

COSOLVENT-ENHANCED ELECTROKINETIC REMEDIATION OF SOILS CONTAMINATED WITH PHENANTHRENE

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ABSTRACT: This research was carried out to evaluate feasibility of using an electrokinetic technique to remove hydrophobic organic pollutants from soils, with the assistance of a cosolvent (*n*-butylamine, tetrahydrofuran, or acetone) added to the conducting fluid. The experiments were carried out on glacial till clay with phenanthrene as the test compound. Desorption equilibrium was investigated by batch tests. The electrokinetic experiments were conducted using a 19.1 cm long \times 6.2 cm inside diameter column under controlled voltage. Water or 20% (volume) cosolvent solution was constantly supplied at the anode. The concentration of phenanthrene in the effluent collected at the cathode was monitored. Each experiment lasted for 100 to 145 days. Results showed that the presence of *n*-butylamine significantly enhanced the desorption and electrokinetic transport of phenanthrene; about 43% of the phenanthrene was removed after 127 days or 9 pore volumes. The effect of acetone was not as significant as butylamine. The effluent flow in the tetrahydrofuran experiments was minimal, and phenanthrene was not detected in the effluent. The use of water as the conducting solution did not cause observable phenanthrene migration.

INTRODUCTION

During the last decade, a great deal of research has been conducted to develop technology for treating contaminated soils and groundwater. In-situ methods are generally more attractive because of potential lower cost, less disruption to the environment, and reduced worker exposure to the hazardous materials. However, in-situ treatments such as bioremediation, vapor extraction, and pump-and-treat have been found rather ineffective when applied to the low-permeability soils present at many contaminated sites (Ho et al. 1995).

Recently, the use of electrokinetics (EK) as an in-situ method for soil remediation has received increasing attention due to its unique applicability to low-permeability soils (Acar and Alshwabkeh 1993; Reddy and Parupudi 1997; Reddy and Shirani 1997; Reddy et al. 1997). EK remediation involves application of a low direct current or voltage to electrodes that are inserted into the ground. As a result of the electrical gradient, charged species in soil pore water migrate to either the cathode or anode in a process known as electromigration. As water is continuously replenished at anodes, dissolved contaminants, either charged or uncharged, are flushed toward the cathode due to electroosmosis, where they can be extracted and further treated by various conventional wastewater treatment methods. Most of the previous investigations on EK remediation focused on metals; only a few were targeted on the organic pollutants, including some gasoline hydrocarbons, phenols, and trichloroethylene (Acar et al. 1992; Bruell et al. 1992). Due to the nonionic nature of most organic compounds, their movement due to electromigration is not expected to be significant. For hydrophobic organic chemicals (HOCs) that dissolve in water in negligible amounts, but have a high tendency to adsorb on soil, transport by electroosmosis is also not expected to produce considerable removal when water is used as conducting fluid during EK remediation. For this reason, EK was classified as "not applicable" toward petroleum

hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), and polychlorinated biphenyls (PCBs) (MacDonald and Rao 1997).

Many water-miscible organic solvents, when present in water as cosolvents, can significantly increase the solubility and decrease the sorption of hydrophobic contaminants. In-situ solvent flushing (SF) involves injecting a solvent mixture, mostly water plus a miscible cosolvent, into the vadose or saturated zone upgradient of the contaminated area. The solvent with the removed contaminants is then extracted downgradient and treated above ground. SF has been used in pilot and field-scale studies for in-situ soil remediation. The cosolvents often used were lower alcohols, ketones, and alkyl amines (USEPA 1995). The limitation of SF, however, is often due to the characteristics of the soil, especially the particle size distribution. While sandy soils may result in uncontrolled fluid migration, clayey soils with a particle size less than 60 μm are often considered unsuitable for in-situ SF remediation due to low soil permeability.

A research program was initiated based on the expectation that the combination of EK and SF techniques promises to efficiently remediate HOC-contaminated soils with low permeability. The goal of this research is to assess the potential of the electrokinetic technique for effective removal of hydrophobic organic contaminants from soils and to evaluate the effects of cosolvents on EK removal efficiency. The results of this research may expand the application of electrokinetic remediation to hydrophobic organic chemicals combined with heavy metals, since both are frequently found at the same site.

THEORY AND BACKGROUND

Electrokinetics and Electroosmosis

Generally, soils such as clay and silt possess negatively charged surfaces due to isomorphic substitutions and broken bonds. The cations in pore water are attracted to the soil, forming a diffusive double layer. By applying a low DC voltage to the soil medium, the hydrated cations in the diffusive double layer, primarily, and the cations in free water, consequently, move toward the cathode. This advective movement drags the molecules of water with it, which results in electroosmotic flow toward the cathode. The electroosmotic flow rate, Q_e , is defined with an empirical relationship:

$$Q_e = k_e i_e A = k_i I \quad (1)$$

where k_e = coefficient of electroosmotic permeability ($\text{cm}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$); k_i = electroosmotic water transport efficiency (cm^3 -

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$\cdot s^{-1} \cdot A^{-1}$); i_e = electrical potential gradient ($V \cdot cm^{-1}$); A = cross-sectional area (cm^2); and I = current (A). The magnitude of k_f is a function of the zeta potential, soil porosity, viscosity and permittivity of the media, and effective bulk electrical conductivity (Acar and Alshwabkeh 1993). The electrochemical reactions occurring in electrokinetics are oxidation and reduction, with the extent being determined by their standard electrode potentials of the half reactions. The reactants involved may be the constituents of the conducting pore water, the soil matrix, or electrode materials.

