

# Application of the electrokinetic-Fenton process for the remediation of kaolinite contaminated with phenanthrene

Soo-Sam Kim<sup>a</sup>, Jung-Hwan Kim<sup>b,\*</sup>, Sang-Jae Han<sup>a</sup>

<sup>a</sup> Department of Civil and Environmental Engineering, Hanyang University, 1271 sa-1 dong, Aansan, Kyunggi-do 425-791, South Korea

<sup>b</sup> National Research Laboratory for Environmental Remediation, Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology (Kaist), 373-1 Guseong-dong, Yuseong-gu, Daejeon 305-701, South Korea

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## Abstract

This study explored the feasibility of applying the electrokinetic-Fenton process (EK-Fenton process) for the remediation of contaminant sorbed onto soil possessing low-permeability. The relationship of H<sub>2</sub>O<sub>2</sub> stability and phenanthrene treatment, and the variation in the monitoring values were also investigated during the EK-Fenton process when catalyzed by heterogeneous minerals. Phenanthrene was chosen to represent hydrophobic organic contaminants (HOCs), which are widespread in the environment, and kaolinite was used as the low-permeability soil. In these experiments, the H<sub>2</sub>O<sub>2</sub> concentrations in pore water, the electrical potential distributions and the electrical currents were measured or monitored to assess the electrochemical effect in relation to injections of H<sub>2</sub>O<sub>2</sub> from the anode. The results suggested that intermediate anions (HO<sub>2</sub><sup>-</sup>, O<sub>2</sub><sup>-</sup>) with Fenton-like reaction affected significantly the variations in the electrical current during the EK-Fenton process. The addition of 0.01 N H<sub>2</sub>SO<sub>4</sub> to the anode reservoir improved the H<sub>2</sub>O<sub>2</sub> stability and the treatment of phenanthrene in the entire soil specimen. Therefore, use of H<sub>2</sub>O<sub>2</sub> and dilute acid, as an anode purging solution is a possible method for treating HOCs in low-permeability subsurface environments.

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## 1. Introduction

The in situ remediation of soils contaminated with organics is a significant problem as such soils are the complex media with many sorbed contaminants. It is particularly difficult to treat or remove contaminants possessing low water solubility and high octanol–water partition coefficients characteristics, such as HOCs. Thus, both the pump-and-treat and in situ soil flushing methods typically require movement of significant quantities of water during the long period for remediating contaminated soils. Furthermore, these technologies often are not directly applicable to fine-grain soils and sediments with low-permeability. Electrokinetic (EK) tech-

nologies are particularly useful for fine grained soils where the aforementioned technologies are impractical or impossible to use. EK is a process in which a low-intensity dc electrical current is applied across electrode pairs. The application of EK process is governed by electromigration and electro-osmosis with electrolysis reactions occurring at the electrodes [1,2]. The electrolysis of water produces hydrogen ions at the anode and hydroxyl ions at the cathode. The hydrogen ions generated at the anode produce an acid front. This front advances toward the cathode by electromigration, diffusions and advection (including the electro-osmotic flow). The electromigration of cation and anion towards their opposite electrodes is proportional to the ion concentration and the electric field strength. The electro-osmotic flow rate, due to the advection by electrical gradients is proportional to the zeta potential.

\* Corresponding author.

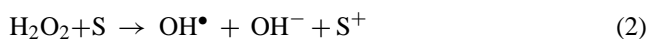
E-mail address: genkjh@wm.cau.ac.kr (J.-H. Kim).

During the last few years, EK technology has been applied successfully in the remediation of inorganic contaminant [1–4]. EK has also been shown to be highly efficient in the removal of partially dissociated organic species, such as acetic acid and phenol [5,6]. However, because of their low solubilities and slow desorption rates, HOCs are difficult to remove from subsurface environments with traditional EK technology. Therefore, the remediation process of these compounds using the EK method has been combined with other treatment process, such as flushing, bioremediation and chemical oxidation (Fenton process). Among these methods, the Fenton process has received much interest due to its ability to treat a wide range of contaminants in soils. Recently, this process has been extended to treating contaminated soils and groundwater, through the in situ injection of Fenton's reagents. Watts and his research group have conducted extensive studies on using a modified Fenton process for the treatment of soils contaminated with various organic pollutants.

In the Fenton's reaction, iron(II) catalyzes the decomposition of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) to hydroxyl radicals [7].



Similarly, the reaction of hydrogen peroxide with heterogeneous soil possessing iron mineral is usually defined by so called "Fenton-like reaction" [8].



where S is the surface of the heterogeneous soil possessing iron minerals. Miller and Valentine [9] studied the oxidation of organic contaminants in the presence of aquifer sand coated by iron. Hydrogen peroxide decomposition generates transient oxygen species in the mineral surface through a Fenton-like reaction. They proposed chain reactions with reaction catalyzed aquifer sand where superoxide anion ( $\text{O}_2^{\bullet-}$ ) and hydroperoxyl radicals ( $\text{HO}_2^\bullet$ ) form the hydroxyl radical. These radical species generating through this chain reaction degraded quinoline. They also suggested that the contaminant reaction rate was first and second order in relation to both the oxide and hydrogen peroxide concentrations.

$$\frac{d[\text{H}_2\text{O}_2]}{dt} = k_{\text{obs}}[\text{H}_2\text{O}_2] = k_{\text{mass}}[\text{H}_2\text{O}_2][\text{oxide}] \quad (3)$$

$$\frac{d[C_{\text{con}}]}{dt} = k_{\text{con}}[C_{\text{con}}][\text{H}_2\text{O}_2] \quad (4)$$

where  $k_{\text{obs}}$  is the observed first order decay coefficient of hydrogen peroxide,  $k_{\text{mass}} = k_{\text{obs}}/(\text{oxide})$ ; and  $(\text{oxide}) =$  concentration of oxide,  $k_{\text{con}}$  the second order degradation coefficient of contaminant;  $C_{\text{con}}$  the concentration of contaminant.

Watts et al. [10] investigated the sensitivity to other parameters, such as pH and iron mineral concentration. The rate of hydrogen peroxide decomposition increased as the pH and iron mineral concentration increased. The rate of nitrobenzene degradation also increased as the pH decreased. If the

other conditions, such as mineral composition, moisture content and chemical component of pore water, are common, the rates of hydrogen peroxide decomposition and contaminant degradation by mineral catalysis are dependent on the soil pH. Therefore, during in situ oxidation process, the soil-buffering capacity is an important factor to be considered.

