidative conditions. *Water Res.*, *40*: 1240–1248.