Contaminant Desorption and Transport

For nonionic organic contaminants, it is reasonable to assume that desorption of the contaminants from soil particles into the pore fluid, and transport with the electroosmotic movement of the fluid, are the most important processes during the EK remediation.

Sorption of chemicals on soil is frequently described by the Freundlich isotherm:

$$C_s = KC_w^n \quad (2)$$

where C is the concentration of solute in soil sorbent (subscript s) and in aqueous liquid (subscript w), K is the Freundlich constant, and n is a measure of the nonlinearity involved. Over limited ranges, particularly at low levels of C_w , the linear sorption isotherm, that is, $n = 1$, is often observed. Then, the equilibrium distribution ratio of the solute in the sorbed and solution phases, K_d , is used, which is numerically equal to K in the case of linear sorption.

$$K_d = C_s/C_w \quad (3)$$

Values of K_d depend on a large number of factors, including the properties of the sorbate (solute) and the compositions of both the aqueous phase and soil sorbent. The complex nature of K_d is described in Schwarzenbach et al. (1993).

Once dissolved into the pore fluid, the contaminant will move with the fluid through the tortuous path of the media. During this process, sorption and desorption will continue. Assuming that the solute sorption is reversible and fast relative to the flow rate of water, the transport of the solute can be described by its velocity of transport relative to that of water, which is measured by the retardation factor R :

$$R = 1 + \rho_s K_d (1 - \phi) / \phi \quad (4)$$

where ρ_s is the density of the soil solids and ϕ is the porosity of the soil.

The commonly used 1D transport equation for chemicals with negligible chemical reactions but significant adsorption in the soil is (Logan 1998)

$$R \frac{\partial C}{\partial t} + u \frac{\partial C}{\partial x} - D_L \frac{\partial^2 C}{\partial x^2} = 0 \quad (5)$$

where C is the concentration of the contaminant in the soil, x is the distance, t is the time, u is the average linear flow velocity, and D_L is the coefficient of dispersion in the direction of the flow. The magnitude of D_L depends on u , the pore dimension, and the molecular diffusivity of the contaminant in water, which is a function of the molecular mass. Assuming the sorbate chemical is in equilibrium with the soil and pore fluid, the differential equation can be solved under boundary conditions presented by Bruell et al. (1992): $C(x, 0) = C_0$ for $x > 0$; $C(0, t) = 0$ for $t \geq 0$; and $C(\infty, t) = C_0$ for $t \geq 0$. The solution is a breakthrough curve described by

$$\frac{C}{C_0} = 1 - \frac{1}{2} \operatorname{erfc} \frac{xR - ut}{(4RD_L t)^{0.5}} \quad (6)$$

where C_0 is the initial concentration of the contaminant in the soil, and erfc is the complementary error function.

Effect of Cosolvent

Cosolvency phenomena refer to the changes in the behavior, including the solubility, sorption equilibrium and kinetics, and transport velocity of solute chemicals upon the addition of one or more organic solvents (cosolvents) to aqueous solution (Rao et al. 1991).

The role of a cosolvent in the sorption and transport of hydrophobic organic chemicals in soil lies in its ability to alter the apparent values of K_d . The extent of the effect on K_d caused by adding a cosolvent can be estimated with (7) below, which relates the apparent distribution ratio in the water-cosolvent mixture K'_d to that in pure water, K_d . In (7), f_c is the volume fraction of the cosolvent in the solvent mixture.

$$\log(K'_d/K_d) = -\alpha\beta\sigma f_c \quad (7)$$

In this equation, α , β , σ measure the effects of various molecular interactions between cosolvent and sorbent, cosolvent and water, and cosolvent and solute, respectively (Rao et al. 1991). The values of σ can be estimated from the knowledge of solute solubilities in pure water (S_w) and in pure cosolvent (S_c) by (8). Then, β can be obtained by equation (9), in which S_m is the solute solubility in solvent mixture with cosolvent volume fraction f_c . Finally, (7) can be used to calculate α .

$$\sigma = \log(S_c/S_w) \quad (8)$$

$$\beta = \log(S_m/S_w)/\sigma f_c \quad (9)$$

From (4) and (7), the cosolvent effect on the solute retardation factor R can be derived:

$$\log[(R' - 1)/(R - 1)] = -\alpha\beta\sigma f_c \quad (10)$$

Strictly, the nature and extent of the interaction parameters α and β may well be functions of f_c . Therefore, (7) is often nonlinear with respect to the cosolvent fraction f_c . At a specified f_c , a higher product $\alpha\beta\sigma$ will indicate a stronger cosolvent effect in assisting the desorption and transport of hydrophobic organic contaminants in soil.