Another phenomenon is sorption at the soil surface. Sorption not only retards the rate of transport of hazardous contaminants and decreases the transfer rate to the liquid phase, but it also significantly affects the rates of contaminant degradation with Fenton-like reaction. In most cases, a contaminant partition on soil organic matter or a mineral surface is not in direct contact with the agents responsible for its transformation [11]. Therefore, desorption is responsible for controlling the transformation of hazardous organic contaminants in soils. However, the addition of excess  $\text{H}_2\text{O}_2$  (0.3 M) has been shown to enhance the oxidative treatment of sorbed and NAPL contaminants [12]. This condition may not provide the reactants necessary to promote desorption of sorbed contaminants, but these same conditions may also enhance the oxidation of HOCs by a vigorous Fenton-like reaction. Kakala and Watts [13] performed column tests to treat hexadecane-sorbed soils. They showed that aggressive Fenton-like reactions had the potential to oxidize sorbed contaminants.

Yang et al. [14,15] conducted research on a combined EK and Fenton process. They gave this process the name "EK-Fenton process". After the artificially contaminated soils with phenol or TCE had been prepared in the cell, and iron powders established at the near anode and cathode, hydrogen peroxide and ferrous sulfate were injected from the anode chamber. The combined effects of the treatment and removal effectively realized remediation of the contaminants.

The EK-Fenton phenomenon is characterized by a complex process, which includes the effects of electro-osmosis, electromigration, electrolysis reactions and the mineral catalyzed Fenton-like reaction (hydrogen peroxide decomposition, organic contaminant degradation, etc.). Fig. 1 shows a schematic diagram of the EK-Fenton process treatment scheme. The transport rate of  $\text{H}_2\text{O}_2$  in soil is influenced by the advection resulting from electro-osmosis and decomposition, with Fenton-like reaction, at mineral surface. And the degradation and desorption of sorbed organic contaminants is also promoted by the radical species produced from the reaction between the introduced hydrogen peroxide and the heterogeneous soil particles.

The  $\text{H}_2\text{O}_2$  introduced from the anode chamber is transferred toward the cathode by the electro-osmotic flow, which is accompanied by the decomposition on the mineral surface, where the anions ( $\text{O}_2^{\bullet-}$ ,  $\text{HO}_2^-$ ) may move toward the anode due to electromigration. Particularly, since the rate of a Fenton-like reaction and the electro-osmosis are governed by the soil pH, the transport rate of the acid front during the EK-Fenton process affects the contaminant remediation and  $\text{H}_2\text{O}_2$  stabilization. Therefore,  $\text{H}_2\text{O}_2$  injected into the soil from the anode treats any organic contaminants by a Fenton-like reaction. During this series of procedures, the charac-

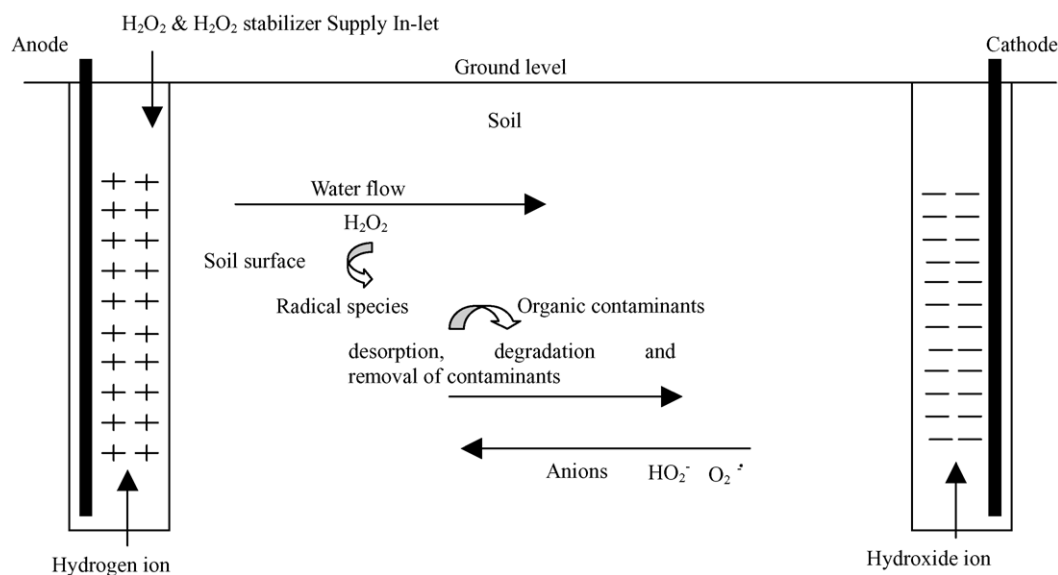


Fig. 1. Schematic diagram of electrokinetic-Fenton process catalyzed by minerals in the subsurface.

teristics of soils and their contaminants affect the treatment efficiency of the contaminants.

This research investigated the treatment availability of organic contaminant sorbed on the soil surface through the EK-Fenton process. The application of EK-Fenton technology in treating contaminated soil, with emphasis on strongly sorbed HOCs in the low-permeability soil, such as kaolinite, have not been studied, and the effect of the EK-Fenton process on the stability of  $H_2O_2$  remains to be investigated. Therefore, this research was conducted to see if the EK-Fenton process not only provides enhanced treatment of sorbed phenanthrene by mineral catalysis, but also improves the potential for stabilizing  $H_2O_2$  in the kaolinite. Namely, the behavior characteristics of  $H_2O_2$ , such as its decomposition, transport and stabilization, were evaluated, and the correlation of phenanthrene treatment and  $H_2O_2$  behavior was also assessed, during the EK-Fenton process. The role of  $H_2SO_4$  as the anode solution was investigated for improvement of treatment efficiency of phenanthrene. Phenol as the probe compound was selected to investigate the influence of ionic species on the stabilization of  $H_2O_2$  during the EK-Fenton process.

