

Surfactant-enhanced electrokinetic removal of phenanthrene from kaolinite

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Abstract

Removal of hydrophobic organic contaminants (HOCs) using surfactant-enhanced electrokinetic (EK) method was studied in a model system. Kaolinite and phenanthrene were selected as a model clay soil and a representative HOC, respectively. Three different types of surfactants: APG (alkyl polyglucoside), Brij30 (polyoxyethylene-4-lauryl ether), and SDS (sodium dodecyl sulfate), were used to enhance the solubility of HOC. Characteristics of surfactants, such as surface tension, HOC solubility, and biodegradability were measured. In the case of Brij30 solution, phenanthrene solubility was higher than that of others. After 4 days, APG and Brij30 were degraded by 65% and 26% of the initial amount, respectively. However, degradation of SDS was hardly detected. Electroosmotic flow (EOF) of Brij30 solution was lower than others when the 0.1 M NaCl was used as electrolyte. Addition of the acetate buffer solution increased the EOF of Brij30 solution and enhanced removal of phenanthrene. Among three different surfactants tested, APG showed the highest removal efficiency.
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1. Introduction

Recently, as the demand for a new, innovative and cost-effective technology for *in situ* soil remediation has grown, the efforts to utilize the electrical conduction phenomena in soils under the influence of an electrical field have been performed [1–8]. Electrokinetics is a process that separates and extracts heavy metals, radionuclides and HOCs from saturated or unsaturated soils, sludges and sediments. A direct current of low intensity is applied across electrodes that have been implanted in the ground on each side of the contaminated soil. Electrical phenomena then cause the transport of various species in the ground. In comparison with researches on the heavy metal removal using EK, however, few researches on HOCs removal have been reported due to low solubility in water and high tendency to sorb on soil surface [9–12].

Bruell et al. [10] reported that hexane and isooctane showed lower removal rates than the other compounds, such as benzene,

toluene and TCE. These results were due to the strong sorption of insoluble organics on soil surface. In the electrokinetic removal of HOCs, the electrophoretic mobility effect could hardly be expected because most HOCs were not polar compounds. In this regard, methods to increase the solubility of HOCs need to be incorporated with the electrokinetic removal.

Surfactant, which has both hydrophobic and hydrophilic group, tends to form micelles at the amount greater than the critical micelle concentration (CMC). HOCs accommodate to the interior of micelles with hydrophobicity [13–18]. In the solubility-enhanced electrokinetic process, two steps of HOCs removal are dissolution of HOCs into surfactant micelles and transport of micelles containing HOCs in electric field. The complex interactions among HOCs, soils, surfactants, and solution composition involved in EK operation were investigated in a series of papers by Ko et al. [19–21]. Surfactant losses due to sorption on soil surface and pore blockage may potentially reduce the effectiveness of EK remediation. Surfactant remained in soil after treatment may be another contaminant itself and cause a secondary contamination by improving the mobility of remained HOCs. Therefore, the following characteristics of surfactants should be considered prior to EK application: good

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HOCs solubility, biodegradability to reduce the secondary contamination, small sorption to minimize decrease of the removal rates, high mobility to transport HOCs, and low CMC for high removal rates with small amount of surfactants.

Abrupt change of soil pH in EK treatment affects soil activity. When a buffer solution is used to control the soil pH, it can decrease the pH difference between anode and cathode and increase the soil conductivity. Thus, pH control by the buffer solution can enhance the effectiveness of contaminants removal.

The objective of this research is to demonstrate the feasibility of EK remediation enhanced by surfactant to remove HOCs from contaminated soil of low permeability. Surface tension, HOC solubility, and biodegradability of three different surfactants were compared. The changes of electrolyte pH, EOF, and removal efficiency according to different electrolyte conditions were investigated.

2. Experimental methods

2.1. Specimen preparation

The model clay soil used in this study was Kyungnam-Sancheong Kaolinite (<150 μm , Dong-Bang Corporation, Korea). Phenanthrene (Sigma) was chosen as a representative HOC. Air-dried kaolinite was mixed with a phenanthrene–acetone solution and contaminated at a concentration of 600–700 mg phenanthrene/kg dry soil.

Two nonionic surfactants, alkyl polyglucoside (APG) and polyoxyethylene-4-lauryl ether (Brij30) were separately obtained from Aldrich and Henkel Korea, respectively. An anionic surfactant, sodium dodecyl sulfate (SDS), was obtained from Sigma.