MATERIALS AND METHODS

Chemicals

Phenanthrene was chosen as the representative HOC in this study. It was purchased from Aldrich Chemical Company (Milwaukee, Wisc.) with 98% purity. The organic solvents used in this study were all purchased from Fisher Scientific Company. Methanol, isopropanol, and acetone were high-pressure liquid chromatography (HPLC) grade with 99.9% purity. Ethanol was denatured with a purity of 97.8%, and *n*-butylamine was 98.9% pure certified grade. The analytical solvents hexane and dichloromethane had purity of >99.9%. Water passing through a Milli-Q system was used in all experiments.

Soil Preparation

Glacial till soil obtained from a project site near Chicago was used for this study. Reddy and Shirani (1997) performed various physical and chemical tests to characterize this soil, and a summary of the test results is provided in Table 1. In accordance with the Unified Soil Classification System, ASTM D 2487, the soil is classified as silty clay. The mineralogy of the soil, based on X-ray diffraction and other analyses, was found to be 31% quartz, 13% feldspar, 35% carbonates, 15% illite, 4–6% chlorite, 0.5% vermiculite and trace smectite.

In preparing the soil, a known amount of phenanthrene was dissolved in hexane. Then, a known amount of glacial till was

TABLE 1. Characterization of Glacial Till (Reddy and Shirani 1997)

Soil property (1)	Value (2)
% Sand	16
% Silt	47
% Clay	37
Optimum moisture content (%)	14.9
Coefficient of permeability (cm/s)	8.77×10^{-8}
Activity	0.41
Organic content (%)	2.8
pH	7.7
Cation exchange capacity (meq/100 g)	13

added and mixed well with the hexane solution. The soil was then placed in a fume hood overnight for hexane to evaporate. During the evaporation of hexane, some of the phenanthrene was lost. The phenanthrene concentration in the soil was then determined by chemical analysis described in the following section. After the hexane was completely removed, a known amount of water was added to the soil to obtain a desired moisture content. For the soil used in *n*-butylamine experiment, the concentration of phenanthrene in the soil was 26 mg/kg, the moisture content was 30%, and the porosity was 0.43. For other experiments, the soil contained 19.5 mg/kg of phenanthrene and had a moisture content of 18% and porosity of 0.36.

Solubility and Batch Desorption Experiments

In order to choose the most effective cosolvents, phenanthrene solubilities in pure water, six pure organic cosolvents, and aqueous solutions containing 20% by volume of one of the six cosolvents were determined. Glass centrifuge tubes were filled with 10 mL of solvent and excess amount of crystalline phenanthrene. They were rotated at 18 rpm and room temperature ($23 \pm 2^\circ\text{C}$) for at least 48 h to achieve equilibrium. The tubes were then centrifuged at 3,000 rpm for 60 min. The supernatants were carefully drawn, diluted with pure cosolvent or methanol, and analyzed for phenanthrene analysis. All samples were prepared in duplicates to ensure accuracy.

Batch desorption experiments were carried out at room temperature with 20% *n*-butylamine, 20% tetrahydrofuran, 20% acetone solutions, and pure water. The soil was prepared by

the procedure described previously and had a phenanthrene concentration of 19 mg/kg. About 5–8 g of dry soil were added to 25 mL of solvent mixture or pure water in a 30 mL centrifuge glass tube with a Teflon-lined screw cap. All test samples were equilibrated for a period of 48 h by rotation at 18 rpm on the tube rotator. After being centrifuged at 3,000 rpm for 8 h, the supernatants were analyzed for phenanthrene concentration. The amount of phenanthrene adsorbed to the soil were calculated from the difference between the amounts added and extracted by the aqueous solution.

Electrokinetic Experiments

The apparatus setup and test procedure developed by Reddy and Shirani (1997) and Reddy et al. (1997) were used for the electrokinetic experiments. A schematic diagram of the apparatus is shown in Fig. 1. This setup was designed to simulate the 1D contaminant migration due to the voltage gradient (Reddy and Parupudi 1997). The electrokinetic cell used for the tests was made of Plexiglas, and it is 6.2 cm in diameter and 19.1 cm long. Slotted graphite electrodes were placed in contact with the reservoirs. The electrodes were located at each end of the test cell so that the soil was only in contact with one face of each electrode. A filter paper was used at the end of the sample to remove particulate matter. A porous stone was then placed next to the electrode to separate the current and voltage anodes followed by another filter paper. The nylon valve (PVC) at each of the cells was used to control the inflow and outflow of the solution. Gas vents were provided in the electrode reservoirs for the escape of any gases resulting from the electrolysis reactions. An HP Model 6205B dual DC generator provided a constant voltage over the electrodes.

The contaminated soil was placed into the cell over the cathode assembly and well compacted using a hand held pestle to avoid any voids across the sample. The anode reservoir was filled with the mobile phase solution. A constant voltage of 19 V (1 V DC/cm) was applied for the *n*-butylamine experiment. For the experiments with acetone, tetrahydrofuran, and water, the voltage was maintained at 19 V (1 V DC/cm) for the first 45 days and then increased to 34 V (1.8 V DC/cm) in an attempt to enhance the effluent flow rate. The effluent from the cell was collected up to 50–75 mL in amber glass bottles and analyzed for phenanthrene within 3 or 4 days.

