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Enhancement with Carbon Nanotube Barrier on 1,2-Dichlorobenzene Removal from Soil by Surfactant-Assisted Electrokinetic (SAEK) Process – The Effect of Processing Fluid

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Abstract: A surfactant assisted electrokinetic remediation (SAEK) process coupled with CNT barrier has been investigated for 1,2 DCB removal under potential gradient of 2.0 V/cm. A better removal of 1,2 DCB up to 75.5% was achieved in EK/CNT system with SDS as processing fluid. Lower removal was found in system with PANNOX 110, which might be due to low affinity of 1,2 DCB in PANNOX 110 micelle. Removal of 1,2 DCB in EK/CNT system was mainly contributed by surface sorption on CNT rather than by EK process. Among the electrical removal mechanisms, electrophoresis became more critical with the surfactant as processing fluid.

Keywords: Carbon nanotube, dichlorobenzene, electrokinetic, permeable barrier, soil remediation, surfactant

INTRODUCTION

Contamination of groundwater and soils due to anthropogenic activities has long been a significant problem in most countries. Dichlorobenzenes

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are so widely used in industrial and domestic uses, such as intermediates in the synthesis of other chemicals, solvents, hygiene products, and components of dielectric fluids (1). As a consequence, it results as ubiquitous in all major environmental compartments for dichlorobenzene. By their nature, they are highly toxic and poorly biodegradable in the environment. It is difficult to remove dichlorobenzenes from subsurface environments using traditional pump-and treat technologies (2,3). Most technologies have been focused on removal of 1,2 dichlorobenzene (1,2 DCB) in aqueous phase, such as adsorption, membrane separation (4), catalytic reduction (5), and biotransformation (6). However, less attention was focused on 1,2 DCB remediation in soil. There is a definite need for efficient methods of decontamination of 1,2 DCB from soil.

The electrokinetic (EK) remediation process is a promising innovative technology for decontamination in low hydraulic permeability media. Basically, the EK technique is upon the action of an electric field generated between inserted electrodes in the medium by applying a direct current or a constant voltage. The applied potential causes the migration of electrolyte solution and soluble contaminants toward the electrodes via electromigration, electroosmosis, and electrophoresis (7,8). Various enhancement techniques, i.e., careful management of the pH within the electrode (9,10), addition of hydroxyl ion membranes (11), chelating agent (12,13), and enhancing reagent (14,15) in the cathode reservoir, have been proposed to improve the effectiveness of the EK system. Additional parameters affecting EK performance included potential gradient and processing time, which was dependant on the characteristics of soils and contaminants. Many researches have shown excellent electrokinetic removal efficiencies for metals from low permeable subsurface environments (16–19). However, the removal efficiencies for hydrophobic organic compounds (HOCs) by electrokinetics are still low.

Surfactants can enhance HOCs solubility in aqueous phase. They are amphipillic molecules and can improve the mass-transfer of HOCs from the solid or nonaqueous phase into aqueous phase by decreasing the interfacial tension and by solubilizing the HOCs into the micelles. As a consequence, surfactant-assisted electrokinetic remediation (SAEK) becomes an effective solution for in-situ remediation of organic contaminated soils with low hydraulic conductivities. The SAEK process has been extensively studied in recent years for HOCs removal from soil and nonaqueous phases. Effect of cationic surfactants (cetyltrimethylammonium bromide, CTAB) on hydrocarbon removal by electrokinetics was investigated by Ranjan et al. (20). It was reported that CTAB coupled with the electrokinetic method retarded the removal of hydrocarbons due to strong interaction of CTAB with soil particles. Mixture of anionic and nonionic surfactants was investigated to enhance the electrokinetic removal of ethyl benzene from clay (21). It was concluded that surfactant addition resulted in 1.6 to 2.4 times more removal than electrokinetic alone. Removal characteristics of Phenanthrene using a surfactant-enhanced electrokinetic (EK) process were investigated by Yang et al. (22). Results showed alkyl polyglucosides (APG) micelles containing phenanthrene easily migrated to the cathode reservoir by electroosmosis flow (EOF). Calfax 16L-35, an anionic surfactant, did not enhance the removal efficiency even at the highest concentration because higher adsorption of Calfax 16L-35 was found in the soil phase. It was thought that, during the electrokinetic process, Calfax 16L-35 was adsorbed onto soil and the migration of the surfactant from cathode to anode was superior to EOF due to anionic charges of Calfax 16L-35. A nonionic surfactant, APG, seems to be suitable for surfactant-enhanced electrokinetic remediation. A highly insoluable compound, DDT, has been treated by surfactant-assisted electrokinetic process (SAEK) (24). It was reported that the aqueous solubility of DDT was enhanced from 0.01% to 13% and yielded a better electrokinetic removal performance. The migration of DDT overcame the opposite electrosmotic flow and, consequently, transported toward the anode within the negatively charged micelles (SDBS). This was highly attributed to the lower interaction between the soil and SDBS.

