

The use of 2D non-uniform electric field to enhance in situ bioremediation of 2,4-dichlorophenol-contaminated soil

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Abstract

In situ bioremediation is a safe and cost-effective technology for the cleanup of organic-contaminated soil, but its remediation rate is usually very slow, which results primarily from limited mass transfer of pollutants to the degrading bacteria in soil media. This study investigated the feasibility of adopting 2D non-uniform electric field to enhance in situ bioremediation process by promoting the mass transfer of organics to degrading bacteria under in situ conditions. For this purpose, a 2D non-uniform electrokinetic system was designed and tested at bench-scale with a sandy loam as the model soil and 2,4-dichlorophenol (2,4-DCP) as the model organic pollutant at two common operation modes (bidirectional and rotational). Periodically, the electric field reverses its direction at bidirectional mode and revolves a given angle at rotational mode. The results demonstrated that the non-uniform electric field could effectively stimulate the desorption and the movement of 2,4-DCP in the soil. The 2,4-DCP was mobilized through soil media towards the anode at a rate of about $1.0 \text{ cm d}^{-1} \text{ V}^{-1}$. The results also showed that in situ biodegradation of 2,4-DCP in the soil was greatly enhanced by the applied 2D electric field upon operational mode. At the bidirectional mode, an average 2,4-DCP removal of 73.4% was achieved in 15 days, and the in situ biodegradation of 2,4-DCP was increased by about three times as compared with that uncoupled with electric field, whereas, 34.8% of 2,4-DCP was removed on average in the same time period at the rotational mode. In terms of maintaining remediation uniformity in soil, the rotational operation remarkably excelled the bidirectional operation. In the hexagonal treatment area, the 2,4-DCP removal efficiency adversely increase with the distance to the central electrode at the bidirectional mode, while the rotational mode generated almost uniform removal in soil bed.

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1. Introduction

Chlorinated phenols, as recalcitrant organic pollutants, have posed serious environmental problems due to their wide use as biocides, wood preservatives and organic precursors of pesticides [1,2]. Soil chlorophenol contamination mainly resulted from spilling or dripping chlorophenol–solvent mixture onto the ground. Chlorophenols tend to remain in the soil phase for a long time period due to their toxicity and hydrophobicity. Despite chlorophenol toxicity, it has been found that a variety of bacteria are able to degrade different chlorophenol isomers [3–6]. Biological treatment of chlorophenols-contaminated sites attracted

more and more attention than physical and chemical methods due to its cost effectiveness and no secondary contamination. Ex situ biological treatment such as soil slurry reactor would inevitably disturb the local environments; while in situ bioremediation is usually less efficient, primarily due to limited pollutants mobilization to the degrading bacteria in soil media [7].

Electric fields have been applied in soil to increase contact opportunities between pollutants and bacteria [8]. The electric field imposed on a soil matrix can induce, complex, coupled electrochemical and geochemical processes in the soil matrix including electroosmosis, electromigration and electrophoresis [9–12]. Electroosmosis is the movement of pore fluids in an electric field, which mobilizes the water-soluble composition of the organics along with pore fluid from the anode to the cathode [13]. Electromigration is the transport of ions and ion complexes to the electrode of opposite charge, and is often at least one order

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of magnitude greater than electroosmosis [14]. Thus, in an electric field, ionizable organic pollutants and ionic nutrients are transported in soil media predominantly by electromigration. Electrophoresis is the transport of charged particles, including clay particles and bacterial cells, toward the electrode of opposite polarity [15]. These principal electrokinetic mechanisms play the critical roles in motivating organic molecules, bacterial cells and nutrients crossing soil matrix and thus have the potentials for accelerating the mass transfer and interactions among organic pollutants, bacterial cells and nutrients during in situ bioremediation [16].