All experiments lasted for a period of 3 to 4 months. Then the soil was extruded carefully from the cell by a mechanical

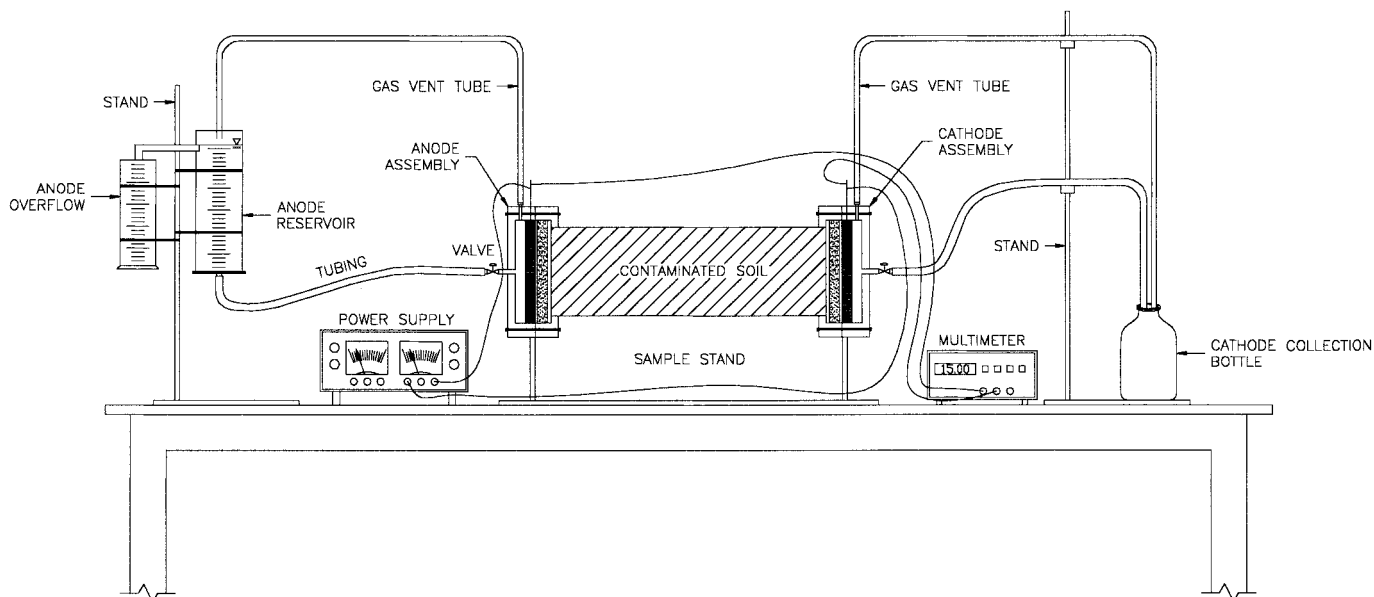


FIG. 1. Schematic of Apparatus Used in Electrokinetic Experiment

extruder and sectioned into 6 parts as 0–3.2, 3.2–6.4, 6.5–9.7, 9.8–13, 13.1–16.3, and 16.4–19.1 cm from the cathode. Each sectioned sample was well mixed by stirring. Representative portions of each section were taken for phenanthrene concentration, moisture content, and pH determinations. The moisture content of each sample was determined by placing the sample in an oven at 130°C for 24 h and then measuring the weight loss. The soil pH was determined using an Orion Model 720A pH meter.

Chemical Analysis

An aliquot of the soil sample was mixed with about 20 g of activated Na₂SO₄, and extracted using Soxhlet apparatus with 300 mL of 1:1 dichloromethane:methanol mixture for 24–48 h. Phenanthrene in liquid samples was extracted by triple liquid-liquid extraction using a total of about 50 mL dichloromethane. The volume of the extract was reduced using a Kuderna-Danish concentrator, and the solvent was exchanged to methanol.

Phenanthrene concentration was determined using a Hewlett-Packard Model 1100 HPLC equipped with an Alltech Econosphere reversed-phase C18 column (250 × 4.6 mm, 5 μm particle size) and a diode array UV detector. All samples were filtered through 0.22 μm Cameo 13F PTFE membrane prior to injection. Each sample was introduced into the HPLC through a manual injector with a 20 μL sample loop. A mixture of water and methanol, 25:75, was used as the mobile phase at a constant flow rate of 1.0 mL/min. The detector wavelength was set at 254 nm.

Two series of calibration standards were prepared for phenanthrene quantification in two different concentration ranges. Each series contained four standard solutions and covered at least one order of magnitude in concentration. Linearity of the HPLC response was determined on each analysis day, and the average regression coefficient R^2 was 0.996. The analytical system was proven to be free of contamination by running method blanks. The phenanthrene recovery of matrix spike samples was 101 and 99.5% for soil and liquid samples, respectively. An average relative standard deviation (RSD) of 25% was obtained for samples analyzed in duplicates at the early stage of the study, and it was later improved to about 10% for most phenanthrene analysis.

RESULTS

The experimental phenanthrene solubilities in pure cosolvent and 20% cosolvent aqueous solution are summarized in Table 2, along with values of σ and β calculated from (8) and (9), respectively. The results showed that *n*-butylamine, tetrahydrofuran, and acetone were more efficient to dissolve phenanthrene than the alcohols. These three cosolvents were therefore further investigated in the subsequent desorption and electrokinetic experiments.