## 2. Experimental

### 2.1. Soil and chemicals

The EPK kaolinite was purchased from Feldspar Corporation. The test soil used was high quality kaolin clay, which was washed with water. Kaolin is often used for electrokinetic laboratory experiments because it has a low organic content and cation exchange capacity. The important properties are listed in Table 1. The iron and manganese concentrations, in different forms, were determined by a sequential extraction procedure that was proposed by the Commission of the Eu-

ropean Communities Bureau of Reference (BCR) [16]. The concentrations of the extracted ions were measured using an inductive coupled plasma-mass spectrophotometer (ICP-MS). The scheme differentiates the following four groups of elements: exchangeable and bound to carbonate; bound to Fe/Mn oxide; bound to organic matter and sulfide; residual fraction. Generally, the first three fractions are the soluble and amorphous solid representing more readily available sources for the Fenton-like reaction. Conversely, the residual solid in the fourth fraction should contain mainly primary and secondary minerals, incorporating elements in their crystalline structure that would be sparingly available. As shown in Table 2, the EPK kaolinite possesses much lesser amounts of Mn, while possessing appreciable amounts

Table 1  
Chemical and physical characteristics of EPK kaolinite

Parameter	EPK kaolinite
Major mineral component (XRD)	Kaolinite
Specific gravity of solid particles (ASTM D 854)	2.65
Particle size (%) (ASTM D 422)	
Clay	97
Silt	3
Sand	0
Specific surface area ( $m^2/g$ )	24.3
Organic carbon content (%) (Walkley and Black, 1934 <sup>a</sup> )	<0.1
Cation exchange capacity (meq/100 g) (U.S. Soil conservation service, 1972 <sup>b</sup> )	5.5–6
Extractable salts concentration (mg/kg)	
$SO_4^{2-}$ (extracted with 0.01 M HCl)	42
$NO_3^-$ (extracted with 0.01 M HCl)	13
Carbonate ions (soluble with de-ionized water)	N.D.
$Cl^-$ (soluble with de-ionized water)	N.D.
Initial soil pH (50%, water–solid)	5.6

<sup>a</sup> Reference [24].

<sup>b</sup> Reference [25].

Table 2  
Distribution of the different iron and manganese fractions in EPK kaolinite

	Fe (mg/kg)	Mn (mg/kg)
Exchangable and bound to carbonates	68.6	2.3
Bound to Fe-and Mn-oxides	184.9	0.2
Bound to organic substances	43.8	0.2
Residual fraction	3865.8	7
Total	4163.1	9.7

of Fe. The most solid Fe has crystalline structures, such as hematite and goethite. The concentrations of extractable  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  in the soil were determined by 0.01 M HCl extraction, and the soluble  $\text{Cl}^-$  and carbonate concentration in the soil by de-ionized water but the salts in the soils were only trace amount. In addition, the titration tests of pH versus acid inputs for the EPK kaolin and blank conducted for investigation of acid buffer capacity in relation to carbonate dissolution [17]. The results show that difference of two titration curve was not nearly, and then indicate that the carbonate dissolution from EPK kaolin generated not nearly.

Phenanthrene was selected as the representative HOC in this study and phenol was chosen as the probe compound. The phenanthrene (98%) and phenol (99.9%) were purchased from Aldrich Chemical Company.

The 35% hydrogen peroxide was supplied by Junsei Chemical Corporation. All other chemicals were purchased

from Fiser Scientific, and were reagent grade or high-pressure liquid chromatography (HPLC) grade. The double-deionized water ( $>18 \text{ M}\Omega \text{ cm}$ ) was purified with a Barnstead Nanopure-ultrapure system.

## 2.2. Electrokinetic apparatus

The basic electrokinetic apparatus was set up as shown in Fig. 2. The experimental apparatus was divided into four parts: two electrode chambers, an electrolyte solution reservoirs and a soil cell, where the soil was placed. The electrokinetic cell used for the tests was made of Plexiglas, and was 8 cm in diameter and 20 cm long. Seven passive electrodes were inserted into the soil cell and graphite electrodes were placed in contact with the chambers.

The electrodes were located at each end of the cell so that the electrolyte solution was only in contact with one face of each electrode. A filter paper was used at the end of the sample. The space of each chamber was placed between a porous stone and an electrode.

Nylon valves (PVC), at each of the cells, were used to control the inflow and outflow of the solution. The inlet at the bottom of the anode chamber was connected to a reservoir containing 2000 ml of anolyte solution, which was circulated using peristaltic pump.

A graduated cylinder (2000 ml volume) was used as a catholyte solution reservoir to measure the water volume transported. Gas vents were provided in the electrode cham-

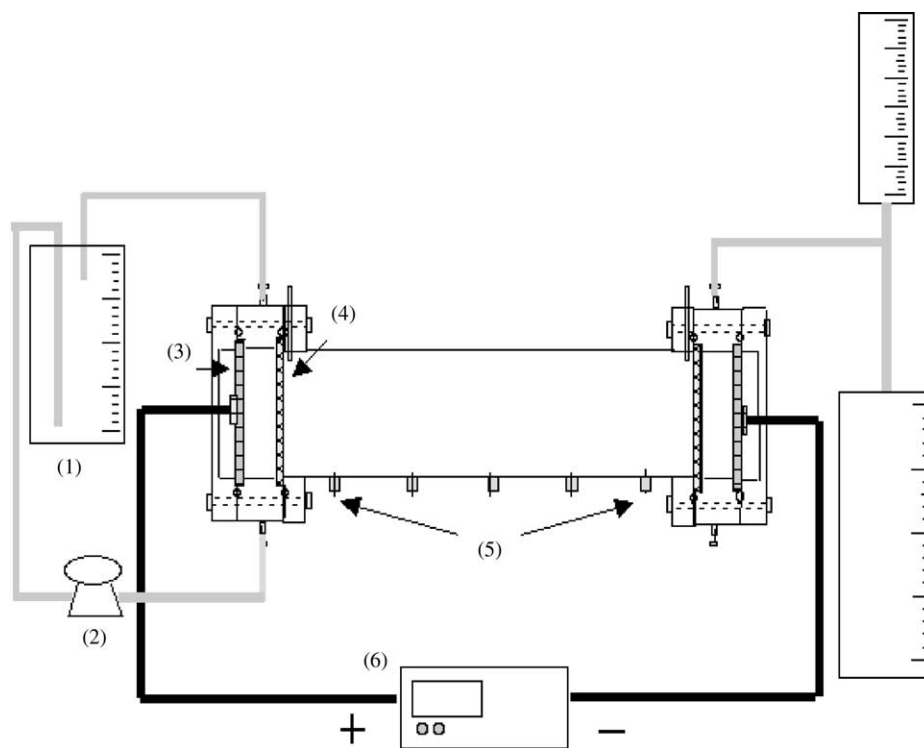


Fig. 2. Schematic diagram of electrokinetic apparatus: (1) anode reservoir; (2) peristaltic pump; (3) graphite electrode; (4) porous stone; (5) passive electrode; (6) power supply.

Table 3  
Summary of test program

Parameter	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7
Permeating fluid at the anode chamber	H <sub>2</sub> O <sub>2</sub> (7%)	H <sub>2</sub> O <sub>2</sub> (7%)	H <sub>2</sub> O <sub>2</sub> (7%) H <sub>2</sub> SO <sub>4</sub> (10 mN)	H <sub>2</sub> O <sub>2</sub> (3.5%)	H <sub>2</sub> O <sub>2</sub> (3.5%)	De-ionized water	De-ionized water
Duration (h)	240	486	312	240	240	240	240
Initial water content (%)	42.1	42.3	42.5	42.3	42.1	42	41.8
Initial soil pH	5.6				5.4		5.6
Initial concentration of spiked compound (mg/kg)	Phenanthrene (200)				Phenol (200)		Phenanthrene (200)

bers for the escape of any gases resulting from the electrolysis reactions.

