Mobilization of phenol and dichlorophenol in unsaturated soils by non-uniform electrokinetics

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Abstract

The poor mobility of organic pollutants in contaminated sites frequently results in slow remediation processes. Organics, especially hydrophobic compounds, are generally retained strongly in soil matrix as a result of sorption, sequestration, or even formation into non-aqueous-phase liquids and their mobility is thus greatly reduced. The objective of this study was to evaluate the feasibility of using non-uniform electrokinetic transport processes to enhance the mobility of organic pollutants in unsaturated soils with no injection reagents. Phenol and 2,4-dichlorophenol (2,4-DCP), and kaolin and a natural sandy loam soil were selected as model organics and soils, respectively. The results showed that non-uniform electrokinetics can accelerate the desorption and movement of phenol and 2,4-DCP in unsaturated soils. Electromigration and electroosmotic flow were the main driving forces, and their role in the mobilization of phenol and 2,4-DCP varied with soil pH. The movement of 2,4-DCP in the sandy loam towards the anode (about 1.0 cm d^-1 V^-1) was 1.0–1.5 cm d^-1 V^-1 slower than that in the kaolin soil, but about 0.5 cm d^-1 V^-1 greater than that of phenol in the sandy loam. When the sandy loam was adjusted to pH 9.3, the movement of phenol and 2,4-DCP towards the anode was about twice and five times faster than that at pH 7.7, respectively. The results also demonstrated that the movement of phenol and 2,4-DCP in soils can be easily controlled by regulating the operational mode of electric field. It is believed that non-uniform electrokinetics has the potential for practical application to in situ remediation of organics-contaminated sites.

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1. Introduction

The slow movement of organic pollutants frequently lowers the remediation rate of organics-contaminated sites (Simoni et al., 2001). When organic chemicals, especially hydrophobic compounds, are released into subsurface environments, their mobility are reduced typically...
through adsorption on soil particle surface, partitioning into soil organic matter, sequestration within extremely small pores, and formation into non-aqueous-phase liquids (NAPL) (Pignatello and Xing, 1996). The poor mobility is traditionally overcome by applying surfactants to enhance the dissolution of NAPL and the desorption of sorbed organics, and by use of a hydraulic head gradient to drive organics through subsurface (Saba et al., 2001). Unfortunately, these techniques are, in most cases, not effective due to the heterogeneity of soil matrix and the shortcomings of hydraulically-driven transport processes. Besides, the energy-consumption and costs associated with these methods are considerable.

One of the recent techniques for subsurface remediation is electrokinetic soil processing. It is carried out by employing a low direct current (DC) density or electrical potential gradient to transport species through soils (Alshawabkeh and Bricka, 2000). A vast majority of this effort has been focused on removal of inorganic species such as heavy metals and radionuclides from saturated clays; however, less effort has been directed toward the transport of organics in unsaturated soils. Many organic pollutants lie within unsaturated soils as a result of leaking chemical storage tanks, landfills, and pipelines (Mattson et al., 2002). Electrokinetically-induced transport processes might provide a remediation alternative to unsaturated soils with organic chemicals.

The efficiency and the cost of electrokinetic treatment are related to the type of electric field, especially when it is scaled up to a field process. Uniform electric field achieved by electrode sheets is mostly adopted in current studies. Using electrode sheets requires trenches, which inevitably disturbs the natural environments (Virkutyte et al., 2002). Electrokinetically-induced transport processes might provide a remediation alternative to unsaturated soils with organic chemicals.

In addition, the current electrokinetic cell usually consists of an open-flow arrangement at the electrodes, which permits injection of processing fluid into the treated soils and later removal of the contaminated fluid. In order to obtain the most efficient results, enhancing agents such as surfactants, acid–base buffering chemicals and even clean water are used in most studies (Saichek and Reddy, 2003).

The aim of this study is to investigate the effectiveness of using electrokinetic transport processes induced by non-uniform electric field (that is, non-uniform electrokinetics) to enhance the mobility of organic pollutants in unsaturated soils with no injection of enhancing reagents (that is, under close-flow condition). Phenol and 2,4-dichlorophenol (2,4-DCP) were selected here due to their high toxicity and wide distribution in contaminated soils and groundwater.