Acetate buffer solution of pH 4 was composed of 18.5 mL of 2 M $\text{CH}_3\text{COONa}\cdot 3\text{H}_2\text{O}$ and 81.5 mL of 2 M CH_3COOH in 1 L. Acetate buffer was used to inhibit a sudden change of soil pH for the maintenance of EOF and soil activity. In addition, acetate buffer played a role to improve electrical conductivity of soil and then save energy cost in EK process.

2.2. Characteristics of surfactants

The surface tension of surfactants was measured in both systems with or without soil. Soil-to-solution mass ratio for surfactant was 1:10. The bottle was filled with 20 mL of surfactant solution based on a 0.1 M NaCl and the pH was 4. Concentration of surfactant stock solutions was from zero to well above the CMC values. After an equilibrium was reached, surface tension was measured by a tensiometer (KRÜSS Digital Tensiometer, K10ST).

To measure the phenanthrene solubility in surfactants with the presence or absence of soil, experiments were performed in a glass bottle containing excess phenanthrene in the same condition for the measurement of surface tension. After an equilibrium was reached, the solid was separated from the surfactant solution by filtration and aliquot of the filtrate was taken for analysis.

To examine the biodegradability of surfactants, sludge from the wastewater treatment plant in Daejeon, Korea was used.

The activated sludge of 50 mL which had a concentration of 1700 mg dry cell/L was mixed with 50 mL of three different types of surfactant solutions: 0.1 mL of a trace metal solution, 1.4 mL of $(\text{NH}_4)_2\text{SO}_4$ and 0.6 mL of KH_2PO_4 . The trace metal solution consisted of 25 g/L of $\text{MgSO}_4\cdot 7\text{H}_2\text{O}$, 4.96 g/L of CaCl_2 , 2 g/L of yeast extraction, 0.5 g/L of FeCl_3 , 3 g/L of $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$, 3 g/L of KI, 1 g/L of $\text{MnCl}_2\cdot 4\text{H}_2\text{O}$, 2 g/L of $\text{ZnSO}_4\cdot 7\text{H}_2\text{O}$, 1.4 g/L of $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$, 1 g/L of $\text{Na}_2\text{MoO}_4\cdot 2\text{H}_2\text{O}$ and 1.27 g/L of EDTA sodium salt. COD changes of the complex sludge were recorded during the cultivation in a shaking incubator at 150 rpm and 30 °C. COD induced by the remained surfactants was quantified using DR/2010 spectrophotometer and COD kit (HACH) [22].

2.3. Electrokinetic set-up

Soil was loaded into an electrokinetic column with a length of 10 cm and a diameter of 4 cm, and consolidated to a void ratio of 1.03–1.13 to obtain a saturated sample containing a uniform distribution of contaminant. The column cell was made of glass to minimize the sorption of phenanthrene onto the cell wall. However, the phenanthrene amount in effluent was analyzed to check the mass adsorbed on the cell wall or remained in the soil pore and surface after extraction for the analysis. Initial water content and pH of soil sample were determined along the cylindrically consolidated clay specimens. The initial water content varied from 40% to 44% and the initial soil pH was between 4.5 and 4.9.

Fig. 1 shows a schematic diagram of the test cell. A constant current, 10 mA (0.8 mA/cm²) across the cell was applied using a power supply with a maximum output of 200 V and voltage was monitored by a voltmeter. The test column was connected to the electrode housing which contained the graphite anode and cathode. Uniform flow across the electrodes was ensured by mini holes uniformly distributed on the electrode surface. Surfactant solutions were continuously supplied to the soil system from anode tank, maintaining the constant hydraulic gradient in the anode compartment.