Nanotechnology has caused considerable attention in recent decades and widely applied to engineering technology. The positive potential effects of nanotechnology to environment include:

a. decreasing materials used;
b. minimizing pollutants production; and
c. enhancing removal efficiency of pollutants in environmental remediation.

Among those, carbon nanotube (CNT) has become a prominent material applied in the removal of aqueous and gaseous pollutants due to the characteristic of high specific surface area, high reaction ability, and high electron transfer capacity (24–26). It is highly expected that CNT becomes a potential barrier material to the removal organic pollutant from subsurface.

The objective of this study is to investigate the enhancement of CNT barrier on SAEK process for removal of 1,2 chlorobenzene from spiked soil. This composite technology involves the application of an electrical field across a porous medium to induce the movement of electrolyte solution and the soluble contaminants will be separated by adsorption onto the CNT barrier. Two different types of CNT, unpurified CNT and acid purified CNT, and two different kinds of surfactants, SDS and PANNOX 110, were chosen as barrier materials and processing fluids in this study, respectively. The effectiveness of 1,2 chlorobezene removal and electrokinetic behavior in each SAEK process were investigated.

EXPERIMENTAL MATERIALS AND METHOD

Soil Selection and Characteristics

Soil samples were collected from a depth of approximately 0.7–1.5 m below the surface within a farmland located in southern Taiwan. Table 1 shows the properties of the soil sample. The texture of this soil was classified as clay. A soil organic matter content of 3.73% was observed by the combustion method (27). The soil pH was measured in water suspensions at 1:1 ratio of soil to solution by volume. The pH of zero point charge (pH_{zpc}) of soil samples was determined by a zeta potential instrument (Pen Kem-Laser Zee 3.0, USA). The solid density of soil was determined according to the method of ASTM D854-92. The specific surface areas of soil was measured by a BET surface areas analyzer (ASAP 2010, Micromeritics, USA) and the particle diameter was measured by a laser particle analyzer (Coulfer Ls100, England). The hydraulic conductivity for the soil sample was measured by a falling-head permeameter, which was less than 10^{-8} cm/sec.

After removing debris and air-dry, the soil sample was sieved to less than 2 mm in diameter and then treated by pressure sterilization of 117.6 kPa for 5 min. The soil sample was then crushed and the 1,2 Dichlorobenzene (1,2 DCB) contaminated soil was prepared by adding 0.7 mL of 1,2 DCB in 100 mL of dichloromethane and 300 g of the soil sample into a 2 L pyrex glass bottle. The mixture was then mixed by hand until dichloromethane was vaporized completely to achieve spiked uniformly. Five gram of 1,2DCB contaminated soil sample was then dissolved in 15 mL of dichloromethane and rotated at a speed of 150 rpm for 20 min. The 1,2 DCB in dichloromethane solution was then determined by means of gas chromatography (HP 6890, USA) with FID detector at initial temperature of 40°C for 1 min and then increased to 150°C for 1 min by a rate of 70°C/min. Triplicate soil samples were analyzed for quantification. This 1,2 DCB spiked soil sample was then ready for EK experiments.

Processing Fluids and PRB Media

Two types of processing fluids were selected as processing fluid in this study, which properties were shown in Table 1. One is a local

Table 1. Characteristics of experimental materials

Characteristics	Values	Characteristics	Values
	I. Soil		
Texture	Clay	Solid density (g/cm^3)	2.64
Organic matter content (%)	3.73	BET areas (m^2/g)	16.4
pH	8.5	CEC (meq/100 g)	0.66
pH$_{ZPC}$	2.4	Hydraulic conductivity (cm/s)	$<10^{-8}$

Anions	Values (meq/L)	Cations	Values (meq/L)
	II. Groundwater		
SO_4^{2-}	3.39	Mg^{2+}	2.21
Cl^-	1.65	Ca^{2+}	1.75
NO_3^-	0.27	K^+	1.33
pH			7.9

Types	Formula	cmc (mM)	Hydrophile–lipophile balance	Water solubility	Company
		III. Surfactants[a]			
SDS	$C_{12}H_{25}SO_4Na$	8.0	40	10% in water	Sigma USA
PANNOX 110	$C_9H_{19}C_6H_4O(C_2H_4O)_{9\cdot 9}H$	0.01	13.3	Complete miscible	Pan-Asia Chemical Corp., Taiwan

Materials	pH$_{ZPC}$	BET area (m^2/g)	Pore volume (cm^3/g)
	IV Barrier		
Unpurified CNT	2.4	75.2	0.29
CNT[b]	2.6	122.2	0.44

[a] Data were provided by manufacturers.