### 2.3. Methods

#### 2.3.1. Preparation of the test specimen

In this test, phenanthrene, dissolved in hexane, was mixed with the soil to obtain the required concentration of 200 mg/kg of dry soil, and the hexane allowed evaporating. This soil was then made up to a moisture content of 70% with de-ionized water. The contaminated soil with phenol was prepared using phenol stock solution prepared in de-ionized water. The soil was then statically compacted into a cell using an air pressure of 150 kPa for 7 days. The cell was, then, inserted into the main testing chamber.

#### 2.3.2. Operating conditions

An electrical potential of 30 V was applied to the EK apparatus for the entire test. For tests 1–7, the testing program is summarized in Table 3. Tests 1–4 were spiked with phenanthrene. Tests carried out room temperature at 25 °C. In tests 1–3, 7% hydrogen peroxide was used as the anode reservoir fluid. In tests 1 and 2, only 7% hydrogen peroxide was used as the anode purging solution, and test 2 was a long-term experiment of test 1. Test 3 used an anode purging solution of 10 mN H<sub>2</sub>SO<sub>4</sub> and 7% hydrogen peroxide.

Tests 1 and 4 were conducted under the same conditions, with exception of a 3.5% hydrogen peroxide injection from the anode chamber. Test 7 was blank test for soil spiked with phenanthrene. These tests were run under different conditions to examine the effects of the sorbed contamination treatment on the EK-Fenton process. Tests 5 and 6 were spiked with phenol, and 3.5% hydrogen peroxide and de-ionized water used as the purging solutions, respectively.

Tests were also conducted to investigate the effects due to the characteristics of the spiking compounds. For all the tests, de-ionized water was used as the cathode reservoir fluid.

#### 2.3.3. Chemical analysis

At the end of each experiment, the cell filling was sliced into layers of approximately 2 cm, and each sectioned sample well mixed. The 10-sectional soil samples were measured for

pH and moisture content. Soil-pH-values were measured in a mixture of 5 g-soil and 25 ml-deionized.

The phenanthrene in the liquid samples was extracted by triple liquid–liquid extraction, using a total of about 50 ml dichloromethane. To extract the phenanthrene from the soil, the soil sample (2.5 g) was transferred to a 10 ml borosilicate screw-top tube. An amount of 7.5 ml of a 1:1 dichloromethane:methanol mixture was added to the soil, and the soil–solvent suspension shaken (200 rpm) for 72 h at 30 °C. The tube was then centrifuged for 15 min, and the solvent mixture transferred to a 10 ml test tube. An amount of 1 g of anhydrous sodium sulfate was mixed with the phenanthrene-containing solvent to completely remove residual water. The phenanthrene concentration was determined using a Gibson 305 system equipped with UV and fluorescence detectors. A mixture of water and methanol, 20:80, was used as the mobile phase at a constant flow rate of 1.0 ml/min. The detector wavelength was set at 254 nm. Using this procedure, 75% of the phenanthrene spiked into EPK kaolinite was recovered. This result indicates that some irreversible sorption/partitioning of the phenanthrene into EPK kaolinite might have occurred, due to EPK kaolinite possessing soil properties of a small particle size and high soil surface area. After the phenanthrene concentration of 10-sectional sample had been analyzed by HPLC, the average value of the adjacent parts was used as the representative phenanthrene concentration.

After the soil had been diluted and centrifuged, the residual hydrogen peroxide concentration in the supernatant was analyzed by iodometric titration [18].

## 3. Results and discussion

### 3.1. Correlation of electro-osmotic flow, electrical potential and electrical current

Fig. 3 shows the variation in the electrical current with time. In all the tests using the kaolinite spiked with phenanthrene and phenol, the electrical current initially increased rapidly, reached a peak within 1–24 h, then decreased and stabilized at a nearly constant value. Tests 1, 3, 4 and 7 using kaolinite contaminated with phenanthrene, were conducted



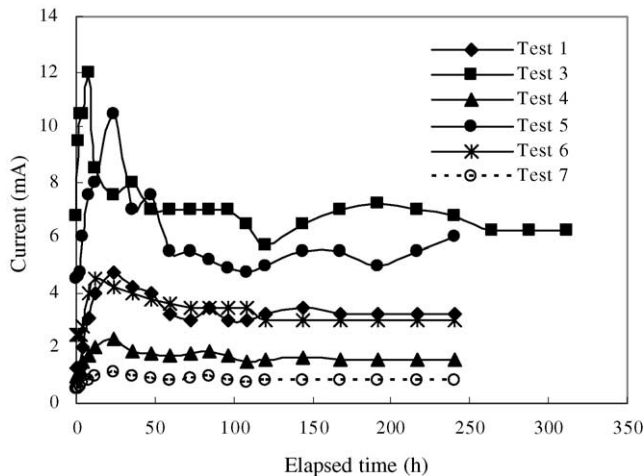


Fig. 3. Electrical current measurements.

to study variation in the current as a function of the different anode purging solution.

It was clear, in test 1 using only 7%  $\text{H}_2\text{O}_2$  as the anode purging solution, the electrical current was higher than that in test 4, where only 3.5%  $\text{H}_2\text{O}_2$  was used. Furthermore, in test 3, that was higher compare to test 7 using de-ionized water as the anode purging solution. By comparing tests 5 and 6 using kaolinite spiked with phenol, the electrical current in test 5 using 3.5%  $\text{H}_2\text{O}_2$  solution was higher than that in test 6 that used de-ionized water as the anode introduction solution.

These results show that the electrical current increased as the  $\text{H}_2\text{O}_2$  concentration of the anode purging solution increased. The reason for the electrical current increase was the generation of ionic compositions in the pore water and chambers. The trends shown in Fig. 3 suggest that the ionic concentration of pore water was increased by the spread of  $\text{H}_2\text{O}_2$  from the anode chamber. In Table 1, the salts, such as  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{HCO}_3^-$  and  $\text{Cl}^-$ , released from the soils was at very trace levels. Therefore, based on the chain reaction in Eqs. (2)–(4), theory of electrical neutrality in the pore solution [19] and the results of Fig. 3, the generation of  $\text{O}_2^{\bullet-}$  or  $\text{HO}_2^-$  anions with Fenton-like reaction increased electrical conductivity in the pore solution, which resulted in increase of an electrical current during the EK-Fenton process.