Parameters associated with each experimental condition are listed in Table 1. About 0.1 M NaCl of pH 4 and acetate buffer solution of pH 4 were used as background electrolytes to simulate the contaminated soil system. Surfactant solutions of 5 g/L

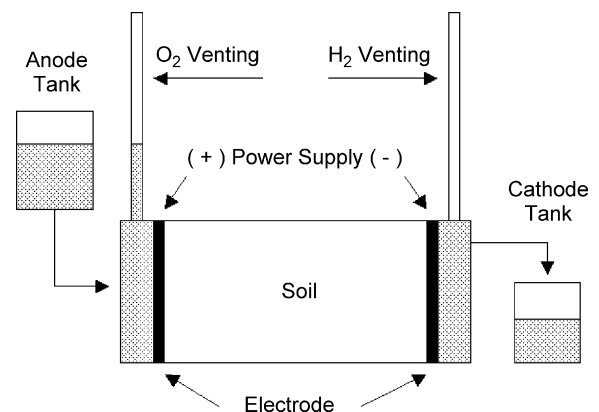


Fig. 1. Schematic diagram of electrokinetic remediation test cell.

Table 1
Experimental conditions^a for electrokinetic tests

Electrolyte	Washing solution	Period (weeks)
0.1 M NaCl	Water, 5 g/L APG, 5 g/L Brij30, 5 g/L SDS	2
	Water, 5 g/L APG, 5 g/L Brij30	4
Acetate buffer solution	Water, 5 g/L APG, 5 g/L Brij30, 5 g/L SDS	2
	Water, 5 g/L APG, 5 g/L Brij30	4

^a Initial pH 4 and constant current, 10 mA.

were prepared using the background electrolytes. The periods of operation were 2 and 4 weeks for each experiment, where 0.1 M NaCl and acetate buffer solution were separately used as electrolytes. SDS solution was used only in 2 weeks experiment.

2.4. Measurement and analyses

During the experiment, which was operated under a constant current condition, the cell voltage and amount of accumulated EOF through the soil system were measured periodically. Electrolyte pH at the anode and cathode compartments was also monitored throughout the experiment. At the end of each run (2 and 4 weeks), the clay sample was promptly removed from the cell and sliced into 11 segments of uniform thickness. Each segment was analyzed for the soil pH and phenanthrene content. The soil pH was measured after the mixture of 1 g of dry soil and 10 mL of 0.1 M KCl was shaken for 12 h. To obtain the distribution of phenanthrene content, 1 g of dry clay was mixed with 10 mL of methanol, and the slurry was shaken for 24 h at room temperature. After filtering, the phenanthrene content of the filtrate was measured by a high performance liquid chromatography (HPLC, Waters) with C₁₈ symmetry column and UV detector. All analytical determinations utilized the standard calibration curve of phenanthrene dissolved in methanol from 0.5 to 80 mg/L.

3. Results and discussion

3.1. Surface tension, solubility and biodegradability of surfactants

Surface tension profiles of the solution are shown in Fig. 2, in which CMC of each surfactant can be identified: 1.0, 0.1 and 0.6 g/L for APG, Brij30 and SDS, respectively. Because Brij30 had lower CMC than others, a higher removal rate with small amount of surfactant can be expected. When soil existed in a surfactant solution, the surface tension increased due to sorption of surfactant onto the soil surface. However, in the concentration ranges above CMC, the profiles of surface tension were almost same for both cases.

Fig. 3 shows the amount of phenanthrene dissolved in the surfactant solution. In the case of the Brij30 solution, the amount of dissolved phenanthrene turned out to be much higher than that of other two-surfactant solutions. The amount of dissolved

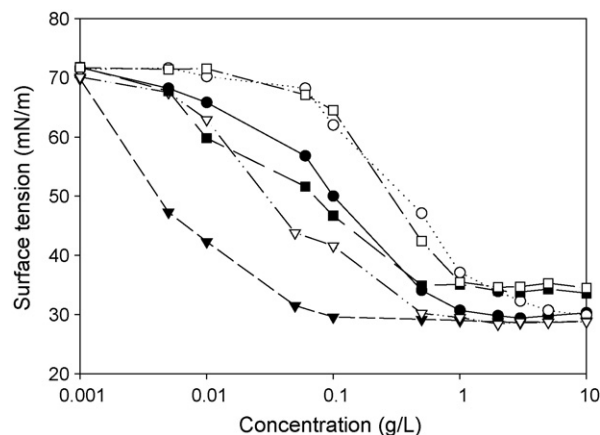


Fig. 2. Surface tension of surfactant solution ((●) APG, (○) APG with soil, (▼) Brij30, (▽) Brij30 with soil, (■) SDS and (□) SDS with soil).

phenanthrene under the presence of soil was again lower than that without soil because some portion of surfactant was sorbed onto the soil surface. When concentrations of APG, Brij30, and SDS became five times of CMC, the dissolved phenanthrene concentration was 23, 30 and 38 mg/L, respectively. This result implies that three different surfactants have similar phenanthrene solubility in respect of CMC in this concentration range.