[b] It was purified with 3 M HNO_3 solution at 120°C for 2 hours.

groundwater in field, which was mainly consisted of anions of SO_4^{2-}, Cl^-, and K^+ and cations of Mg^{2+} and Ca^{2+}. The second is biodegradable surfactants including sodium dodecylsulfate (SDS, an anionic type) (28) and nonylphenol polyethylene glycol ether (PANNOX 110, a nonionic type), which critical micelle concentrations (cmcs) were 8 and 0.01 mM, respectively. These surfactants were used without further purification. Carbon nanotube (CNT) was used as barrier media, which was classified as multi-walled texture. Both CNT before and after HNO_3-purification would be investigated in this study, whose characteristics were listed in Table 1.

Setup of EK Experiments

Nine EK experiments were conducted in a glass cell of 4.2 cm (ϕ) × 22 cm (L), consisting of three compartments: cathode reservoir with 5 cm in length, anode reservoir with 5 cm in length, and soil specimen chamber with 12 cm in length, which was shown in Fig. 1. The processing fluid was initially placed into both anode and cathode reservoirs and replenished in the anode reservoir every half day. All experiments were conducted under potential gradient of 2.0 V/cm for 5 day with CNT barrier located at 6 cm away from the anode in EK cell. The CNT barrier was composed with 0.5–2.0 g of CNT and 10 g of Ottwa sand, in which the addition of Ottwa sand was aimed to extend the retention time of 1,2 DCB in barrier. The electric current, reservoir pH, concentrations of 1,2 DCB, and the quantity of the electroosmostic flow were monitored during the test periods. Eight soils pHs were determined after treatment for each test. Among them, two were sampled at the end of anode and cathode side and the other six were sampled every 2 cm of soil specimen. The residual concentration of 1,2 DCB in soil phase was analyzed by means of gas chromatography (HP 6890, USA) with FID detector.

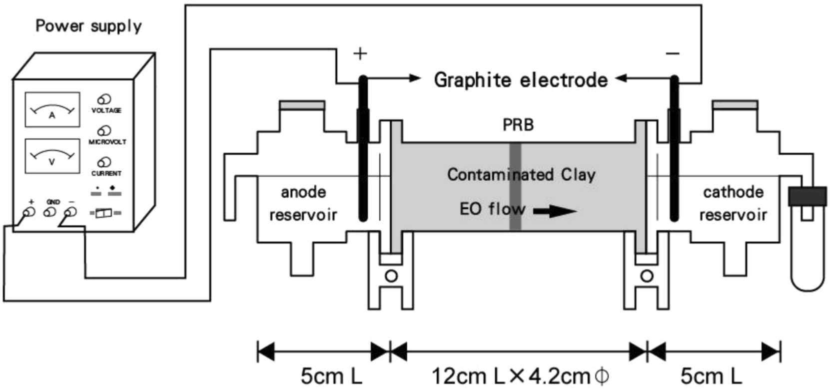

Figure 1. Schematic of EK-CNT barrier decontamination process.

RESULTS AND DISCUSSIONS

The experimental results are summarized in Table 2 and further discussed in the following sections.

Aqueous Adsorption of 1,2 DCB on CNT

Figure 2 shows the aqueous equilibrium adsorption of 1,2 DCB with CNT at different pHs. It was showed that high 1,2 DCB uptake on CNT was found at pH range of 4–8 but lower uptake was found at extreme acid and basic environment. The 1,2 DCB uptake was 20–98 mg/g at pH of 2.0, increased to 25–168 mg/g in the range of 6–8, and finally largely dropped to 24–68 mg/g at pH of 12.5. It was implied that the adsorption of 1,2 DCB by CNT was limited at acid and basic environment. Lower uptake of 1,2 DCB was found at extreme acid and basic conditions. This might be largely attributed to

a. competing adsorption between other species and 1,2 DCB on CNT; and
b. surface chemical characteristic of CNT changing at that pH environment.

As the concentration of CNT was less than 18 mg/L, the effect of pH on 1,2 DCB uptake was insignificant at the pH range of 4–8. Furthermore, the uptake of 1,2 DCB was increased as increasing concentration of CNT.