2. Background

A DC electric field imposed on soil matrix can induce complex and coupled electrochemical and geochemical processes. The principal electrokinetic phenomena related to the mobilization of organic pollutants in soils are electroosmosis, electromigration, and electrolysis reactions.

Electroosmosis is the movement of pore fluid in an electric field. The soil particle surface is generally negatively charged, and the resulting electroosmotic flow is typically towards the cathode. The average electroosmotic flow velocity ($V_{eo}$) can be expressed by (Musso, 2003):

$$V_{eo} = -\frac{i_o \eta}{n_i} = k_e l_e$$  (1)

where $i_o$ is the applied electrical gradient, $\zeta$ is the zeta potential on soil particle surfaces, $\eta$ is dielectric constant, $n_i$ is the viscosity of pore fluids, $n$ is the effective porosity of soils, $k_e$ is the electroosmotic permeability coefficient. Electroosmotic flow is able to drag the free-phase dissolved and even sorbed organics toward the cathode (Acar et al., 1992; Chang, 2000).

Electromigration is the transport of charged species in an electrical field. The cations move towards the cathode, the anions towards the anode. The electromigration velocity ($V_{em}$) is proportional to the applied electrical gradient ($i_e$) and the effective mobility of the species in soils ($u^*$); the latter is affected by the ionic mobility in free dilute solutions ($u$), the tortuosity ($\tau$) and porosity ($n$) of the soils (Mattson et al., 2002):

$$V_{em} = n u \tau i_e = u^* i_e$$  (2)

The charged species are mobilized simultaneously by electromigration and electroosmosis. The movement of cationic species is enhanced as both mechanisms drive the cations towards the cathode, whereas the electromigration of anionic species towards the anode is reduced by the opposite electroosmotic flow. The actual velocities of cationic species (c) and anionic species (a) are then given, respectively, by (Baraud et al., 1999):

$$V_c = (u_c^* + k_e) i_e$$  (3)

$$V_a = (u_a^* - k_e) i_e$$  (4)

In general, the electromigration rate is at least one order of magnitude greater than the electroosmotic flow, and hence electromigration generally dominates mass transport during electrokinetic treatment (Virkutyte et al., 2002).
Importantly, when an electric potential is applied to wet soils through inert electrodes, electrolysis of pore fluid occurs at the electrodes (Saichek and Reddy, 2003):

At the anode: \[ 2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + \text{O}_2(\text{g}) + 4\text{e}^- \quad (5) \]

At the cathode: \[ 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^- + \text{H}_2(\text{g}) \quad (6) \]

Oxidation at the anode generates an acid front while reduction at the cathode generates a base front. These acids and bases will advance through soil matrix and change the soil pH. The change in soil pH will affect the sorption and dissociation of organics in soils, and will exert significant impact on the efficiency of electrokinetic treatment. Therefore, pH control is of significance for electrokinetic treatment. Applying conditioning agents and constructing modified reactors are the two common strategies (Lee and Yang, 2000), and yet alternate polarity-reversal of the electric field may be a simple solution under in situ conditions.

Phenol and 2,4-DCP are both ionizable organics, and can exist in both neutral and ionized forms depending upon the pH of environmental media (Fytianos et al., 2000; Li et al., 2000). The concentration of ionized species will increase with pH. The sorption of phenol and 2,4-DCP by soil media depends partly upon their form. The neutral phenol and 2,4-DCP are expected to undergo more sorption than their ionized forms. On the other hand, the ionized and unionized species are moved mainly by electromigration and electroosmotic flow, respectively; therefore, the mobilization of phenol and 2,4-DCP may vary with the degree of dissociation, ultimately with the soil pH.

This study was deliberately performed under the background pH condition. No attempt was made to control the soil pH values. The results should thus be able to reflect the variation of transport mechanism and the effect of electrolysis reaction during the electrokinetic test.

3. Materials and methods

3.1. Experimental soils

Kaolin and a natural soil were used as experimental soils. The natural soil was obtained from the topsoil layer (0–30 cm) of a woodland near Tsinghua University. Tree roots and debris were first removed, and the soil was air-dried. After that, the soil sample was sieved through a 10-mesh screen. The fraction finer than 2 mm was stored for later analyses and experiments. The kaolin soil was purchased from Xudong Chemical Com. in Beijing. The natural soil (designated as soil 1) and the kaolin (designated as soil 2) were categorized as sandy loam and light clay, respectively, with various characteristics listed in Table 1. The corresponding analytical methods were referred to Lu (2000). In addition, the zeta potential and acid–base buffering capacities of soil were measured using the methods described by Yeung et al. (1997).