The profile of COD changes of surfactant solution in Fig. 4 suggests biodegradability of surfactant tested. After 4 days, APG was degraded by 65% of the initial amount while Brij30 degraded by 26%. However, degradation of SDS was the smallest: <10%.

3.2. Electrical potential gradient and accumulated outflow

Change of electrical potential gradient across the electrodes with time is shown in Fig. 5. Under a constant current condition, the electrical potential gradient between electrodes initially increased with time. It was because the surface polarization

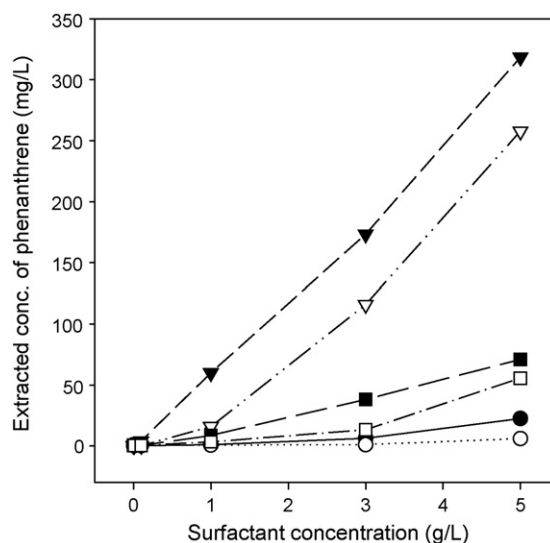


Fig. 3. Phenanthrene solubility of surfactants (0.1 M NaCl)((●) APG, (○) APG with soil, (▼) Brij30, (▽) Brij30 with soil, (■) SDS and (□) SDS with soil).

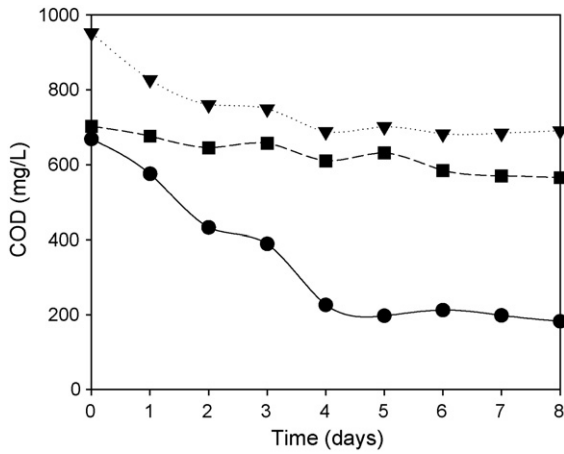


Fig. 4. Profile of COD change of surfactants ((●) APG, (▼) Brij30 and (■) SDS).

increased the soil resistance, therefore increased the electrical potential gradient. When 0.1 M NaCl or Brij30 in 0.1 M NaCl were used as electrolyte solution, the electrical potential gradient reached the maximum, 20 V/cm, within 7 days. In the case with APG in 0.1 M NaCl, the electrical potential gradient initially increased to 10 V/cm, decreased back to 6 V/cm and remained almost constant. When a buffer solution was used as a background electrolyte, the increase of electrical potential gradient was not significant. A constant value of 5 V/cm was maintained thereafter. The acetate buffer solution therefore could be used to reduce the resistance between electrodes and ensure an operation for long period.

When the 0.1 M NaCl was used as a background electrolyte, the accumulated electroosmotic flow (EOF) rapidly increased except for the case of Brij30 solution (Fig. 6). The low accumulation rate of Brij30 in 0.1 M NaCl was due to its relatively low hydrophilicity and a sudden increase of the electrical potential gradient. When the acetate buffer solution was used as a background electrolyte, the accumulated EOF gradually increased with a small but constant slope. It was because the surface