Variation of pH in Reservoir and Soil

During EK experimental periods, the pH of the cathode reservoir increased to 11.6–12.3 and the pH in anode reservoir decreased to 1.0–3.0. It was resulted from the electrolysis of H_2O under an applied electric field (Eqs. (1) and (2)). The generation of H^+ and OH^- results in the movement of acid and basic fronts in EK system and changes the soil pH drastically during EK process (29,30). Moreover, the consumption of hydroxyl ions in precipitation, the surface complexation, and adsorption into the soil, and the formation of complexes in the bulk solution were other factors affecting the pH distribution in EK system (31).

$$\text{Anode}: 2H_2O \rightarrow O_{2(g)}\uparrow + 4H^+ + 4e^- \tag{1}$$

$$\text{Cathode}: 2H_2O + 2e^- \rightarrow H_{2(g)}\uparrow + 2OH^- \tag{2}$$

Table 2. Summary results in EK/CNT system

			PRB						
Test No.	Conc. of 1,2-DCB (mg/kg)	Processing fluid	Medium	Quantity (g)	Position (cm form anode)	Q_e (cm^3/day)	$k_e \times 10^6$ (cm^2/V-s)	Power consumption (kwh/m^3)	Removal efficiency (%)
1	250	Groundwater	–	–	–	10.3	4.4	465	45.9
2	261	Groundwater	Unpurified CNT	1.0	6	7.8	3.2	317	47.5
3	245	Groundwater	CNT	1.0	6	7.8	3.2	427	54.4
4	249	SDS (0.25 cmc)	CNT	1.0	6	7.8	3.3	247	60.9
5	249	SDS (0.5 cmc)	CNT	1.0	6	9.5	4.0	295	62.0
6	252	SDS (1.0 cmc)	CNT	1.0	6	10.3	4.4	303	70.5
7	249	SDS (2.0 cmc)	CNT	1.0	6	12.1	5.0	345	75.5
8	249	PANNOX 110 (0.5 cmc)	CNT	1.0	6	3.5	3.0	380	59.6
9	249	PANNOX 110 (1.0 cmc)	CNT	1.0	6	12.2	3.2	398	61.8

1. All experiments were conducted under potential gradient of 2 V/cm for 5 day.
2. Other than PRB medium mentioned above, 10 g of Ottwa sand was also added into PRB layer.

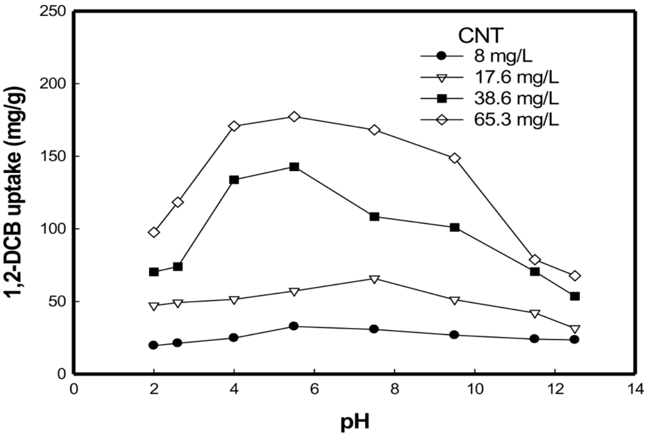

Figure 2. The effect of pH on adsorption of 1,2 DCB on CNT in aqueous phase.

The soil pH profiles along EK cell in EK/CNT systems are shown in Fig. 3. A general trend of a low pH near the anode and a high pH near the cathode was found in all investigated systems. The acid front generated at anode reservoir flushed across the soil specimen, consequently lowering the soil pH value from 8.5 to 2.0–4.2 near the anode side for all cases. At the cathode side, the migration of OH^- advancing toward the anode and the concentration differences of OH^- between reservoirs and soils would make the soil pH increases to 9.8–12.0. Results showed no evident correlations between soil pHs and purification of CNT (Fig. 3a) but higher variance of soil pH was found in EK/CNT systems with various types (Fig. 3b) and concentration (Fig. 3c) of processing fluid.

Current Density and Electroosmotic Permeability

The variations of current density as a function of time in EK/CNT systems are shown in Fig. 4. The current density was gradually increased to 3.2–3.8 mA /cm^2 within 60 hours for Tests 1–3 (Fig. 4a). Similar phenomenon was shown for all other EK/CNT systems. In Fig. 4b, a much lower current density was found for EK/CNT system with PANNOX 110 (Tests 8–9) than SDS at concentration of 0.5 and 1.0 cmc. In Fig. 4c, a higher peak current density was found for EK/CNT system with 2.0 cmc of SDS (Test 7) than other system with SDS of 0.25 $\sim$ 1.0 cmc. It might result from the various solubility of 1,2 DCB in SDS and PANNOX 110. It was inferred that high mobility and solubility of 1,2 DCB were found in the SDS solution, which consequently resulted in high current density, and vice versa for PANNOX 110. As processing greater than

