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Removal of phenanthrene from soil by additive-enhanced electrokinetics

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ABSTRACT: Removal of hydrophobic organic contaminants (HOCs) using an additive-enhanced electrokinetic method was studied in a model system. Kaolinite and phenanthrene were selected as a model clay soil and a representative HOC, respectively. Three different chemically-synthesized surfactants along with two different biosurfactants were used to remove phenanthrene. Hydrogen peroxide was also used to degrade phenanthrene. Electrokinetic (EK) column experiments were performed using these additives. When no additive was used, a removal efficiency of phenanthrene was 4.23% after 2 weeks. When surfactants were added in the EK system, the removal efficiencies after 2 weeks were as follows: APG 11.1%, Brij30 6.31%, SDS 9.97%, MEL 16.2% and BS-UC 17.4%. Among surfactants, biosurfactants had higher removal efficiencies than chemically-synthesized surfactants. When hydrogen peroxide was used, 54.7% of initial amount was removed at a current of 5 mA for 2 weeks. Even a higher removal efficiency was achieved (84.2%) at 10 mA within 1 week. These results suggest a detailed future study on the chemical treatment by hydrogen peroxide incorporated with EK method to remove phenanthrene from clay soil.

Key words: electrokinetic remediation, surfactant, biosurfactant, hydrogen peroxide, soil, phenanthrene

1. INTRODUCTION

Recently, as the demand for a new, innovative and cost-effective *in situ* remediation technology has grown, the efforts to utilize electrical conduction phenomena in soils under the influence of an electrical field have been reported (Hamed et al., 1991; Lageman, 1993; Acar et al., 1993, 1994, 1996; Yeung et al., 1996; Lee et al., 1999). 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 causes the transport mechanisms of various species in the ground.

In comparison with the heavy metal removal using EK, however, HOCs removal is difficult due to their low solubility in water and their high tendency to sorb on soil surface (Acar et al., 1992; Ko et al., 2000; Kim et al., 1999). Bruell et al. (1992) reported that hexane and isooctane showed lower removal rates than the other compounds examined (benzene, toluene, and TCE). These results had been caused by the strong sorption of insoluble organics on soil surface. In the electrokinetic removal of HOCs, the electrophoretic mobility effect was difficult to be expected because most HOCs had the characteristic of non-polarity.

In this regard, in order to achieve the high removal efficiency for insoluble organics, the control methods to increase the solubility of HOCs need to be incorporated in electrokinetic operation. Surfactants and complexing agents can be used to increase the solubility and assist in the movement of the contaminant. Also, reagents and chemicals may be introduced at the electrodes to enhance contaminant removal rates.

Surfactants, which have both hydrophobic and hydrophilic group, start to form micelle at the amount of surfactant above the critical micelle concentration (CMC) and HOCs accommodate to the interior of micelle with hydrophobicity (Edward et al., 1994; Jafvert et al., 1994; Yeom et al., 1996, 1997; Chang et al., 2000). In the solubility-enhanced electrokinetic process, the HOCs removal is occurred by the two mechanisms of the dissolution of HOCs into surfactant micelle and the transportation of HOCs by electric field. Surfactants, therefore, can be used to increase the solubility of HOCs.

Several chemically-synthesized surfactants have been evaluated in soil decontamination tests. But it would be preferable to employ agents that are less toxic than synthetic ones. Biosurfactants produced by bacteria or yeast are potentially useful due to no toxicity, good biodegradability and antimicrobial activity. The feasibility of biosurfactants to remove HOCs from contaminated soils have been demonstrated (Mulligan et al., 2001). When biosurfactants produced using HOCs as carbon source were applied to the field, the adaptability to the specific contaminants was better than other surfactants (Hau et al., 1997).