3.2. Experimental system

A schematic diagram of the testing system was shown in Fig. 1. It consisted of a soil cell, graphite electrodes, an electrode control system, an electric current and voltage real-time monitoring system, and a DC power supply. The soil cell was made of Perspex with an inner size of 24 cm × 12 cm × 7 cm in length × width × height. Columnar graphite electrodes, 6 cm × 0.5 cm in length × diameter, were used to produce the non-uniform electric field, and plate-shaped electrodes, 6 cm × 10 cm × 0.5 cm, were used to generate the uniform electric field. The electrode control apparatus (Omron, Japan) was capable of reversing the polarity of the electric field, thus
allowing a change in the operational mode (i.e. unidirectional or bidirectional) for the test. The data monitoring system was able to monitor electric current and voltage on-line following a preset time step and automatically store them into a personal computer for later analysis. The power supply (Jintong Com., Beijing) provided a constant DC electric voltage in a range from 0 to 60 V for the electrokinetic test.

3.3. Experimental procedures

3.3.1. Sorption experiments

20 ml phenol or 2,4-DCP solutions in water with concentrations ranging from 0 to 800 mg l\(^{-1}\) were added into Teflon-sealed 50 ml glass bottles with 2 g of soil samples. The bottles were then placed on a shaker to equilibrate for 12 h at 150 rpm at room temperature. Centrifugation was carried out at 4000 rpm to obtain a clear supernatant for the determination of phenol and 2,4-DCP. The sorption amount was determined by the difference between the initial and the final concentrations, and expressed as mg phenol or 2,4-DCP per kilogram of dry soil. All tests were performed in duplicate.

3.3.2. Mobilization of phenol and 2,4-DCP under electrokinetics

The contaminated soil was artificially spiked with phenol or 2,4-DCP at a target content, which was determined by the sorption experiments. For the 2,4-DCP contaminated soils, the 2,4-DCP required to yield the target content was measured and then dissolved in 500 ml of anhydrous ethanol. The solution was mixed homogeneously with the tested soil (soil 1 or soil 2). The mixture was placed at a thickness of 1 cm beneath a ventilation hood for about 1.5 d until the ethanol completely evaporated. 2.2 kg of the 2,4-DCP-contaminated soil was mixed with a measured amount of deionized water to obtain the target water content. In order to obtain comparable results for the two soils, all the tests were carried out at an identical water saturation of 53%, that is, the target water content for the soil 1 and soil 2 was 17.5% and 28.4%, respectively. For the phenol-contaminated soils, they were prepared by mixing 2.2 kg of soils directly with the required amount of phenol solution in deionized water.

The moist contaminated soil was then placed into the electrokinetic cell by layers. Each layer was pressed down using a Perspex pestle and vibrated so that the amount of void space was minimized. After that, the soil specimen was compacted for 12 h at a pressure of 0.1 kg cm\(^{-2}\). The extruded pore fluids were removed from the surface layer using bibulous paper. A fraction of the soil specimen was obtained to determine the actual initial content of phenol or 2,4-DCP, soil pH and moisture, since a portion of the pollutants and water could volatilize during the preparation. The electrodes were directly inserted into the wet soil with a distance of 20 cm from each other. DC power supply, electrode control and monitoring equipment were then connected to the electrodes. Once the reactor assembly was completed, the cell was closed with a Perspex cover to prevent excessive water evaporation. The test was run at a constant voltage gradient of 1.0 V cm\(^{-1}\) for 1–14 d. During the test, the electric current and voltage across the soil specimen were automatically measured every 15 min.

At the end of test, soil samples were taken to analyze the soil pH, water content and the residual content of phenol or 2,4-DCP in the soil. In order to reflect the spatial variation of the variables, three sampling lines 4 cm apart and seven sampling points in each line at 3 cm intervals, that is, 21 soil samples in total, were taken for each test. The sampling points were shown in Fig. 1. Two cell experiments were conducted for each test, and a control experiment with no application of electric field was conducted in parallel.