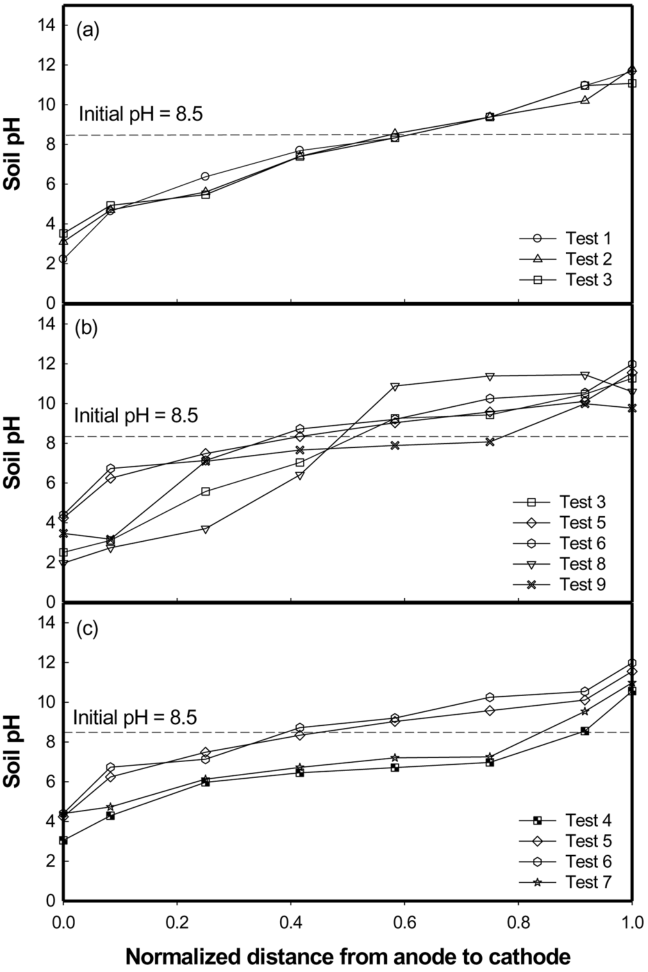

Figure 3. Soil pH profiles according to (a) type of PRB; (b) type of processing fluid; and (c) concentration of SDS.

60 hours, the current density of all investigated systems was decreased to less than 0.5 mA /cm^2. It was largely because the clogging of metal hydroxide precipitates formed near the cathode under basic environment. It was shown that the variance of current density was more significant related to type of processing fluids (Fig. 4b). The results of current density were consisted with As(V) removal with EK systems by Zhou et al. (10) and Yuan and Chiang (32). However, it was less consistent with benzene removal with SAEK system by Yuan and Weng (21). This was largely due to no CNT barrier and lower pH near cathode in SAEK system.

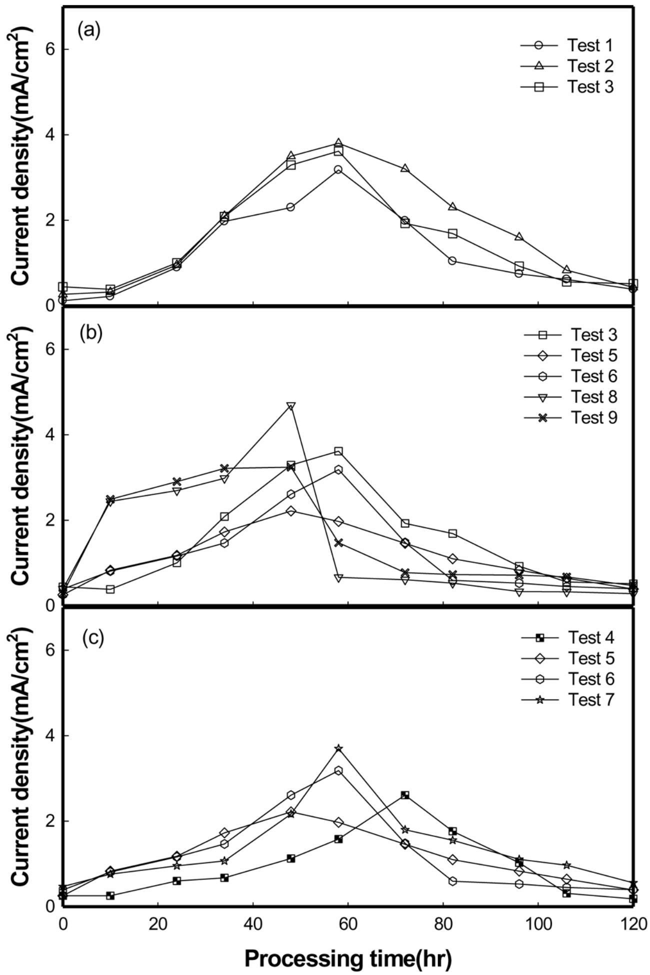

Figure 4. The effect of (a) PRB; (b) processing fluid; and (c) concentration of SDS on current density.