One of chemicals which may be introduced at the electrodes, hydrogen peroxide forms hydroxyl radical when iron ions or iron complexes naturally exist in soil (Yang et al., 1999, 2001). Hydroxyl radical is strong oxidant, and the mechanism of formation is as follows:

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$$H_2O_2 + Fe^{2+} \rightarrow OH\cdot + OH^- + Fe^{3+}$$

If HOCs are present in soil, the reaction includes:

$$RH + OH\cdot \rightarrow H_2O + R\cdot$$

$$R\cdot + Fe^{3+} \rightarrow Fe^{2+} + products$$

High degradation rate of contaminants can be expected from upper reactions (Kong et al., 1998; Watts et al., 1999).

The objective of this research is to demonstrate the effectiveness of EK remediation enhanced by additives such as chemical surfactants, biosurfactants and hydrogen peroxide to remove phenanthrene from contaminated fine soil.

2. MATERIAL AND METHODS

2.1. Specimen Preparation

The model clay soil used in this experiment was kaloinite-white O passing a No. 100 sieve. Phenanthrene was chosen as a representative HOC. Air-dried kaolinite was mixed with a phenanthrene-aceton solution and contaminated at a concentration of 1500 mg phenanthrene/kg dry soil. To remove the extra phenanthrene non-sorbed and remained between soil particles after contamination, the soil sample was washed several times with water and finally obtained the soil sample contaminated at a concentration of 600–700 mg phenanthrene/kg dry soil.

Surfactants were used to investigate the effects of solubility enhancing materials on the efficiency of HOCs removal. Two nonionic surfactants, alkyl polyglucoside (APG) and polyoxyethylene 4 lauryl ether (Brij30) were obtained from Aldrich and Henkel Korea and used as received. An anionic surfactant, sodium dodecyl sulfate (SDS), was obtained from Sigma and used as received. APG is a food grade surfactant which has characteristics of a low toxicity and a high potential for biodegradation. The concentration of chemically-synthesized surfactant solutions was 5 g/L.

Biosurfactants produced by *Candida Antarctica* JWSH–112, mannosylerythritlo lipid (MEL) and BS–UC, were obtained from Lab of Industrial Biotechnology, Southern Yangtz University, China. Biosurfactants were used as mixture of surfactant and culture medium. The concentration of MEL solution was 2.5 g/L. Because an analytical method of BS–UC was not generally known, BS–UC of the same amount with MEL solution was used. Carbon sources were a mixture of soybean oil and kerosene for MEL and undecane for BS–UC. Fermentation was carried out to produce biosurfactants for 7 days in the shaking incubator of 28°C and 200 rpm.

Hydrogen peroxide produces hydroxyl radical in the presence of iron ions and then hydroxyl radical degrades phenanthrene. Hydrogen peroxide of 35% was obtained from Junsei and used after dilution to 3.5%.

2.2. Experimental Set-up

Soil was loaded into an electrokinetic column with a length of 10 cm, a diameter of 4 cm and consolidated to a void ratio of 0.68–0.77 to obtain a saturated sample containing a uniform distribution of contaminant. A column cell was made of glass to minimize the phenanthrene losses due to the sorption to cell wall. The initial water content and pH of consolidated soil sample were determined. The initial water content varied from 40% to 44% and the initial soil pH was between 4.5 and 4.9.

Figure 1 shows a schematic diagram of the electrokinetic remediation test cell. A constant current, 5 or 10 mA (0.4 or 0.8 mA/cm^2) across the cell was applied using a power supply with a maximum output of 200 V and voltage was monitored using a voltmeter. The test column was connected to the electrode reservoir which contained the graphite anode and cathode. Uniform flow across the electrodes was ensured by holes in the electrodes. Solutions of additives were continuously supplied to a soil system from anode tank, maintaining the constant hydraulic gradient in the anode electrode compartment.

Parameters associated with each experiment were listed in Table 1. Experiment 1 was no additive. Chemically-synthesized surfactants of 5 g/L were used in experiment 2 to 4. In experiment 5 to 6, biosurfactants were used and concentration of MEL solution was 2.5 g/L. Hydrogen peroxide of 3.5% was supplied to anode tank in experiment 7 to 8. Experiment 1 to 7 were operated for 14 days and experiment 8 was conducted for just 7 days. Constant current of 5 mA was applied to experiment 7 and the others were 10 mA.