Fig. 4 shows that the electrical potential was induced across the soil specimen ( $E_{\text{cell}}$ ) when the test started with a 30 V electrical potential between both electrodes. Although an electrical potential of 30 V was applied to the EK apparatus, including the electrode chamber, the  $E_{\text{cell}}$  generated a lower value than 30 V. The initial electrical potential across the soil cell was about 12–23.5 V, and monotonically increased to the final range of 23–28 V. In tests 3 and 5, the  $E_{\text{cell}}$  was higher than in the other tests.

Due to the characteristics of the electrolyte solution in the reservoir and the contaminants in the soil, the  $E_{\text{cell}}$  developed indicated different results. The magnitude of  $E_{\text{cell}}$  was proportional to the relative electrical conductance at the electrode chamber in contact with the soil specimen. In tests 3 and

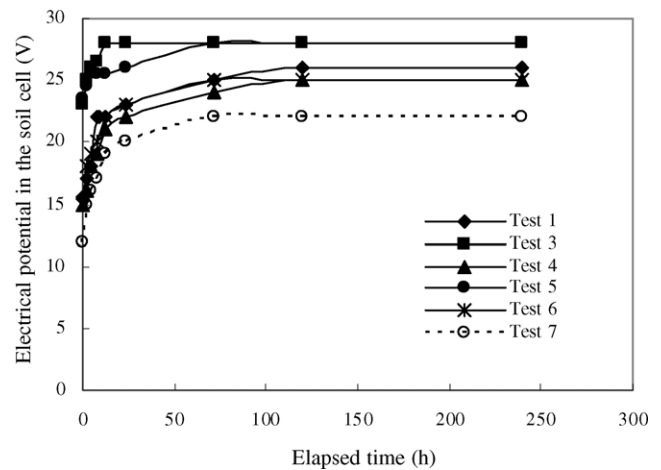


Fig. 4. Electrical potential in the soil cell ( $E_{\text{cell}}$ ) during EK-Fenton process ( $E_{\text{cell}}$  indicate that electrical potential was measured by the passive electrode, which inserted at the both end of the soil specimen).

5, since the concentrations of the ionic species ( $\text{H}^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{HO}_2^-$ ,  $\text{O}_2^{\bullet-}$  and phenolate ( $\text{C}_6\text{H}_5\text{O}^-$ )) at the anode chamber and in the soil were higher, electrolysis rate was higher than in the other tests. Therefore, as the electrical conductance in the electrode chambers increased more than in the other tests, due to increases in the  $\text{H}^+$  and  $\text{OH}^-$  ions in the electrode chambers, the magnitude of the induced electrical potential in the electrode chambers is decreased more than in the other tests, and as a result, the  $E_{\text{cell}}$  was increased more than in the other tests.

Fig. 5 indicates the evolution of a relative electrical potential ( $V/V_{\text{cell}}$ ) distribution during the course of these tests. In tests 1, 2 and 4, from 72 to 240 h, the relative electrical potential difference between the anode end of soil specimen and the passive electrode inserted, 2 cm from the anode end of soil specimen, was larger than in the other regions, and the electrical potential distribution in the soil remained nearly constant as time elapsed. These results indicate that, from 72 to 240 h, the ionic concentration distribution in the soil remained almost constant.

Conversely, in test 3, the potential gradient in the regions near the anode had much smaller values than in the other tests, and a very low potential gradient region gradually developed from the anode end toward the cathode as time elapsed.

The trend in test 3 suggests that the ionic concentration of the pore water gradually increased in the anode region, and that the region of higher ionic concentration extended toward the cathode over time. Wada and Umegaki [19] found that  $\text{Cl}^-$  ions gradually speeded toward the cathode, due to the electro-osmotic flow, when NaCl was injected the anode chamber. This phenomenon could explain the trend in test 3. Namely, the main cause of the potential flattening was the transportation of  $\text{SO}_4^{2-}$  ions toward the cathode due to the electro-osmotic flow.

Test 5, in Fig. 5, indicates that the entire electrical potential gradient trend in the soil specimen was different from that in

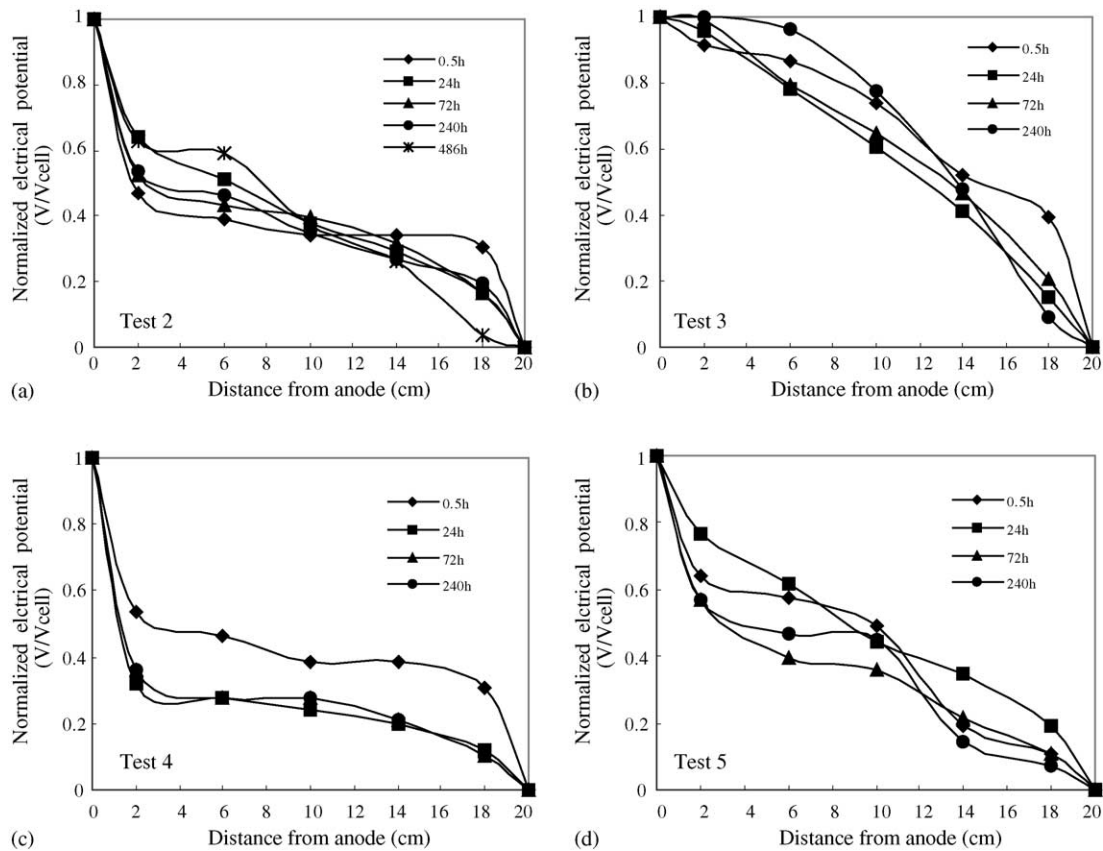


Fig. 5. Development of electrical potential distribution: (a) test 2; (b) test 3; (c) test 4; (d) test 5.

tests 1 and 4. An electrical potential distribution produced relatively irregular variations during the test period. These results signify that the characteristics (ionic and non-ionic compound) of compounds in the soil made the distribution of the ionic concentration change in the soil specimen.