3.4. Analytical methods

Methylene chloride and acetonitrile were used to extract phenol and 2,4-DCP from the soil samples, respectively. 1.0–1.5 g of soil sample was placed in a glass vial, and 10 ml of extractant was added. Vials were tightly sealed and then agitated for 3.0 h at 200 rpm on a shaker. 4–5 ml of the lower methylene chloride or acetonitrile layer was filtered through 0.45 μm Teflon membrane. The filtrate was analyzed on a high performance liquid chromatograph (HPLC) (Hewlett Packard 1050) equipped with a reverse-phase C18 column (4.6×250 mm) (Agilent extended-C18). The 2,4-DCP was measured at 284 nm, and a mixture of methanol and 5% acetic acid water solution (67:33, v:v) as the mobile phase. The phenol was determined at 284 nm, and a mixture of methanol and 2% acetic acid water solution (60:40, v:v) as the mobile phase. The HPLC was calibrated using four external standards prior to performing analyses, and the detection limit was 0.1 mg l\(^{-1}\).

In addition, soil pH was determined using a soil to water ratio of 1:2.5 and water content was determined using the methods described by Lu (2000).

3.5. Quality control and mass balance

The Perspex cells were specifically constructed for the tests. The electrodes were all new from the manufacturer. All the testing equipment, such as the electrode control system, monitoring apparatus, power supplies, and pH meters, were in good condition and were calibrated. All the glassware such as vials and sample bottles were verified to be clean. The chemicals used as solvents or in analyses were fresh and high grade purity.
Phenol and 2,4-DCP were used as an external standard for calibration. Sample blanks were injected regularly to ensure that the system remained uncontaminated. Standard samples were commonly injected to certify a uniform response. The syringe was rinsed with solvent between sample injections to eliminate cross-contamination.

After the electrokinetic tests were completed, a mass balance was conducted for the phenol and 2,4-DCP in the cells. Over the test periods of 1–14 d, 77–96% of the initial phenol was recovered from soil 1, while over the periods of 1–10 d, 88–91% and 90–94% of the initial 2,4-DCP were recovered, respectively, from soil 1 and soil 2. These showed that there was an overall mass balance of phenol and 2,4-DCP before and after the test. The discrepancies in the mass balance might be caused by volatilization of phenol and 2,4-DCP throughout the test, and by adsorption to the electrokinetic equipment, such as the Plexiglas cells, electrodes and sample vials.

4. Results and discussion

4.1. Characterization of experimental soils

Two soils with distinct properties as shown in Table 1 were used to evaluate the effect of soil properties on the mobilization of organics under electrokinetics. Soil 2 was chosen due to its low organic matter content, fine-grained particles and large surface area. It basically consists of kaolinite mineral and is fairly nonreactive. In contrast, soil 1 has a larger particle size, less surface area, and greater content of organic matter. As a natural soil, soil 1 has many complex and unknown active components, which would affect the test in an uncertain way.

The zeta potential and pH relationships for the two soils were presented in Fig. 2a. The zeta potential of soil 2 was greater than that of soil 1 in the range of greater than pH 3, indicating that the negative charge on the particle surface of soil 2 was more than that of soil 1 in this pH range. According to Eq. (1), greater electroosmotic flow would be induced in soil 2 than in soil 1. The acid–base buffering capacities for the soils were showed in Fig. 2b. The acid–base buffering capacity of soil 1 was much greater than that of soil 2 in the range of less than pH 9. The acid–base buffering capacity is related to soil pH change due to electrolysis reaction; the greater the acid–base capacity is, the less the soil pH changes, and vice versa.

4.2. Sorption of phenol and 2,4-DCP by the soils

Sorption is known to reduce the mobility of organic pollutants in soils (Simoni et al., 2001). Sorption experiments were thus conducted to evaluate the sorption of phenol and 2,4-DCP by the tested soils. The results were shown in Fig. 3. The sorption of 2,4-DCP on soil 1 and soil 2 followed the Freundlich equation and the linear equation, respectively; while the sorption of phenol on soil 1 followed the Langmuir equation. The sorption data could be fitted to the following equations:

\[ \frac{x}{m} = 0.075C_e^{1.307} \quad (R^2 = 0.985) \]  

\[ \frac{x}{m} = 1.530C_e/(1 + 0.029C_e) \quad (R^2 = 0.952) \]  

\[ \frac{x}{m} = 1.464C_e \quad (R^2 = 0.988) \]  

Fig. 2. Zeta–pH relationships (a) and acid–base buffering capacities (b) of the tested soils; soil 1 (●); soil 2 (□).