2.3. Measurement and Analyses

During the experiment, which was operated under a constant current condition, the cell voltage and amount of accu-

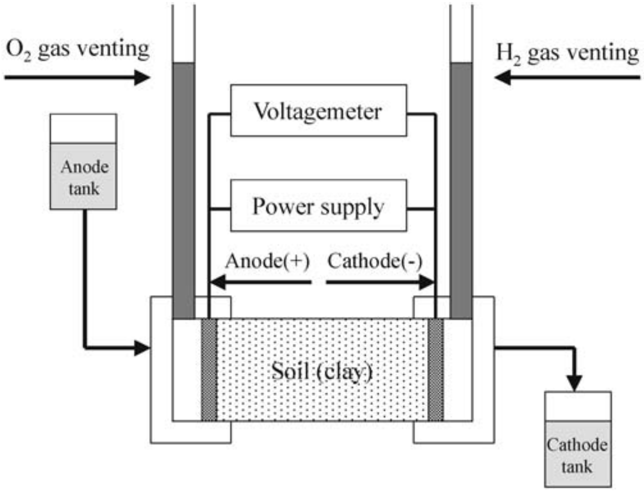

Fig. 1. Schematic diagram of electrokinetic remediation test cell.

Table 1. Experimental conditions for electrokinetic tests.

Experiment	Additive	Concentration	Time (days)	Current (mA)
1	Water	-	14	10
2	APG	5 g/L	14	10
3	Brij30	5 g/L	14	10
4	SDS	5 g/L	14	10
5	MEL	2.5 g/L	14	10
6	BS-UC	-	14	10
7	H_2O_2	3.5%	14	5
8	H_2O_2	3.5%	7	10

mulated electroosmotic flow through the soil system were measured with time. At the end of a specific experimental run time, the clay sample was promptly removed from the cell and segmented into 11 slices. Each slice was used to measure phenanthrene content. The distribution of phenanthrene content was measured by mixing 1 g of dry clay with 10 mL of methanol, and shaking the slurry for 24 hours at room temperature. After filtering, the phenanthrene content of the filtrate was measured by a high performance liquid chromatography (HPLC). The HPLC equipped with an autosampler (Water 717 plus) was used to determine phenanthrene concentration. All analytical determinations utilized the standard calibration curve of phenanthrene dissolved in methanol from 0.5 mg/L to 80 mg/L.

3. RESULTS AND DISCUSSION

3.1. Electrical Potential Gradient and Accumulated Outflow

Difference of voltage between two electrodes causes the flow of solution supplied to anode tank and can be represented as electrical potential gradient, V/cm. Development of electrical potential gradient across the cell electrodes with time is shown in Figure 2. Under a constant current condition, the electrical potential gradient between electrodes initially increased with time. It was caused by decrease of zeta potential due to a rise of concentration of hydrogen ions in the soil system and increase of repulsion between soil particles and hydrogen ions. In this experiment, the maximum possible electrical potential gradient was 20 V/cm. When H_2O_2 were applied to a model soil at constant current of 10 mA, the electrical potential gradient reached maximum values in 4 days and its trend was similar to the case of water. The electrical potential gradient of H_2O_2 at 5 mA was lower than that at 10 mA and the final value was 8.8 V/cm. While the current decreased by half, the electrical potential gradient decreased more than half. This influenced the amount of accumulated electroosmotic flow (EOF) and removal efficiency of phenanthrene in soil.