The values of equilibrium soil/solution distribution ratio K_d of phenanthrene determined from batch tests are summarized in Table 3. By comparing the K_d value of 214 with water alone, the effect of adding 20% cosolvent is remarkable. It was observed that *n*-butylamine decreased the K_d by two orders of magnitude, making it the most effective among the three cosolvents in assisting phenanthrene to desorb from soil. Less than one order of magnitude decrease in K_d was observed in 20% tetrahydrofuran and 20% acetone. Values of α estimated using (7) are also included in Table 3.

Results of the electrokinetic experiments are illustrated in Figs. 2 to 5. In brief, the use of 20% *n*-butylamine aqueous solution as a conducting fluid resulted in remarkable phenanthrene movement toward the cathode, and 43% of added phenanthrene was removed from the soil after 127 days. However,

TABLE 2. Phenanthrene Solubility

Cosolvent (1)	S_c (mg/L) (2)	S_m^a (mg/L) (3)	σ^b (4)	β^c (5)
<i>n</i> -Butylamine	2.03×10^5	1,001	5.2	2.8
Acetone	2.19×10^5	22	5.2	1.2
Tetrahydrofuran	4.2×10^5	78	5.5	1.6
Ethanol	1.36×10^4	5	4.0	0.7
Methanol	1.38×10^4	2	4.0	0.2
Isopropanol	1.4×10^4	10	4.0	1.1

^aMeasured with $f_c = 0.2$.

^bCalculated by Eq. (8) with $S_w = 1.4$ mg/L (Li and Yalkowsky 1998a).

^cCalculated by Eq. (9) with $S_w = 1.4$ mg/L and $f_c = 0.2$.

TABLE 3. Desorption Equilibrium of Phenanthrene

Cosolvent (1)	K_d (mL g ⁻¹) ^a (2)	α^b (3)
Water	214 ± 94	—
20% <i>n</i> -Butylamine	3.0 ± 1.5	0.65
20% Acetone	65.6 ± 4.7	0.43
20% Tetrahydrofuran	32.3 ± 12.1	0.47

^aMean ± standard deviation ($n = 3$).

^bCalculated by Eq. (7).

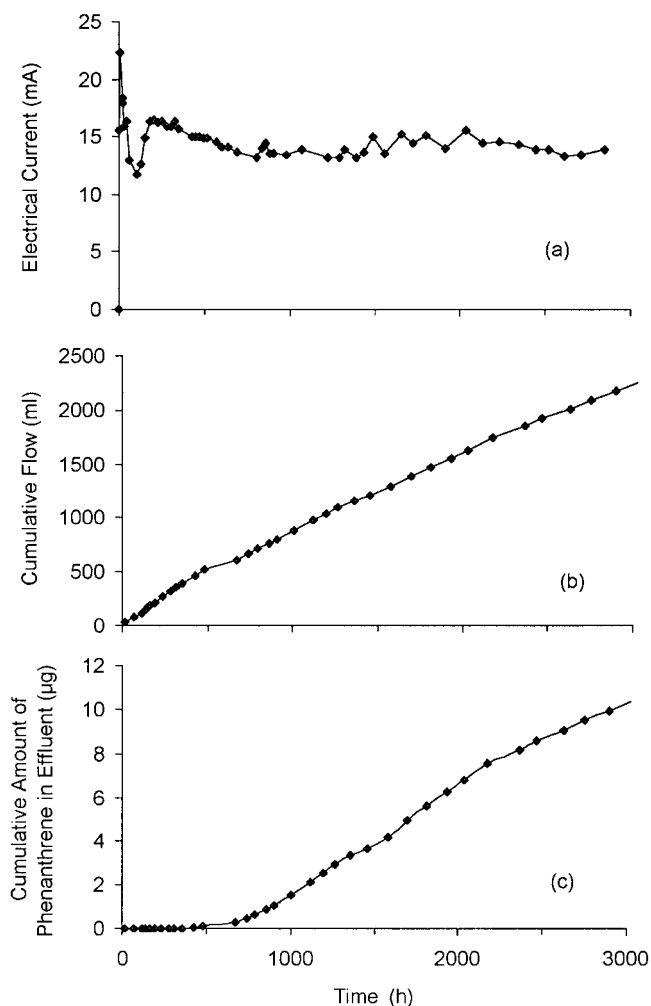


FIG. 2. Results of Electrokinetic Experiment with 20% *n*-Butylamine: (a) Measured Electrical Current; (b) Cumulative Volume of Effluent Flow; (c) Cumulative Mass of Phenanthrene in Effluent

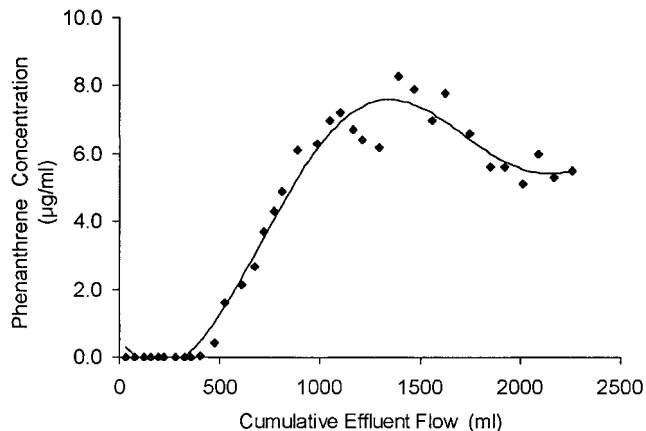


FIG. 3. Phenanthrene Concentration in Effluent Flow in 20% *n*-Butylamine Electrokinetic Experiment