In the EK process, the movement of electrolyte solution driven by an electrical field, which carries the removed pollutants toward the electrodes, is considered to be one of the mechanisms leading to the pollutants removal from soils. The movement of electrolyte solution, i.e., electroosmotic flow, Q_e (mL/d), for a cylindrical soil core is directly proportional to the applied electric potential gradient, i_e (V/cm):

$$Q_e = k_e \times i_e \times A \qquad (3)$$

where A (cm^2) is a cross-section area of the soil core and k_e(cm^2/V-s) is electroosmotic permeability. As shown in Table 2, the EO flow was in the range of 3.5–12.1 cm^3/day and it was increased with k_e for all experiments. The calculated k_e values listed in Table 2 for all experiments were in the ranges of 3.0×10^{-6}–5.0×10^{-6} cm^2/V-s. These values were similar to those observed in the electrokinetic remediation of phenanthrene-contaminated kaolin and glacialtill soils (33,34) and benzene group-contaminated soil (21), whereas they are slightly less than those (10^{-6}–4.0×10^{-5} cm^2/V-s) reported in electrokinetic remediation of soil contaminated with heavy metals (35,36). This suggested that the strong sorption affinity of hydrophobic organics in soil matrix influence the contaminant mobility in electrokinetic system. It was confirmed that installation of CNT barrier in EK system would retard transportation of contaminants as compared with k_e for Test 1 and Tests 2–3 in Table 2. As using higher concentration of SDS in EK/CNT systems (Tests 4–7), the higher k_e up to 5.0×10^{-6} cm^2/V-s was found (Test 7). It might result from solubility enhancement of 1,2 DCB by SDS micelle. The EO permeability, however, was not enhanced by PANNOX 110 (Tests 8–9). It was inferred that lower affinity of 1,2 DCB was in PANNOX 110 micelles.

The experimental results in Table 2 indicated that the constituent of the CNT barrier and processing fluid affected the removal of 1,2-DCB from clay. With groundwater as processing fluid, the EK removal efficiency of 1,2 DCB was only 45.9% (Test 1) and it increased to 47.5% and 54.4% as inserted unpurified CNT barrier and purified CNT by HNO_3 solution in EK system, respectively (Tests 2 and 3). With SDS concentration less than cmc in EK/CNT systems (Tests 4–5), 1,2 DCB removal was restrictively enhanced to 62%. This resulted from low affinity of 1,2 DCB with SDS monomers. As concentration of SDS increased above cmc (Tests 6–7), higher 1,2 DCB removal was achieved to 75.5%. It was largely attributed to micelle formation and resulted in more release of 1,2 DCB from soil matrix to aqueous. Whereas less 1,2 DCB removal enhancement was found in system with PAANOX 110 as processing fluid (Tests 8–9). Due to effect of solubility enhancement, it concluded that type and concentration of surfactant plays a positive effect on EO permeability and remediation efficiency of 1,2 DCB.

Energy expenditure in EK systems is calculated as follows:

$$E_u = \frac{P}{V_s} = \frac{1}{V_s}\int VIdt \tag{4}$$

where E_u = energy expenditure per unit volume of soil (kWh/m^3); P = energy expenditure (kWh); V_s = volume of soil (m^3); V = voltage

(V); I = current (A); t = time (h). In the tests of constant-voltage condition, the energy expenditure is directly related to the time integral of the current across the cell. The calculated energy consumption were 465, 317, 247–427 kWh/m^3 of soil for EK, EK/unpurified CNT, and EK/CNT systems (see Table 2), respectively. It is apparent that installation of the CNT layer and type and concentration of processing fluid are the controlling factors with respect to energy consumption. Considering 1,2 DCB removal performance, it is clear that energy applied is not enough for completion of remediation. However, this can be improved by prolonging the treatment periods and increasing potential gradient.

Removal Mechanisms of 1,2 DCB in EK/CNT System

Large agglomerate contaminants in soil matrix will either move toward counter-electrode reservoir by electrophoresis or toward cathode reservoir by electroosmosis flow during EK process (8,18). As installation of CNT layer in EK system, sorption of organic contaminants onto CNT becomes another major removal mechanism due to high surface area of CNT.

Fractional distribution of 1,2 DCB in investigated system are shown in Table 3. The 1,2 DCB was existed either

1. in the soil phase, which represented the portion that can not be removed by EK/CNT process,
2. in the reservoir solution, which represented the portion of removal by EK process, or
3. on the CNT surface, which represented the portion of removal by the barrier.