On the application of the electrical potential, the pore water was transported to the cathode chamber by electro-osmotic flow. Fig. 6 indicates the cumulative volume of the effluent

against the elapsed time. The results show that the differences in the anode reagents and compounds in the soil had a significant effect on the flow rate for this process. In 240 h, the cumulative volumes produced in tests 1 and 2 were 292 and 294 ml, respectively, and those in tests 3, 4, 5 and 6 generated 429, 179, 433 and 316 ml, respectively. Test 7 produced the smallest cumulative volume of 120 ml. Test 2 produced a total flow of 479 ml in 486 h, while test 3 produced a total flow of 498 ml in 312 h.

These results suggested that the electro-osmotic flow rate during these tests were affected by factors in the soil, such as the  $E_{\text{cell}}$ , electrical current and electrical potential distribution. It is likely that differences in these monitoring values led also to the variations in the electro-osmotic flow rates.

Tests 3 and 5, in Figs. 4 and 5, show a higher  $E_{\text{cell}}$  than in the other tests and a lower electrical potential loss than in the other tests. Therefore, in the cases of tests 3 and 5 in Fig. 5, these phenomena result in the faster electro-osmotic flow rate compare to the other tests. Similarly, the electro-osmotic flow rate was faster in test 1 than in test 4. These results were attributed to the higher  $E_{\text{cell}}$  in test 1 compared to test 4, and that the electrical potential loss in the anode region was lower in test 1 than in test 4.

Furthermore, by comparing all the tests, the electro-osmotic flow rates were proportional to the current magnitude

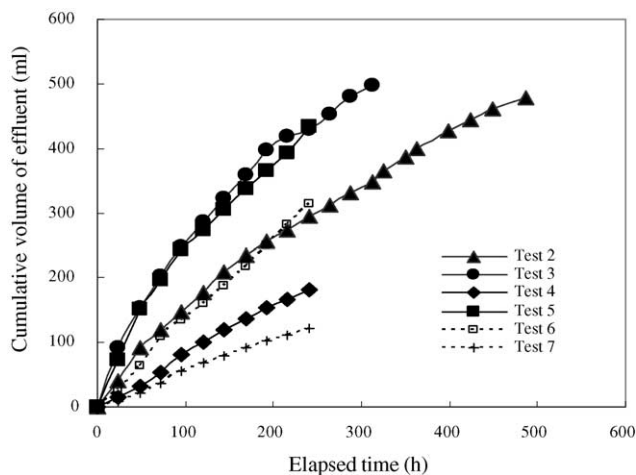


Fig. 6. Cumulative volume of effluent plotted against elapsed time.

generated during the test periods. These results were in agreement with the research results of Hamed and Bhadra [20], where the electro-osmotic flow rates increased as the electrical current densities increased.

Consequently, these results suggest that the cumulative electro-osmotic flow quantity increased as the value of  $E_{\text{cell}}$  increased [21], and as the electrical potential loss in the anode region decreased, the electrical current increased.

### 3.2. pH and residual concentration of $\text{H}_2\text{O}_2$ in the soil specimen after tests

After the tests, the residual  $\text{H}_2\text{O}_2$  concentration and pH in the soil specimens, in relation to the kind of anode purging solution, contaminant in the soil and test period, are shown in Fig. 7. In addition, after the tests,  $\text{H}_2\text{O}_2$  concentration in the anode chamber measured same value compared to initial concentration of  $\text{H}_2\text{O}_2$ .

Tests 1 and 2 were conducted to compare the effect of the test period, 240 and 486 h, respectively. The data in Fig. 7(a) show that the residual  $\text{H}_2\text{O}_2$  concentration in test 2 was 3.97% in the  $z=0.05$  region, and remained detectable to the  $z=0.95$

region ( $z$  is the normalized distance from the anode end in the soil column; i.e.,  $z=Z/L$ , where  $Z$  is the distance from anode end in the soil column and  $L$  the soil column length). On the other hand, the residual  $\text{H}_2\text{O}_2$  concentration in test 1 was 2.45% in the  $z=0.05$  region, and could be detected to the  $z=0.75$ . In addition, the residual  $\text{H}_2\text{O}_2$  concentrations in the entire soil specimens were higher in test 2 than in test 1. After these tests, the pH values in the soil specimen were lower in test 2 than in test 1 with the exception of the  $z=0.95$  region.

These results signify that, although  $\text{H}_2\text{O}_2$  was decomposed by catalysis of the soil surface during the movement toward the cathode from the anode chamber,  $\text{H}_2\text{O}_2$  gradually speeded toward the cathode. Namely, as time elapsed, the increase of the residual  $\text{H}_2\text{O}_2$  concentration was attributed to the  $\text{H}_2\text{O}_2$  transport rate toward the cathode overcoming the  $\text{H}_2\text{O}_2$  decomposition rate in the soil specimen. By comparing tests 1 and 2, the residual concentration of  $\text{H}_2\text{O}_2$  increased over time. These results were attributed to the decomposition rate of  $\text{H}_2\text{O}_2$  in the soil specimen decreasing as the acid front was transported toward the cathode, over time, although the flow rate decreased slightly during the test period in test 2.