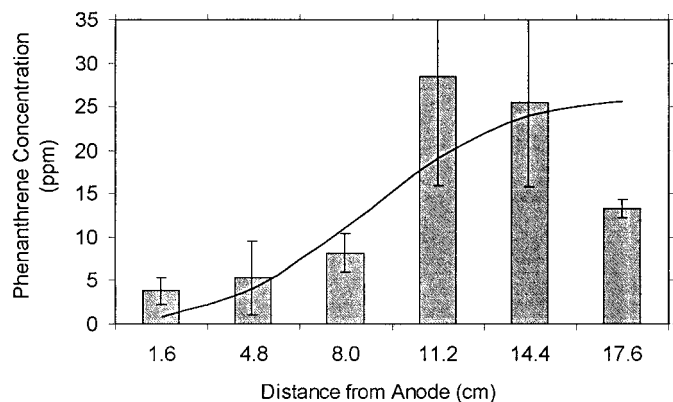


FIG. 4. Phenanthrene Concentration in Soil Sections after Electrokinetic Experiment with 20% *n*-butylamine. Predicted Breakthrough Curve Is Based on Eq. (6)

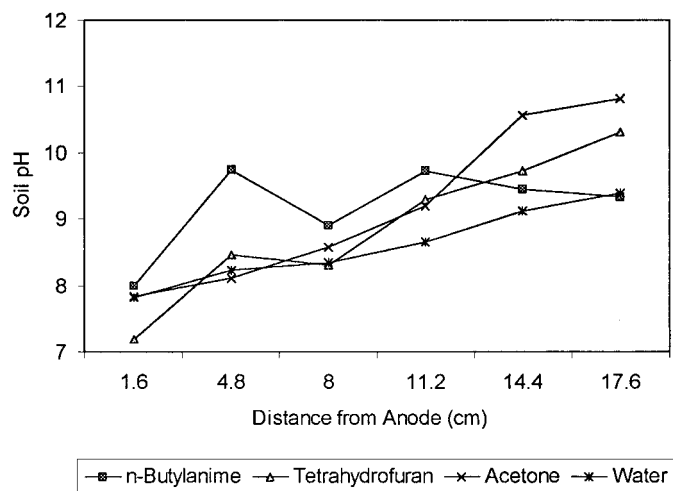


FIG. 5. Profiles of Soil pH in Electrokinetic Cells

the experiments with water alone, 20% acetone, or 20% tetrahydrofuran did not generate observable phenanthrene movement or removal after more than 3 months.

The effectiveness of the electrokinetic process in removing phenanthrene using 20% *n*-butylamine aqueous solution is illustrated in Figs. 2, 3, and 4. The electrical current increased at the beginning, and then became stabilized at about 15 mA with a constant electrical potential of 19 V or 1 V DC/cm [Fig. 2(a)]. After a few hours of initial lagging, the effluent flow increased rapidly to about 1 mL/h (linear flow velocity of 0.033 cm/h) and maintained as such throughout the entire ex-

periment [Fig. 2(b)]. For these conditions, the coefficient of electroosmotic permeability (k_e) is calculated as 5.5×10^{-4} cm²/V min (9.2×10^{-10} m²/V s). This value falls within the lower range of k_e values (10^{-9} to 10^{-8} m²/V s) given by Mitchell (1992). The phenanthrene concentration in the effluent collected at the cathode was not detected until the total volume of flow reached about 500 mL. After that, the phenanthrene concentration increased steadily to about 6 to 8 µg/mL and lasted for about a month, and then slightly decreased before the experiment stopped (Fig. 3). This resulted in a steady removal of phenanthrene from the electrokinetic cell [Fig. 2(c)]. After 3,000 hours or 9 pore volumes, about 43% of the phenanthrene mass added to the soil had been removed. The results of after-run destructive sampling of the soil column confirmed the movement of phenanthrene toward the cathode, with 85% of the phenanthrene remaining in the cell concentrated within 50% of the column length closest to the cathode (Fig. 4).

By contrast, experiments with 20% tetrahydrofuran, 20% acetone, and water alone showed little success. For these experiments, a constant voltage of 19 V was applied during the first 44 days, then increased to 34 V in an attempt to increase the electric current and effluent flow rate. The electric current in the experiment using 20% acetone increased at the early stage then stabilized at only about 4 mA, and a fairly constant effluent flow rate of about 0.25 mL/h was maintained. Meanwhile, the effluent flow had nondetectable phenanthrene until the last 100 mL of effluent flow, in which phenanthrene concentrations of 0.03 to 0.06 µg/mL were detected. The experiment with 20% acetone was stopped at 3,500 h, the longest run in this study. The electric current demonstrated an inconsistent pattern of electrical potential in the tetrahydrofuran experiment, and that on the experiment using water alone diminished sharply after an initial rise before 1,000 h passed. Both 20% tetrahydrofuran and water experiments were stopped at 2,500 h with about, respectively, 1.7 and 1.5 pore volumes of effluent collected. All of the effluent samples collected from tetrahydrofuran and water experiments had phenanthrene concentrations below the detection limit. After each run, the soil column inside each cell was sectioned and analyzed. No significant phenanthrene migration was observed in these experiments.