Fig. 3. Adsorption isotherms of phenol and 2,4-DCP by the tested soils phenol by soil 1 (●); 2,4-DCP by soil 1 (●); 2,4-DCP by soil 2 (∆).
where \( C_e \) was the equilibrium concentration of 2,4-DCP or phenol in solution (mg l\(^{-1}\)), \( x/m \) was the amount of 2,4-DCP or phenol sorbed per unit of soils (mg kg\(^{-1}\)). The average sorption amount of phenol by soil 1 was about 2.6 times greater than that of 2,4-DCP in the range of equilibrium concentration from 0 to about 450 mg l\(^{-1}\), and the average sorption of 2,4-DCP by soil 2 was about 3.6 times greater than by soil 1. Moreover, the saturation sorptive capacity of phenol on soil 1 was about 240 mg kg\(^{-1}\), but it was not possible to obtain the saturation sorptive capacity of 2,4-DCP on both soil 1 and soil 2 from the sorption isotherms. In addition, methylene chloride and acetonitrile were used to extract phenol and 2,4-DCP from the soils, respectively. An average extraction efficiency of 83%, 89% and 94% was obtained respectively for phenol in soil 1, 2,4-DCP in soil 1, and 2,4-DCP in soil 2. These suggested that soil 1 retained phenol more strongly than 2,4-DCP, but the retention of 2,4-DCP by soil 2 was weaker than by soil 1.

The fraction of soil organic matter (SOM) is generally regarded as the main sorbent (Chang, 2000). The SOM in soil 1 was more than four times greater than soil 2 (Table 1), which might partly contribute the greater sorption of phenol. On the other hand, the neutral phenol and 2,4-DCP undergo more sorption than their ionized forms (Li et al., 2000). The phenol and 2,4-DCP may dissociate to different degrees depending on the solution pH. 2,4-DCP–soil 2 solution and 2,4-DCP–soil 1 solution have average pH values of 5.74 and 8.68, respectively. With a \( pK_a \) value of 7.85, the 2,4-DCP in the soil 1 solution is expected to exist primarily as more hydrophilic phenolate anions, instead of the more hydrophobic neutral form in the soil 2 mixture. In contrast, phenol has a \( pK_a \) of 9.99 while the phenol–soil 1 solution has an average pH of 8.72; hence the phenol in the soil 1 mixture should exist mainly in its neutral form, which might further contribute to the greater phenol sorption by soil 1.

Judging from the initial pH of the tested soils (Table 1), the sorption isotherms provided in Fig. 3 would be reasonably valid at much higher solids content. It was decided to use a phenol content of about 200 mg kg\(^{-1}\) for soil 1 since most phenol at this content would be sorbed, and removal would require its desorption and migration through the soil specimens (Acar et al., 1992). Taking into account the relatively low retention of 2,4-DCP by the soils, a smaller 2,4-DCP content of about 100 mg kg\(^{-1}\) was used for both soil 1 and soil 2.

4.3. Mobilization of phenol and 2,4-DCP under different electrokinetics

The spatial change of phenol and 2,4-DCP in soil 1 under different electrokinetics was shown in Fig. 4. At the beginning of each test, the 2,4-DCP and phenol in the cells were distributed uniformly. After 6 d at 1.0 V cm\(^{-1}\), the 2,4-DCP and the phenol were accumulated in the region of 4–7 cm and 1–4 cm from the cathode, respectively. However, in the control tests with no application of electric field, they were not redistributed (data not shown). This demonstrated that the electrokinetic process could facilitate the desorption and movement of phenol and 2,4-DCP in the soil.