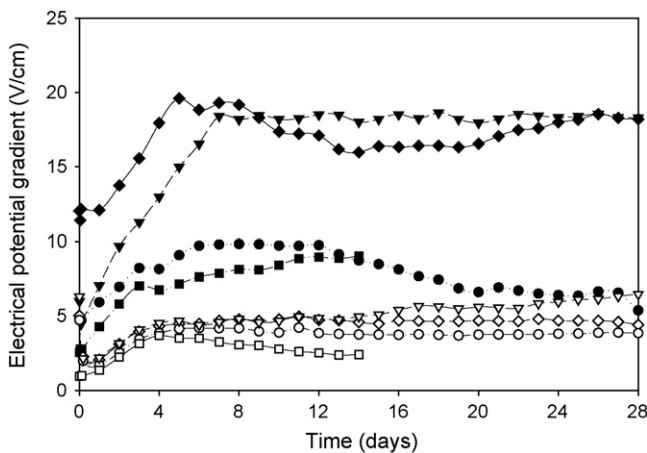


Fig. 5. Electrical potential gradient across the electrodes ((◆) 0.1 M NaCl, (●) APG in 0.1 M NaCl, (▼) Brij30 in 0.1 M NaCl, (■) SDS in 0.1 M NaCl, (◇) acetate buffer solution, (○) APG in acetate buffer solution, (▽) Brij30 in acetate buffer solution and (□) SDS in acetate buffer solution).

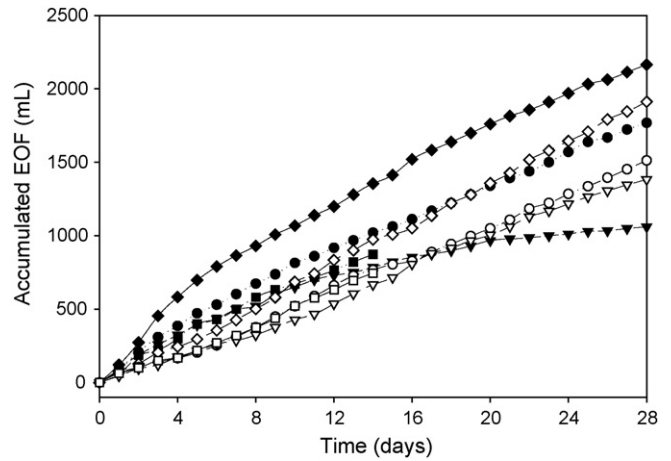


Fig. 6. Accumulated electroosmotic flow ((◆) 0.1 M NaCl, (●) APG in 0.1 M NaCl, (▼) Brij30 in 0.1 M NaCl, (■) SDS in 0.1 M NaCl, (◇) acetate buffer solution, (○) APG in acetate buffer solution, (▽) Brij30 in acetate buffer solution and (□) SDS in acetate buffer solution).

polarization increased the repulsion between soil mineral and hydrogen peroxide and then inhibited EOF. In the case of Brij30 in buffer solution, although the accumulated amount of flow was initially lower than in the case of Brij30 in 0.1 M NaCl, the condition was reversed after 17 days. Therefore, application of the buffer solution could enhance the flow rate of Brij30 in EK process.

To understand the transport of pore water in detail, the electroosmotic coefficient of permeability, k_e , was calculated [1]. Change of electroosmotic permeability in two kinds of electrolytes is shown in Fig. 7. Since k_e is inversely proportional to electrical potential gradient at a constant current, k_e decreased while electrical potential gradient increased with time and became stable due to the constant supplement of ions from anode tank. When acetate buffer was used as electrolyte, k_e was higher than that of NaCl because ionic concentration in acetate buffer was higher.

3.3. Electrolyte pH

pH profiles in the anode and cathode compartments are shown in Fig. 8. When the 0.1 M NaCl was used as a background electrolyte, at the start of the experiment, the pH values were very acidic (pH 2–3) within the anode compartment and very alkaline (pH 11–12) in the cathode compartment as a result of the electrolytic reaction of water. The pH in the anode compartment slightly decreased. In the cathode compartment, the final pH became 7–10, because the acid front from the anode had reached the cathode compartment neutralizing the base front between the cathode and anode. Catholyte pH of SDS in 0.1 M NaCl slightly decreased because the amount of neutralized OH^- ions was relatively small due to competed transport between sodium ions from SDS and hydrogen ions toward cathode.