The 1,2 DCB could be collected in cathode reservoirs via electroosmosic flow and in anode reservoir via electrophoresis, by which 1,2 DCB was dissolved in center of SDS micelle with anionic charge. Results showed that 1,2 DCB removal in EK system (Test 1) was only by EK process as expected, among which was dominated by EO flow (73.4%). With groundwater as processing fluid, the removal fraction of 1,2 DCB by sorption on barrier was increased from 80.2% in EK/unpurified CNT system (Test 2) to above 97.9% in EK/CNT systems (Test 3–9). It indicated that the sorption of 1,2 DCB on the barrier became the major removal mechanism in EK/PRB system. Moreover, the estimated adsorption capacity of 1,2 DCB on purified CNT was 33.9 mg/g (Test 3) which was 1.3 times greater than that in EK/unpurified CNT system (Test 2).

Table 3. Fractional distribution of 1,2 DCB in EK/CNT systems

			Fraction of 1,2-DCB					Fractional removal of 1,2-DCB	
				Reservoir					
Test No.	(1) Initial 1,2-DCB (mg)	(2) CNT (g)	(3) Soil phase residual (mg)	(4) Anode (mg)	(5) Cathode (mg)	(6) Sorbed on CNT (mg)	(7) Adsorption capacity (mg/g)	(8) EK process (%)	(9) Sorption on CNT (%)
1	62.8	–	34.0	7.56 (26.6%)[a]	20.84 (73.4%)[b]	–	–	98.5	–
2	68.4	1	36.2	1.37 (21.4%)[a]	5.01 (78.6%)[b]	25.9	25.9	19.8	80.2
3	63.5	1	29.0	0.16 (25.2%)[a]	0.49 (74.8%)[b]	33.9	33.9	1.9	98.1
4	65.7	1	25.7	0.30 (48.4%)[a]	0.32 (51.6%)[b]	39.4	39.4	1.5	98.5
5	65.7	1	24.8	0.30 (44.8%)[a]	0.37 (55.2%)[b]	40.2	40.2	1.6	98.4
6	70.9	1	20.9	0.42 (42.4%)[a]	0.58 (57.6%)[b]	49.0	49.0	2.0	98.0
7	63.6	1	15.6	0.32 (45.8%)[a]	0.38 (54.2%)[b]	47.3	47.3	1.4	98.6
8	62.7	1	25.3	0.37 (46.3%)[a]	0.43 (53.7%)[b]	36.6	36.6	2.1	97.9
9	62.3	1	23.8	0.34 (42.5%)[a]	0.46 (57.5%)[b]	37.7	37.7	2.1	97.9

[a] = (4) ÷ [(4)+(5)].

[b] = (5) ÷ [(4)+(5)].

(6) = (1)−[(3)+(4)+(5)].

(7) = (6) ÷ (2).

(8) = [(4)+(5)] ÷ [(1)−(3)].

(9) = (6) ÷ [(1)−(3)].

It was largely because the metal catalysts on the CNT surface was removed after HNO_3-purification and resulted in higher specific surface area (see Table 1). For Tests 4–7, it was also shown that the 1,2 DCB collected in anode and cathode reservoirs were respectively in the range of 42.0–48.4% and 51.6–58.0% (Columns 4 and 5 in Table 3). It was inferred that the 1,2 DCB removal via electrophoresis became more important when using anionic surfactant of SDS as processing fluid. A similar trend was also found in systems with PAANOX 110 as processing fluid (Tests 8–9).

It was concluded that both the EK process and the sorption on the barrier media contributed to the removal of 1,2DCB in the EK systems with the barrier. It was found that sorption of 1,2 DCB on CNT w/o HNO_3 purification become the major mechanism in EK/CNT system. Among the electrical removal mechanisms, 1,2 DCB removal via electrophoresis became more critical when using surfactant as processing fluid.

1,2 DCB Residual Profile in EK/CNT System

The residual 1,2 DCB in investigated systems presented as a function of the normalized distance from anode to cathode are shown in Fig. 5. It was found that residual 1,2 DCB was gradually increased from anode to cathode for the EK system with groundwater as processing fluid (Test 1), which was consistent with direction of EO flow. It was clearly confirmed that 1,2 DCB in soil matrix was pushed by EO flow and collected in cathode reservoir in EK system alone (Table 3). As the inserted CNT barrier without purification (Test 2), due to lower sorption affinity of 1,2 DCB, a concentrated residual was found near cathode side as expected.

A higher residual 1,2 DCB was found in the section between anode side and CNT barrier in Tests 3–9.

This might because of either

(a) no sorption contribution by CNT barrier, or
(b) migration of anionic SDS micelles associated with 1,2 DCB toward anode by electrophoresis.

Moreover, a lower 1,2 DCB residual was found between CNT layer and cathode side. This resulted from sorption of 1,2 DCB onto CNT when concentration front passed through CNT barrier, which could be confirmed by the result of the adsorption capacity in Table 3.