When a uniform electric field was applied, the content of phenol or 2,4-DCP along line \(-A, 0 \) and \(+A\) had a discrepancy of less than 10%. When a non-uniform electric field was applied, the content of phenol or 2,4-DCP along line \(-A, 0 \) and \(+A\) had a discrepancy of less than 10%.
form electric field was applied, the 2,4-DCP and phenol in the region of line 0 were concentrated at a distance of 7 cm and 4 cm from the cathode, respectively, with an increase of 124% and 98% over the 6-d period, respectively; however, the 2,4-DCP and phenol in the lines −A and +A were mobilized to a relatively low degree. These results showed that the mobilization of organics in the soil would vary with the type of electric field applied.

The spatial distribution of phenol or 2,4-DCP in the cells accorded, as a whole, with the distribution of electric field density in the corresponding system. In uniform electrokinetic cells, the electric field density across the soil specimen distributed uniformly along lines −A, 0 and +A. However, in non-uniform electrokinetic cells, the electric field density in the region of line 0 was greater than that in the lines −A and +A (Betts, 1995; Luo et al., 2004b). According to Eqs. (1) and (2), non-uniform electric field could produce a greater driving force in the region of line 0 than in lines −A and +A, and induce faster movement in this region accordingly (Luo et al., 2004a).

Fig. 4 also showed that the mobilization of organics under electrokinetics depended upon the organic species. Over the 6-d period, the peak values for 2,4-DCP and phenol in the line 0 appeared in the region of 7 and 4 cm from the cathode, respectively, indicating that the movement of 2,4-DCP in soil 1 towards the anode was about 0.5 cm d−1 V−1 faster than that of phenol under the same conditions.

The soil 1 had an average pH value of 7.74, closer to the pK_a of 2,4-DCP and yet much less than the pK_a of phenol. Therefore, the 2,4-DCP in soil 1, especially in the cathode region, could be moved in its ionized form by electromigration, while the phenol might be mobilized mainly in its neutral form by electroosmotic flow before the soil pH was increased enough due to the electrolysis reaction at the cathode. On the other hand, the 2,4-DCP in soil 1 was not as strongly retained as the phenol, and thus was easier to desorb into the pore fluid. These might be the reasons for the faster movement of 2,4-DCP in soil 1.

4.4. Mobilization of phenol and 2,4-DCP under close-flow condition

Fig. 5 shows the temporal variation of phenol and 2,4-DCP in the region of line 0 in the non-uniform electrokinetic cells under closed-flow conditions.

As described in Fig. 5a, the phenol in soil 1 was moved mainly towards the cathode over the 6-d period. However, the phenol content in the 1-cm region near the cathode was gradually reduced from 1 d onwards; especially over the 14-d period, the phenol in both the anode and cathode region was reduced significantly while the peak content of phenol appeared in the middle of the cells. These indicated that the phenol was initially mobilized towards the cathode region, and then towards the anode region under closed-flow conditions.

A similar trend existed in the mobilization of 2,4-DCP in soil 1 as presented in Fig. 5b. Over the period of 3, 6 and 10 d, the peak content of 2,4-DCP along line 0 existed in the region of 4, 7 and 10 cm from the cathode, with an increase of 62%, 124% and 54%, respectively. With the treatment time increased, the 2,4-DCP in the cathode region was gradually reduced, while in the anode region it increased slightly. These findings indicated that the 2,4-DCP was moved, as a whole, towards the anode region. Based on the movement of 2,4-DCP peaks, it was estimated that the 2,4-DCP was mobilized through soil 1 towards the anode at a rate of about 1.0 cm d−1 V−1.

The 2,4-DCP in soil 2 was moved much faster than in soil 1 despite their similar properties as shown in Fig. 5c. At the start of test, the 2,4-DCP in the anode region was mobilized much easier in soil 2 than in soil 1, but in the cathode region it was more difficult to mobilize than in
soil 1. Over the period of 3 and 6 d, the peak content of 2,4-DCP in soil 2 appeared in the region of 7 and 10 cm from the cathode, respectively, instead of in the region of 4 and 7 cm in soil 1, indicating that the 2,4-DCP in soil 2 was moved towards the anode at a rate of about 1.0–1.5 cm d$^{-1}$ V$^{-1}$ faster than in soil 1.

During the test, the soil pH near the anode region reduced gradually, while near the cathode region it increased (Fig. 7d). The ionized 2,4-DCP and phenol near cathode region would increase with time, and consequently an increasing amount of 2,4-DCP and phenol was mobilized by electromigration towards the anode. At the same time, the electroosmotic flow towards the cathode region would gradually decrease as a result of the reduction in soil pH near anode region (Yeung et al., 1997), and hence a decreasing amount of phenol and 2,4-DCP was dragged towards the cathode by the electroosmotic flow. This might be responsible for the movement toward the anode of phenol and 2,4-DCP under closed-flow conditions.