When the acetate buffer solution was used as a background electrolyte, increases of catholyte pH were smaller than the case of 0.1 M NaCl. It is because nonionic acetic acid with hydrogen ions at low pH was transported to cathode and hydrogen

Table 2
Removal efficiency of phenanthrene and energy expenditure

Electrolyte	Washing solution	Period (weeks)	Removal efficiency (%)	Accumulated EOF (mL)	Removal efficiency/EOF (%/L)	Energy expenditure (kWh/m ³)
0.1 M NaCl	Water	2	23.5	1355	17.3	4307
	APG		57.8	1020	56.7	2189
	Brij30	45.8	785	58.3	3686	
	SDS	55.0	873	63.0	1807	
	Water	4	35.8	2164	16.5	8901
	APG		75.1	1768	42.5	4061
	Brij30		56.5	1060	53.5	8471
Acetate buffer solution	Water	2	20.2	974	20.7	1131
	APG		43.4	768	56.5	971
	Brij30	38.0	667	57.0	1162	
	SDS	44.6	744	59.9	693	
	Water	4	30.9	1912	16.2	2365
	APG		72.5	1512	47.9	1982
	Brij30		71.3	1382	51.6	2683

ions were released back due to high pH in cathode compartment. After 14 days operation, they decreased back to the initial electrolyte pH. The catholyte pH of the acetate buffer solution without surfactant (pH ~4) was certainly attributed to the higher buffering capacity due to larger EOF.

3.4. Removal efficiency of phenanthrene and energy expenditure

Phenanthrene content in soil after each experiment is shown in Fig. 9. Table 2 represents the removal efficiency of phenanthrene in the EK process. The amount of phenanthrene in effluent almost corresponded to the amount of phenanthrene removed

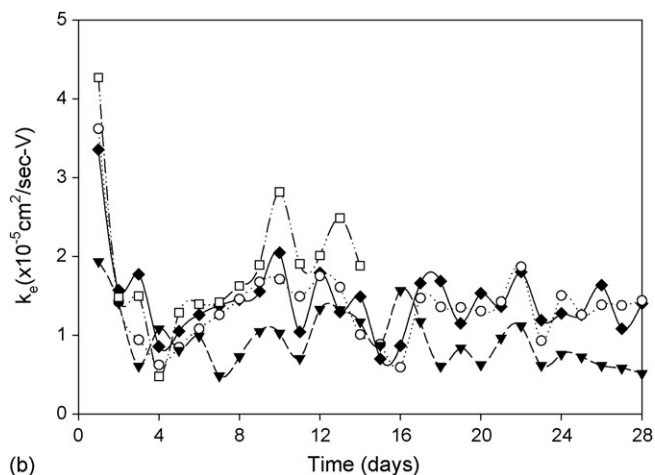
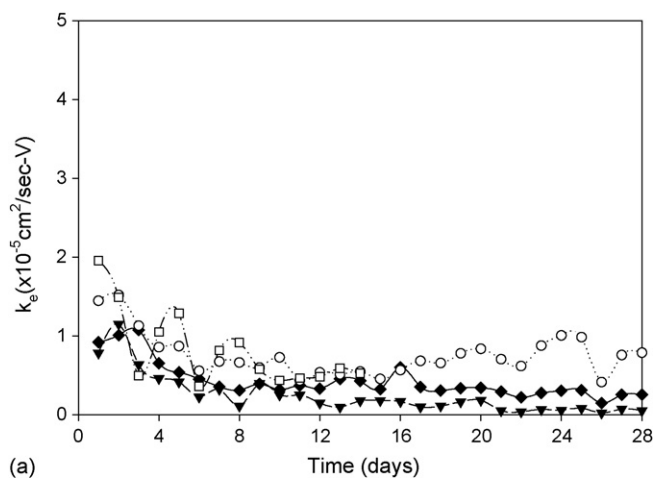


Fig. 7. Change of electroosmotic coefficient of permeability (a) 0.1 M NaCl and (b) acetate buffer solution (◆) water, (○) APG, (▼) Brij30 and (□) SDS.