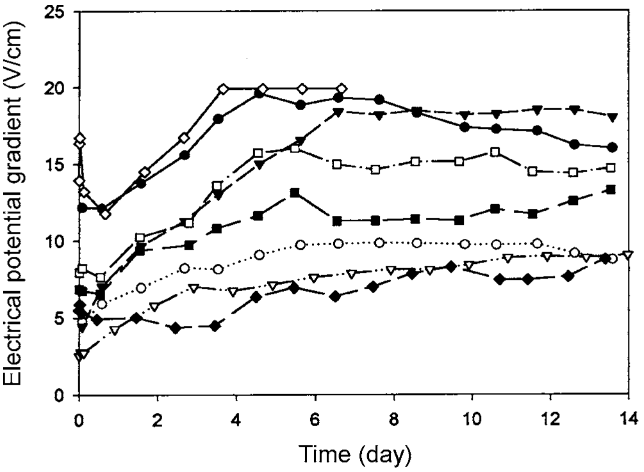

Fig. 2. Electrical potential gradient across the cell electrodes (● : Water, 14 days, 10 mA, ○ : APG, 14 days, 10 mA, ▼: Brij30, 14 days, 10 mA, ▽: SDS, 14 days, 10 mA, ■: MEL, 14 days, 10 mA, □ : BS–UC, 14 days, 10 mA, ◆: H_2O_2, 14 days, 5 mA, ◇ : H_2O_2, 7 days, 10 mA).

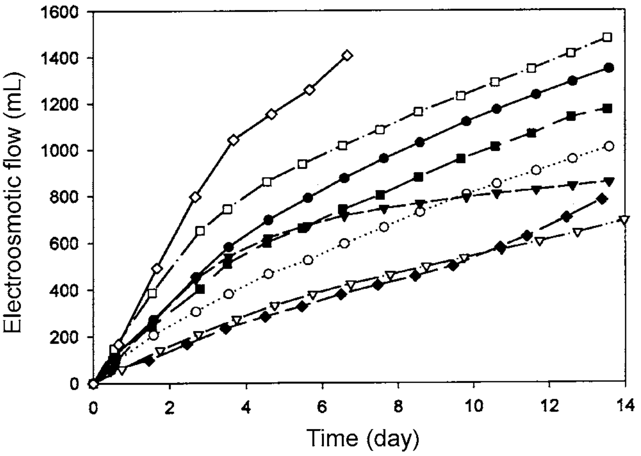

Fig. 3. Accumulated electroosmotic flow (● : Water, 14 days, 10 mA, ○ : APG, 14 days, 10 mA, ▼: Brij30, 14 days, 10 mA, ▽ : SDS, 14 days, 10 mA, ■: MEL, 14 days, 10 mA, □: BS–UC, 14 days, 10 mA, ◆: H_2O_2, 14 days, 5 mA, ◇ : H_2O_2, 7 days, 10 mA).

In the case that APG and SDS were used as additives, the electrical potential gradient initially increased and remained an almost constant value, about 9 V/cm. The electrical potential gradient of MEL, BS–UC, Water, Brij30 was finally reached the values of 13.2, 14.7, 16.0 and 18.0 V/cm after 14 days, respectively.

The difference among profiles of electrical potential gradient causes different EOF at each experimental condition. As to same additives, high electrical potential gradient usually induces high EOF and high removal efficiency. Except for the case of Brij30, EOF gradually increased with different slopes (Fig. 3). The slope of EOF of Brij30 decreased as to time due to its relatively low hydrophilicity. Three

Table 2. Removal efficiency of phenanthrene in soil.

Experiment	Additive	Removal efficiency (%)	EOF (mL)
1	Water	4.23	1345
2	APG	11.1	1006
3	Brij30	6.31	857
4	SDS	9.97	695
5	MEL	16.2	1171
6	BS-UC	17.4	1478
7	H_2O_2	54.7	779
8	H_2O_2	84.2	1406

experiments using chemical surfactants showed low EOF values because surfactants hindered the transport of solution to penetrate between soil particles. When H_2O_2 was added, EOF for 7 days was 379 mL at 5 mA and 1406 mL at 10 mA which was 3.7 times of amount at 5 mA. Accumulated EOF rapidly reduced when the constant current decreased by half because the electrical potential gradient at 5 mA was lower than that at 10 mA. The control of electrical potential gradient to obtain enough EOF is important but difficult because the relation between two parameters is not linear.