Fig. 5 shows the soil pH distributions across the cell column upon completion of the experiments. The pH values of soil near the cathode were 9–11, and those near the anode were 7–8. The increase in pH from anode to the cathode is a direct consequence of the attempt of the acid generated at the anode to migrate towards the cathode by electromigration, diffusion and advection. Theoretically, the acid front generated at the anode should flush across the cell neutralizing the base at the cathode. However, the pH of the soil near anode was somewhat basic (pH ≈ 8). Such observation was also made by Reddy and Parupudi (1997), and the high pH environment across the samples was attributed to the high carbonate content of the glacial till, which increases the acid buffering capacity of the soil.

DISCUSSION

Cosolvent Effect on Desorption

The effect of cosolvents on the desorption of organic pollutants in soils has been the focus of numerous researchers. The results of this study confirm that such effects are remarkable. For neutral organic chemicals, the values of K_d can be fairly reliably estimated from the knowledge of soil organic matter content f_{om} and the solute (sorbate) octanol/water partition coefficient K_{ow} .

$$\log K_d = (a \log K_{ow} + b) + \log f_{om} \quad (11)$$

The experimental log K_{ow} for phenanthrene is 4.57 (Schwarzenbach et al. 1993). The soil used in this study has an f_{om} of 0.028 (Table 1). With the values of a and b being 1.01 and -0.72 , respectively, for aromatic hydrocarbons (Schwarzenbach et al. 1993), the estimated K_d is 223, which is in good agreement with the experimental K_d of 214 obtained in this study (Table 2).

The beneficial effect of adding cosolvent is manifested by the values of σ , β , and α . The σ values (Table 2) for the three cosolvents selected for EK tests are greater than 5, indicating that the ratio of phenanthrene solubility in these pure cosolvents to that in pure water is greater than five orders of magnitude. If the solubilization were a linear function of the cosolvent volume fraction in the solvent mixture, phenanthrene would dissolve in 20:80 cosolvent:water mixture in an amount >10 times as much as that in water, due to the interactions among molecules of the cosolvent and the solute. Positive deviations from such a linear solubilization make β greater than unity, as a result of intermolecular interactions between cosolvent and water. Among all six cosolvents listed in Table 2, *n*-butylamine stands out for its β of 2.8, which indicates a strong positive effect of interactions between *n*-butylamine and water on phenanthrene solubility. Peters and Luthy (1993) also found *n*-butylamine to be a good solvent for coal tar dissolution.

The empirical value of α suggests the extent of cosolvent effect on HOC sorption equilibrium due to the interactions between cosolvent and sorbent. Such effect seems unfavorable to phenanthrene desorption from the soil used in this work, based on the values obtained ($\alpha < 1$; see Table 3). Both $\alpha < 1$ and $\alpha > 1$ cases have been reported in the literature (Rao et al. 1991).

The method of estimating the cosolvent effect on sorption is not readily available at present. Li and Yalkowsky (1998a, b) presented a set of equations to estimate σ from S_w and the K_{ow} of solute (sorbate) and cosolvent. However, estimation methods are not available for β and α . Developing easy-to-use techniques to estimate the cosolvent effects will be useful not only for remediation of soils using solvent flushing, but also for predicting the fate of hazardous pollutants like PAHs and PCBs at sites where substantial amounts of commonly used industrial solvents are present.

Effect of Electrical Field on Desorption

From the batch desorption experiment, a K'_d value of 3.0 mL/g was obtained for phenanthrene in 20% *n*-butylamine aqueous solution (Table 3). At the end of the electrokinetic experiment, the observed phenanthrene concentration in the effluent flow was about 6 $\mu\text{g/mL}$, and the two slices of soil close to the cathode had average phenanthrene concentrations of 13 and 25 $\mu\text{g/g}$, respectively. These correspond to a distribution coefficient of 2 to 4 mL/g near the cathode, which suggests the possibility that the distribution of phenanthrene in the vicinity of the cathode was close to reaching equilibrium. This is all the more possible considering that the retention time of water in the electrokinetic cell is about 24 days, which is long enough for sorption to reach equilibrium. This implies that desorption may not be the limiting step in removing phenanthrene from soil by *n*-butylamine enhanced electrokinetic remediation under the experimental conditions used in this work. The effect of electrical field on desorption, if any, should be negative since it exerts polarizing forces on water molecules. Such a force works only against the solubilization of hydrophobic organic contaminants. However, the effect of the electrical field is very likely to be minimal, based on the results of this study and others (Acar et al. 1992; Bruell et al. 1992).