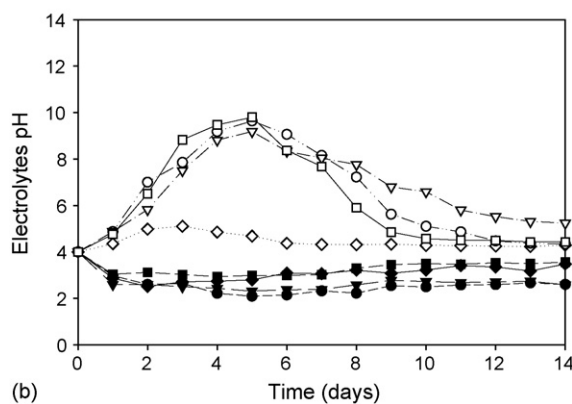
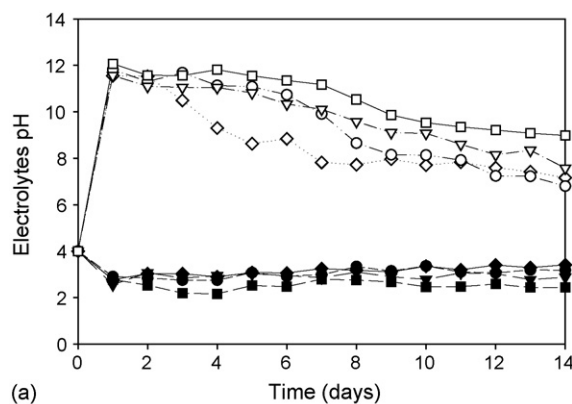


Fig. 8. pH profile of the anolyte and catholyte (a) 0.1 M NaCl and (b) acetate buffer solution (◆) water (anode), (◇) water (cathode), (●) APG (anode), (○) APG (cathode), (▼) Brij30 (anode), (▽) Brij30 (cathode), (■) SDS (anode) and (□) SDS (cathode).

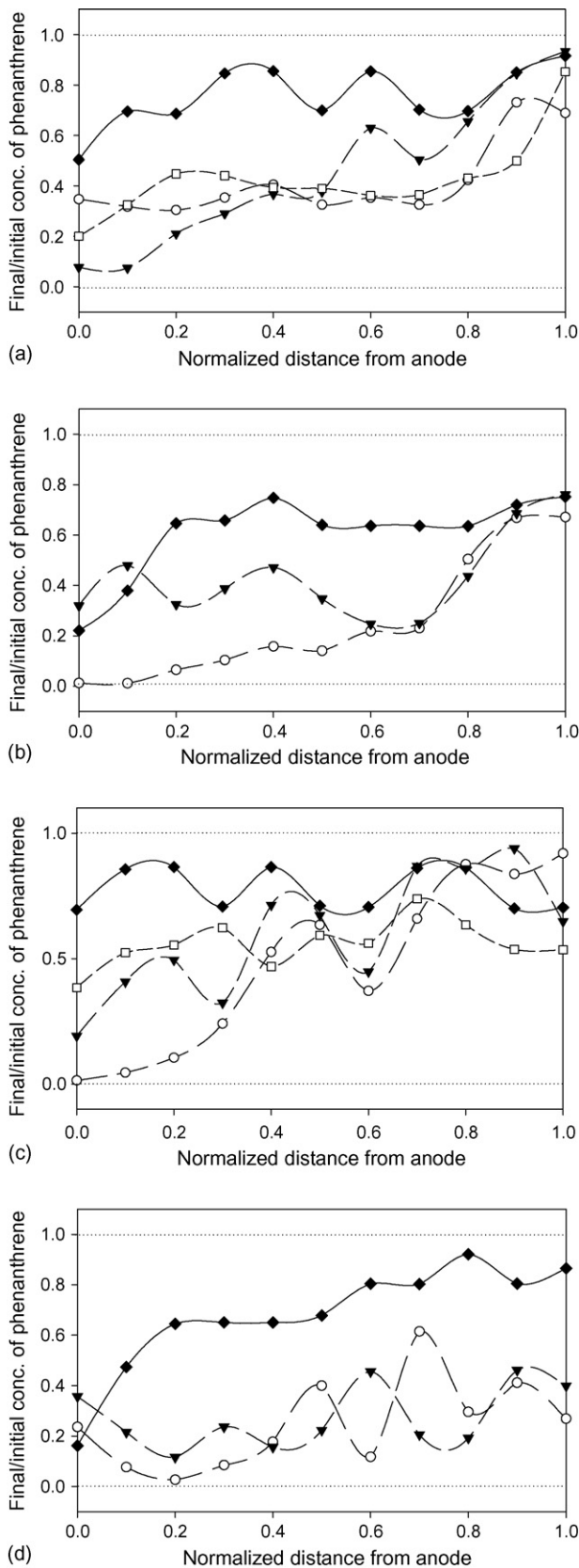


Fig. 9. Content of phenanthrene in soil after operation (a) 2 weeks: 0.1 M NaCl, (b) 4 weeks: 0.1 M NaCl, (c) 2 weeks: acetate buffer solution and (d) 4 weeks: acetate buffer solution ((\blacklozenge) Water, (\circ) APG, (\blacktriangledown) Brij30 and (\square) SDS).