3.2. Phenanthrene Content in the Clay

Table 2 represents a removal efficiency of phenanthrene and accumulated EOF in the EK process. Removal efficiency is usually dependant on the amount of EOF. A removal efficiency by additives in this EK system was various. When H_2O_2 was added in this system, it showed much higher removal efficiency than others because it was the potential oxidation reaction called as Fenton reaction. Among different five kinds of surfactants, MEL and BS-UC had higher removal efficiency than chemically-synthesized surfactants although concentration of biosurfactant solutions was lower than those of chemical surfactant solutions. It is generally known that biosurfactants can obtain high removal efficiency with small amount. BS–UC was slightly higher efficiency than MEL because EOF of BS-UC was higher. In the Lab of Industrial Biotechnology, Southern Yangtz University, China, it was proved that the washing effect of BS–UC was higher than that of MEL at batch experiment (Hau et al., 1997). But the removal efficiencies between two biosurfactants was similar at EK system because surfactant solution at EK experiment continued to flow while solution at batch had no flow. Among three chemical surfactants, APG had higher value. Although APG is chemical surfactant, it is food grade surfactant with less toxicity and its biodegradability was higher than other two chemical ones (Yang et al., 2001). It is desirable to use APG, MEL and BS–UC which have low-toxicity and good biodegradability in EK system because these can minimize the secondary contamination and have environmental compatibility. Of two condition of H_2O_2, when the constant current was 10 mA, it had higher removal efficiency although the running time was just 7 days due to higher electrical potential gradient and higher EOF. Figure 4 shows profile of phenanthrene remained in soil at the end of experiment conducted with H_2O_2. The point 0.0 of x-axis represents starting position at the anode and the point 1.0 is position at the cathode. The direction of flow was from anode to cathode. The area under the curve means phenanthrene remained in soil and one above the curve presents phenanthrene degraded. In this figure, phenanthrene remained in the anode part was smaller amount than that in the cathode part because solution flowed anode to cathode and the anode part contacted with hydroxyl radical more times than the cathode part.

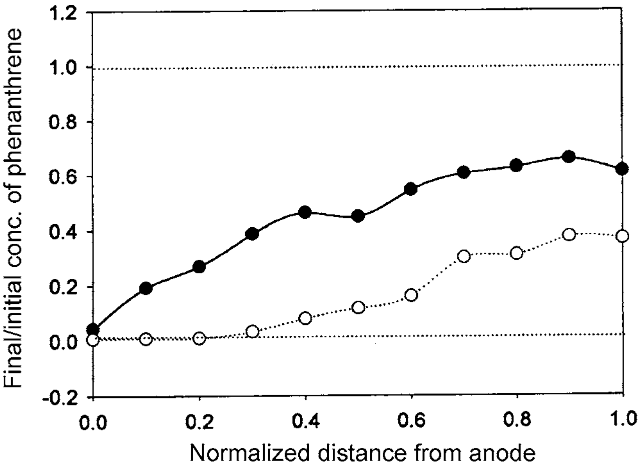

Fig. 4. Phenanthrene profile in the clay (● : H_2O_2, 14 days, 5 mA, ○: H_2O_2, 7 days, 10 mA).

4. CONCLUSIONS

In the removal of HOCs by EK, the control methods to increase removal rate of HOCs need to be incorporated in electrokinetic operation. In this research, surfactant which can enhance the desorption ability and mobility of HOCs existing on soil surface and hydrogen peroxide which has the ability to degrade HOCs rapidly were used as additives.

When H_2O_2 was used as additive, it had much higher removal efficiency than others. Among different five types of surfactants, the removal efficiency of MEL and BS-UC showed higher value than other surfactants. When biosurfactants mixed with culture medium were used, although these concentration was lower than those of chemical surfactant, these represented higher removal efficiencies. From this result, we could notice that soil washing with surfactant in EK system had limitation which could not expect high removal efficiency although it had characteristic of less toxicity to soil. It also has a disadvantage of secondary treatment of wastewater collected in the cathode reservoir. But in the case of H_2O_2, HOCs are immediately degraded to carbon dioxide and water in soil and a secondary treatment are not necessary. If a high removal efficiency of HOCs is achieved with minimum consumption of H_2O_2, the use of H_2O_2 as an additive in EK system will be preferable and environment-friendly.

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