The zeta potential of soil 2 is greater than that of soil 1 in the range of soil pH from about 3 to 14 (Fig. 2a). According to Eq. (1), a greater electroosmotic flow would be induced in soil 2, which might contribute to the easier movement of 2,4-DCP towards the cathode at the start of test. Moreover, soil 2 has a lower acid–base buffering capacity (Fig. 2b). A remarkable change in soil pH and thus 2,4-DCP dissociation could be produced in soil 2 due to electrolysis reaction. This might contribute to the relatively faster movement of 2,4-DCP in soil 2 than in soil 1.

4.5. Effect of polarity-reversal on movement of phenol and 2,4-DCP

When a polarity-reversal of the electric field was performed every 6 h, no significant accumulation of 2,4-DCP or phenol was observed in the cells, as presented in Fig. 6. The movement direction of phenol and 2,4-DCP could be reversed arbitrarily whenever the polarity of the electric field was switched, suggesting that the movement of organics in soils could be easily controlled by regulating the application mode of electric field.

4.6. Effect of soil pH on movement of 2,4-DCP and phenol under electrokinetics

Phenol and 2,4-DCP may dissociate to form phenolate anions depending upon the soil pH, and hence their mobilization might vary with soil pH. In order to evaluate this effect, soil 1 was adjusted to pH 9.3 using NaOH solution and tested under the same conditions as pH 7.7. The results were shown in Fig. 7.

At pH 7.7, the peak content of phenol and 2,4-DCP were both at a distance of 4 cm from the cathode. However, at pH 9.3, the peak phenol and 2,4-DCP was in the region of 10 and 19 cm from the cathode, respectively, with a greater increase of 35% and 63% than at pH 7.7 (Fig. 7a and b). These indicated that the phenol and 2,4-DCP were both moved mainly towards the anode at pH 9.3, and their migration rate was twice and five times greater than that at pH 7.7, respectively. Moreover, the pore fluid moved more significantly towards the cathode at pH 9.3 than at pH 7.7 (Fig. 7c); however, the phenol and 2,4-DCP in the cathode region at pH 9.3 was much less than at pH 7.7. This suggested that the electroosmotic flow played a relatively less significant role in the mobilization of phenol and 2,4-DCP at higher pH values. In addition, the soil pH near the anode decreased while near the cathode it increased (Fig. 7d), which would also affect the movement of phenol and 2,4-DCP in the soils.

4.7. Discussion on potential application of non-uniform electrokinetics

This study demonstrates that non-uniform electrokinetic transport processes can enhance the mobility of organic pollutants in unsaturated soils. By use of the electrokinetically-induced desorption and movement, the organic pollutants dispersed in contaminated sites could be directed to specific treatment zones, into which some reagents and even active bacteria could be added for in situ treatment, or from which the soils containing with high quantities of pollutants could be removed for ex situ treatment. At the same time, it could be used to accelerate the movement of organic pollutants towards
the active indigenous bacteria to increase the bioavailability of target organics during the in situ bioremediation.

In addition, the cost associated with the non-uniform electrokinetic remediation was expected to be lower than the common uniform electrokinetic treatment due to its ease of installation, the small amount of electrode materials. The related studies ongoing also showed that the non-uniform electrokinetic system has advantages over the uniform system in operational stability and maintaining a natural environment (Luo et al., 2004b). Therefore, non-uniform electrokinetics is of significance for potential practical application.

5. Conclusions

(1) Non-uniform electrokinetic transport processes can enhance effectively the desorption and movement of phenol and 2,4-DCP in unsaturated soils, the extent of which is related to the organic species, the soil characteristics, and the operational mode.

(2) Electromigration and electroosmotic flow are the major driving forces for the movement of phenol and 2,4-DCP in the soils, while the electrolysis reaction and soil pH are the main factors affecting the mobilization of organic pollutants under closed-flow conditions.

(3) Non-uniform electrokinetic remediation is of significance for potential practical application to the in situ remediation of contaminated sites.

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