form soil. The result showed that phenanthrene was removed by solubilization by surfactant solution not by biological degradation or accumulation at the electrodes. The removal efficiency by the same surfactant increased with period of operation. APG showed the highest removal efficiency, 75.1%, after 4 weeks in 0.1 M NaCl. Even in 0.1 M NaCl or acetate buffer solution without surfactant, phenanthrene removal was observed 20.2–35.8% for 2 or 4 weeks just by EOF. Surfactant solution had higher removal efficiency although its EOF was smaller than that of 0.1 M NaCl or acetate buffer solution without surfactant. That is, surfactant could enhance the solubility and mobility of phenanthrene and increase the removal efficiency. When the removal efficiency in the same EOF was compared, removal efficiency of Brij30 in 0.1 M NaCl was not low because it had a good ability to enhance solubility of phenanthrene. But Brij30 in 0.1 M NaCl showed low removal efficiency due to low EOF in EK system.

The acetate buffer was used to enhance EOF of Brij30 and expect high removal efficiency. In the experiment using acetate buffer solution as electrolyte, the removal efficiency after 2 weeks slightly reduced due to a little decrease in the amount of EOF. EOF in buffer solution decreased due to the surface polarization. Brij30 in buffer solution, however, had higher removal efficiency than that in 0.1 M NaCl after 4 weeks because EOF of Brij30 solution increased in buffer. Although buffer solution slightly decreased EOF rate, it could cause reasonable EOF due to decrease of resistance.

Because phenanthrene dissolved in APG and Brij30 was transported to cathode tank by EOF, phenanthrene would be extracted out through cathode tank [23–25]. However, in this study, although SDS was an anionic surfactant, washing solution was supplied to anode tank. When SDS was used, transport and removal of phenanthrene near cathode were observed as shown in Fig. 9. Some of the anionic SDS micelle dissolving phenanthrene would exist in anode tank according to its polarity [12,26]. However, because apparent charge density of SDS decreased at low pH [27], SDS micelle in anode tank could be transported toward cathode by EOF. Therefore, phenanthrene near cathode could be removed. In addition, there was a study that some of the anionic surfactant Calfax 16L-35 introduced to anode tank was transported toward cathode in electrokinetic soil flushing [28].

The total energy expenditure is shown in Table 2. During 4 weeks, energy expenditure in 0.1 M NaCl was 4061–8901 kWh/m³ and that in acetate buffer was 1982–2.683 kWh/m³. Energy expenditure of acetate buffer was lower than that of 0.1 M NaCl because of low electrical potential gradient. In this study, the high removal efficiency of phenanthrene was obtained for only 2 or 4 weeks of treatment period at high cell voltage. However, the total amount of EOF and energy expenditure in the present study are similar values to those in other electrokinetic washing processes which were conducted for several months at low current and voltage [23–25]. Because surfactant washing effects in EK process depend on EOF of surfactant solution, it is important to maintain high electroosmotic permeability during the operation.

4. Conclusions

Among three different types of surfactants, APG showed a reasonably high EOF and the best removal efficiency. APG was known to be an environmentally compatible and non-toxic surfactant and the biodegradability test turned out to be sound. Thus, APG could be regarded as an adequate surfactant in EK operation.

Brij30 was known as a good surfactant in the removal of HOCs and the present solubility test proved it. In the EK experiment, however, the EOF of Brij30 in 0.1 M NaCl was lower than that of other two surfactants. Removal efficiency of phenanthrene in an experiment with Brij30 in 0.1 M NaCl was also lower than that with other surfactants. In order to increase the EOF, an acetate buffer could be added to the washing solution. Brij30 in buffer solution showed a high removal efficiency of phenanthrene. So buffer solution could be used to change the condition in soil system.

The results obtained from this study show that EK process using the surfactant washing and pH buffering is a promising technology for HOCs removal in low-permeability subsurface environments.

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