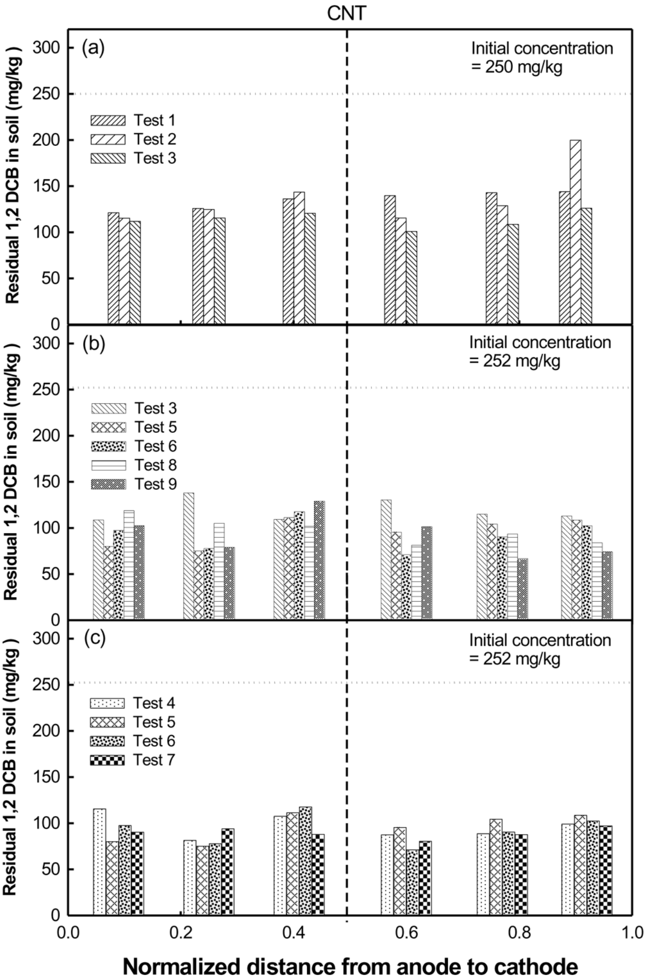

Figure 5. 1,2 DCB residual profiles along EK cell according to (a) type of PRB; (b) type of processing fluid; and (c) concentration of SDS.

Compared with ethylbenzene removal in the surfactant-assisted EK system (21), the residual 1,2 DCB was more evenly distributed along the EK cell. It represented that no significant resistance existed in the soil pore and the external force, i.e., the potential gradient, applied in the EK cell was quite fit for pushing 1,2 DCB migration. To study the 1,2 DCB removal performance in EK/CNT system more thoroughly, using a processing fluid with high solubility of 1,2 DCB and prolonging processing time are recommended in future investigations.

CONCLUSIONS

This study suggests that the electrokinetic remediation of 1,2 DCB in clay was enhanced by surfactant solution and installation of CNT barrier inside. As applied a 2 V/cm potential gradient for 5 days with groundwater as processing fluid, 54.4% of 1,2DCB was removed from clay in EK/CNT systems, which were 1.1 and 1.2 times greater than that in the system of EK/unpurified CNT and EK system alone, respectively. Up to 60.9–75.5% of 1,2 DCB removal was enhanced by SDS solution in EK/CNT system and EO permeability was also increased to $3.3 \times 10^{-6} - 5 \times 10^{-6}\,\mathrm{cm^2/V\text{-}s}$. As SDS concentration above cmc value, significant removal of 1,2 DCB was found. This was largely because of solubility enhancement of 1,2 DCB in SDS micelles. Low soluble affinity of 1,2 DCB in PANNOX 110 micelles resulted in lower removal efficiency (59.6%–61.8%). By EK/CNT treatment, 1,2 DCB as existed either in the soil phase, in the reservoir solution, or on the CNT surface. Results indicated that both the EK process and the sorption on the barrier media contributed to the removal of 1,2 DCB in EK systems with barrier. Sorption of 1,2 DCB on CNT w/o HNO_3 purification become the major mechanism in EK/CNT system. Among the electrical removal mechanisms, 1,2 DCB removal via electrophoresis became more critical when using surfactant as processing fluid. Lower residual was found between CNT barrier and cathode side.

This might largely because

1. sorption of 1,2 DCB was occurred on CNT surface as concentration front passed through barrier via EO flow; and
2. anionic SDS micelles were moved toward the anode by electrophoresis.

To study 1,2 DCB removal performance in EK/CNT system more thoroughly, it is recommended to chose processing fluids with high affinity of 1,2 DCB and prolong the processing time in the future investigations.

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