Retardation and Transport

The retardation factor R is the ratio of the water linear velocity to that of the chemical. Assuming that equilibrium between the soil solids and pore liquid in the electrokinetic column was established, we can estimate the retardation of phenanthrene using (4). With the $K'_d = 3.0$ (Table 3), the soil solids density of 2.65 g/cm^3 , and porosity of 0.43, the retardation factor R is calculated to be 11.5. The retardation factor can also be obtained using the experimental data with the method described by Bruell et al. (1992), in which the location of pollutant concentration of 50% of the original concentration after a known period of time is determined from the breakthrough curve; the average velocity of the retarded pollutant chemical is then obtained. With the run time for the *n*-butylamine experiment being 3,000 h and the position of 50% concentration at about 9 cm (Fig. 4), the linear velocity of phenanthrene was calculated to be 3×10^{-3} cm/h. Dividing the fluid linear velocity (0.33 cm/h) results in an experimental R value of 11, which is the same as the value calculated from the K'_d . Compared with the retardation factor of 753 calculated from $K_d = 214$ when water alone was used, adding 20% *n*-butylamine is highly efficient in mobilizing phenanthrene.

This indicates that, due to the adsorption, phenanthrene will take about 11 times longer to move the same distance in the EK cell than the conducting fluid, 20% *n*-butylamine aqueous solution. With a flow rate of 1.0 mL h^{-1} , or a linear velocity of 0.03 cm h^{-1} , it would take 275 days for phenanthrene originally at the anode to cross the distance of 19 cm to reach the cathode. This compares well with the time for complete removal of phenanthrene calculated from linear extrapolation of the accumulative phenanthrene mass in the effluent [Fig. 2(c)].

A breakthrough curve is constructed based on (6) with an estimated dispersion coefficient D_L of 5×10^{-4} $\text{cm}^2 \text{min}^{-1}$. It is included in Fig. 4 to compare with the after-run experimental phenanthrene concentrations of the soil inside the column. The curve is in general agreement with the experimental observations, especially in the vicinity of the anode. The original concentration of phenanthrene in the test soil was 26 mg/kg . As the treatment time increased, phenanthrene continuously migrated toward the cathode, leaving behind a progressively cleaner soil. Phenanthrene concentration in the middle of the soil column was slightly higher than the initial concentration. A decrease in phenanthrene concentration toward the cathode was observed as a result of migration into the cathode compartment and subsequent removal.

Electroosmotic Flow Rate

As mentioned above, the desorption kinetics may not be the limiting factor in the EK experiment with the use of cosolvent, especially if the sorbate (phenanthrene in this work) is not aged or sequestered by the soil matrix. Then, the key to enhancing the pollutant removal may lie in increasing the electroosmotic flow rate. In this work, the experiments with water alone and 20% tetrahydrofuran aqueous solution did not last as long as we desired due to the diminished effluent flow. The attempt to boost the flow rate by increasing the voltage also failed. The exact reason for such observed flow reduction is unknown. The differences in dielectric constants for the conducting fluids, as well as the zeta potential changes due to pH changes in the soil, may also have led to different electroosmotic flow behavior.

Possible Electrochemical Reactions

Electrolysis of the constituents of the fluid phase will occur at the electrodes. In the absence of significant competitive reactions, water decomposition occurs at the electrodes to re-

lease oxygen gas at the anode and hydrogen gas at the cathode. In this work, reactions involving cosolvents may also occur to a significant extent during our experiments since they were 20% of the fresh liquid added at the anode. Butylamine, for example, might be oxidized at the anode to form various nitrogen-containing compounds with different oxidation states. In addition, components of the soil organic matter may also dissolve into the fluid phase due to the existence of the cosolvent. They may be subject to oxidation at the anode. A small amount of a dark brown liquid was observed at the anode, which may be the result of various oxidation reactions mentioned above. Unfortunately, concentration of the cosolvent in the effluent was not monitored during this study, nor were the gases eluted from the gas vents. Quantitative evaluation of the electrochemical reactions is therefore not possible.

CONCLUSIONS

No study had been performed in the past to assess the effect of cosolvents to enhance the electrokinetic removal of hydrophobic organic contaminants. This research was carried out to evaluate feasibility of using a cosolvent-assisted electrokinetic technique for remediating soils contaminated by hydrophobic organic pollutants. Based on the results obtained from this research, the following conclusions can be drawn.

1. Electrokinetic removal of phenanthrene from contaminated glacial till is moderately effective with the addition of 20% *n*-butylamine in the aqueous mobile phase. Removal efficiency of 43% was achieved in 127 days with 9 pore volumes of effluent.
2. Adding cosolvent to the conducting fluid greatly enhances the desorption of phenanthrene from soil. The distribution coefficient of phenanthrene was significantly lower in 20% *n*-butylamine aqueous solution ($K'_d = 3.0$) than in water ($K_d = 214$). The retardation factor *R* was therefore reduced from 753 in water to 11 in 20% *n*-butylamine solution.
3. Based on the results from the electrokinetic experiment with *n*-butylamine, there appears to be minimal or no effect of the electrical field on the phenanthrene desorption. The ratio of phenanthrene concentrations in soil at the cathode and in effluent is close to the batch experimentally determined apparent K_{ds} , indicating that desorption may not be the limiting step in electrokinetic systems used in this work.
4. Electroosmosis plays an important role in helping a cosolvent to be effective in an electrokinetic remediation process. This depends on the dielectric constant value of the conducting solution and also on the pH changes induced in the soil. The low removal of phenanthrene using

water, tetrahydrofuran, and acetone may be attributed to low electroosmotic flow.

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