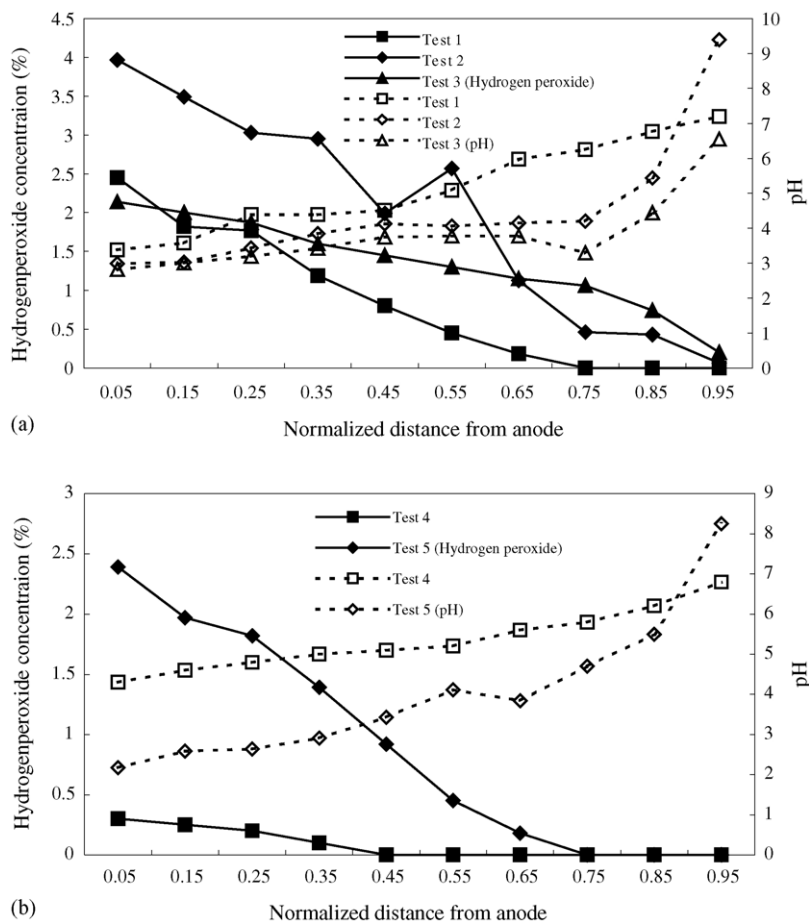


Fig. 7. Residual  $\text{H}_2\text{O}_2$  and pH distribution in the soil specimens after the tests. (a) The tests using kaolinite spiked with phenanthrene to investigate effects in relation to the test period and anode purging solution. (b) The tests using kaolinite, spiked with phenanthrene or phenol, to investigate the effects in relation to the contaminant characteristics (ionic or non-ionic).



The role of  $\text{H}_2\text{SO}_4$  on the stabilization of  $\text{H}_2\text{O}_2$  was investigated in test 3 using 0.01 N  $\text{H}_2\text{SO}_4$  and 7%  $\text{H}_2\text{O}_2$  as the anode purging solution. The residual  $\text{H}_2\text{O}_2$  concentration was 2.14% in the  $z=0.05$  region, and gradually decreased toward the cathode from the anode. By comparing tests 1–3, the residual  $\text{H}_2\text{O}_2$  concentrations in the soil specimen were

higher in test 3 than in test 1, with the exception of  $z=0.05$  region. Furthermore, although the test period in test 2 was longer than that in test 3, the residual  $\text{H}_2\text{O}_2$  concentration in the  $z=0.75$ – $0.95$  regions was higher in test 3 than in test 2. In test 3, the result signifies that the acid front extended to the adjacent regions of the cathode, and that the  $\text{H}_2\text{O}_2$  decompo-

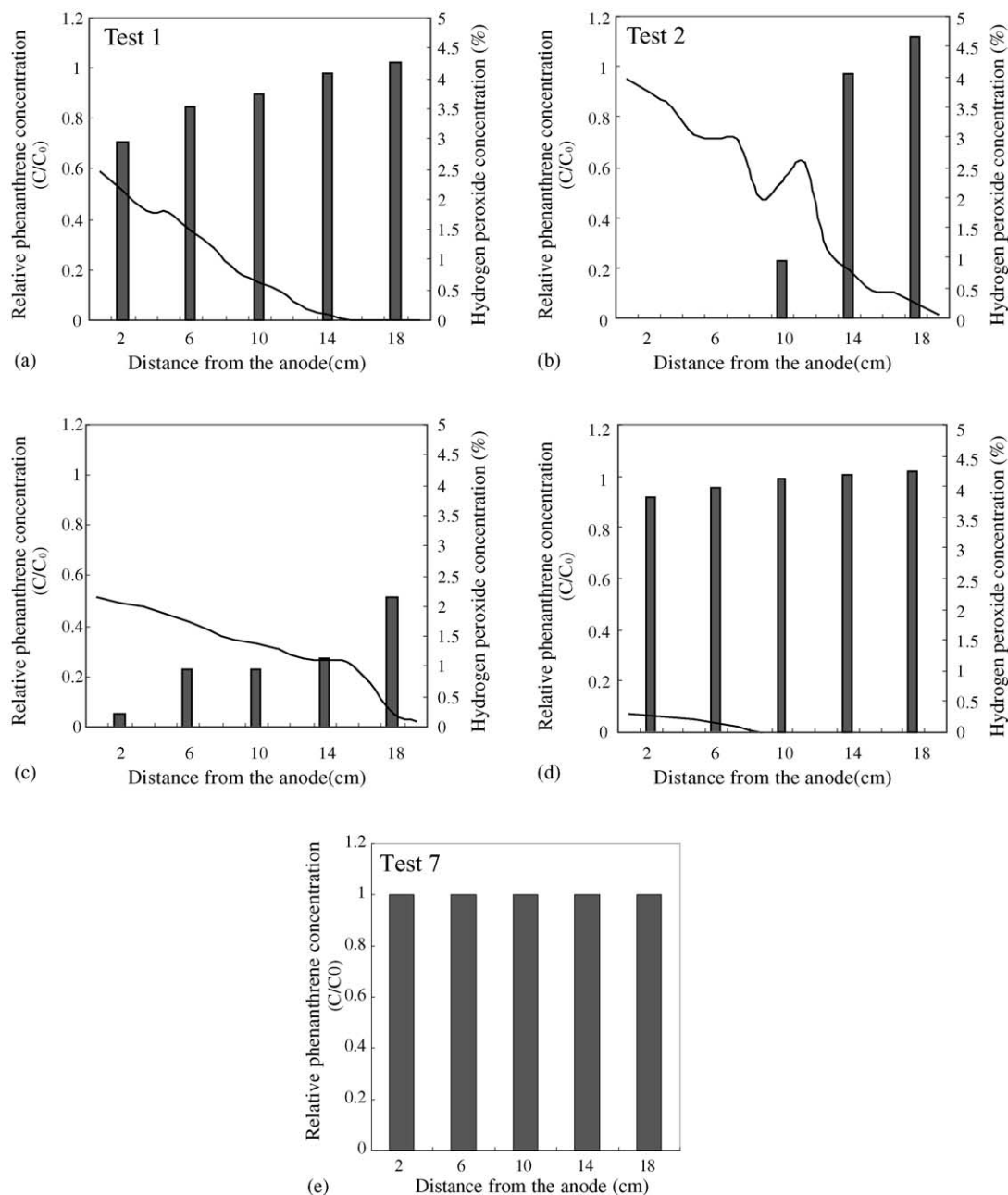


Fig. 8. The distributions of the residual phenanthrene and hydrogen peroxide in the soil specimen after the tests: (a) test 1; (b) test 2; (c) test 3; (d) test 4; (e) test 7.

sition rate in the cathode regions was reduced. In addition, in Fig. 6, the electro-osmotic flow rate was higher in test 3 than in test 1 and 2. For these reasons, in the case of test 3, the stabilization of  $\text{H}_2\text{O}_2$  in the cathode regions improved more than in the other tests.

In Fig. 7(b), the results indicate that the electrolysis reactions at the electrodes, together the transport of the background ions, play a major role in the development of pH in the soil specimen. In test 5, the phenolate ion ( $\text{C}_6\text{H}_5\text{O}^-$ ) concentration in the soil specimen increased the electrical current during the test period. At the same time, the concentration of  $\text{H}^+$  ions in the anode reservoir increased as the rate of the electrolysis reactions at the electrodes increased, and as a result, the advancement rate of the acid front toward the cathode increased. Furthermore, the transport rate of the acid front was higher than that of the base front moving from the cathode [22]. It is for these reasons that the pH in the soil specimen was lower in test 5 than in test 4, with the exception of the  $z=0.95$  region. In the soil specimen, these factors resulted in the reduction of the  $\text{H}_2\text{O}_2$  decomposition rate and the improvement of the  $\text{H}_2\text{O}_2$  stability.

### 3.3. Distribution of phenanthrene after EK-Fenton process

The results combining the residual concentration of the phenanthrene and  $\text{H}_2\text{O}_2$  are shown in Fig. 8. In test 7 using deionized water, treatment of phenanthrene did not generate nearly after test. In tests 1 and 4, using only 7 and 3.5%  $\text{H}_2\text{O}_2$  as the anode purging solution during the 240 h, respectively, the phenanthrene was slightly treated in the region near the anode, compared with tests 2 and 3. In test 2, with identical conditions to test 1, with the exception of the longer experiment period, the residual phenanthrene was not detected within 6 cm from the anode and the phenanthrene in the 10 cm region from the anode was about 80% treated.

However, the phenanthrene in the regions near the cathode was hardly treated and, the residual phenanthrene concentration in the 18 cm region from the anode indicated that about 10% of initial concentration was exceeded. In test 3, using 0.01 N  $\text{H}_2\text{SO}_4$  and 7%  $\text{H}_2\text{O}_2$  as the anode purging solution, the phenanthrene treatment effect was improved in the soil specimen. The phenanthrene in the entire soil specimen was 74% treated, and even 49% treated in the region nearest the cathode.

According to these results, values exceeding the initial phenanthrene concentration in the soil specimen were not measured, with the exception of test 2. However, since an error of  $\pm 10\%$  might be produced by a slightly inhomogeneous phenanthrene concentration in the soil, the excessive value in test 2 might include the error limit. In addition, the phenanthrene in the effluent was not measured. Therefore, under these test conditions, the results suggest that the phenanthrene degradation occurred in the sorbed state, or that the rate of phenanthrene degradation was as fast as the rate of phenan-

threne desorption at the soil surface. When the residual  $\text{H}_2\text{O}_2$  concentration after test was considered, the results agreed with those of Watts and Stanton [12], in that the addition of excess  $\text{H}_2\text{O}_2$  (0.3 M) enhances the oxidative treatment of sorbed contaminants. Consequently, these results signify that the major treatment mechanism of the phenanthrene might not be removal but degradation.

The effect of phenanthrene oxidation in the soil specimen was relevant to the stabilization of the  $\text{H}_2\text{O}_2$  in the soil specimen (Fig. 8). Baciocchi et al. [23] suggested that the efficiency of 3-chlorophenol oxidation increased as  $\text{H}_2\text{O}_2$  life time increased.

In test 4, using 3.5%  $\text{H}_2\text{O}_2$  as the anode purging solution, the phenanthrene was hardly degraded in the soil specimen, since the  $\text{H}_2\text{O}_2$  had hardly been introduced into the soil specimen. In comparison with test 4, the treatment effect in test 1 improved as the  $\text{H}_2\text{O}_2$  stabilization in the soil increased. Furthermore, the results reported in Fig. 8(b and c) indicate that phenanthrene degradation yield increased to a greater extent in tests 2 and 3 than in tests 1 and 4 as the residual  $\text{H}_2\text{O}_2$  concentration increased. Therefore, the correlation between the degradation yield of phenanthrene and the stabilization of  $\text{H}_2\text{O}_2$  in the soil specimen was confirmed.

However, by comparing tests 2 and 3, although the operating time was longer in test 2 than in test 3, and the residual  $\text{H}_2\text{O}_2$  concentration in the 14–20 cm region from the anode were nearly the same, the treatment efficiency in the regions was lower in test 2 than in test 3.

The results suggest that the phenanthrene degradation rate was affected by other factors than the  $\text{H}_2\text{O}_2$  concentration in the soil specimen or the operating time. In Fig. 7, the pH in the regions was lower in test 3 than in test 2. The results suggest that the rate of the acid front advancement affected the phenanthrene degradation rate.

The reaction of hydroxyl radicals formed through the Fenton mechanism was fast at low pH, whereas the rate of hydroxyl radical production decreased at a neutral pH [15]. Since the latter process is the predominant route of oxygen evolution, the contaminant degradation rate is probably low. Consequently, since the advancement rate of the acid front was higher in test 3 than in test 2, the treatment efficiency in the cathode regions increased to a greater extent in test 3 than in test 2.

## 4. Conclusion

This research was conducted to investigating phenomenon and applicability of the EK-Fenton process for the remediation of low-permeability soil contaminated with PAHs.

The present experimental results suggest that, according to increase of  $\text{H}_2\text{O}_2$  addition in the anode solution, the increase of anions ( $\text{HO}_2^-$  and  $\text{O}_2^{\bullet-}$ ) with chain reaction resulted in that of the electrical current. Therefore, when  $\text{H}_2\text{O}_2$  of high concentration introduce from the anode, the generation of intermediate anions with Fenton-like reaction will

affect significantly electrochemical phenomenon during the EK-Fenton process.

The results of this research show that the residual concentration of  $H_2O_2$  was proportional to the transfer rate of the acid front due to acid addition from the anode and increase of electrolysis rate together the transport of ionic composition in the soil. Furthermore, the phenanthrene degradation yield was proportional to the transfer rate of the acid front and  $H_2O_2$  stability.

Therefore, to effectively treat sorbed contaminant on soils during the EK-Fenton process, an injection of acid is necessary, but to an extent that does not decrease the electro-osmotic flow rate.

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