In an electric field, the electrolysis reaction on the surface of electrodes produces acids and bases which advance through soil matrix and change soil pH. The change of soil pH will affect the electrokinetic transport process of chlorophenol and the viability of bacterial cells. Chlorophenol can exist in both the ionized and neutral forms in soil [17]. The ratio of its ionized to neutral form increases as soil pH rises, and vice versa. The existing form of chlorophenol exerts important effects on its transport in soil matrix as the sorption of chlorophenol in soil is, in part, depending upon its form in soil environment [17] and ionized and neutral chlorophenol migrate with different mechanisms (electromigration or electroosmosis). Moreover, the electrolysis caused extreme soil pH affects adversely the viability of bacteria near electrodes especially the cathode [18]. In order to avoid unfavorable effects of extreme pH in electrokinetic bioremediation, some common strategies have been considered involving applying acid–base buffering chemicals, constructing modified reactors and circulating electrolyte solutions in electrode compartments [19]. An emerging strategy is to reverse the polarity of electric field (bidirectional operation) for automatically neutralizing H^+ and OH^- ions electrolyzed at the electrodes. It has been demonstrated that polarity reverse could effectively keep soil pH stable when appropriate intervals were chosen [20–22].

In addition, non-uniform electric field was usually used to minimize the complications associated with electrokinetic treatment such as soil consolidation and cracking, development of steep pH gradient in in situ bioremediation because columnar electrode for non-uniform electric field is of a smaller contact area with soil matrix than planar electrode for uniform [13]. Non-uniform electric field could be one-dimensional (1D) or two-dimensional (2D) depending upon the electrode array. Generally, electrode pairs are adopted to generate 1D electric field, while the configurations of regular polygons are used to produce 2D electric field. In theoretical modeling study, the distribution of 1D and 2D electric field is usually simplified to be linear and radial, respectively, despite more complicated distribution under practical conditions [23]. Previous studies had demonstrated that 1D non-uniform electrical field could effectively enhance the biodegradation of phenolic organics in unsaturated soil [21]. The studies on 2D electrokinetic remediation were rare and concentrated on theoretical aspects. Because of the superiority in modularizing the treatment cell to develop electrode matrix, 2D configuration may be more accessible to large-scale field application than 1D electrode array. It has been proved that many organics such as PAHs and BTEX compounds could be moved by electroosmosis towards the cathode in 2D electric field

[24]. Therefore, it should be possible to combine electrokinetic movement of organics in 2D electric field with biodegradation in situ, thus overcoming the constraints of mass transfer to biodegradation in soil media.

The present study aimed at assessing the feasibility of adopting 2D non-uniform electric field to accelerate in situ bioremediation of chlorophenol-contaminated soil. For this purpose, a 2D non-uniform electrokinetic system was developed and tested in bench-scale experiments at bidirectional and rotational modes. In order to reduce the ineffective area, hexagonal electrode matrix was adopted to produce 2D electric field. In addition, a sandy loam and 2,4-DCP were selected as the model soil and chlorophenol, respectively.

2. Material and methods

2.1. Soil and bacteria

A natural soil used as the experimental soil was categorized as sandy loam, with various characteristics listed in Table 1. The corresponding analytic methods were described by Lu [25]. The natural soil was sterilized three times using an autoclave and dried at 105 °C for bioremediation test. In addition, the contaminated soil was obtained by blending 2,4-DCP solution in anhydrous ethanol into the natural soil and then evaporating the ethanol completely beneath a ventilation hood.

The bacterial species capable of degrading 2,4-DCP were isolated from a soil contaminated with pesticides by using a basic mineral media with 2,4-DCP as the sole carbon source (designated as CP media), as described by Quan et al. [26]. The bacterial cells were grown in CP media on a shaker at 30 °C and 150 rpm and harvested in the exponential growth phase by centrifugation. After washed twice, they were resuspended in sterilized deionized water to obtain bacterial suspension for all of the tests. The preliminary study showed that bacterial suspension added into soil could degrade 2,4-DCP at a content of 200 mg/l in aqueous phase by 91% during 2 days, indicating its high initial activity.

Table 1
The main characteristics of the tested soils

Item determined	Sandy loam
Particle size analysis (%)	
<2 μm	11.21
2–10 μm	5.01
10–50 μm	7.00
50–250 μm	63.31
>250 μm	13.47
BET surface area (m^2/g)	8.10
Carbonate (%)	0.0306
Organic matter (g/kg)	5.33
CEC (cmol/kg)	11.25
pH	7.74
Air-dried density (g/cm)	1.35
Saturated water content (%)	33.0
Point of zero charge	1.5
Liquid limit (%)	19.7
Plastic limit (%)	18.2

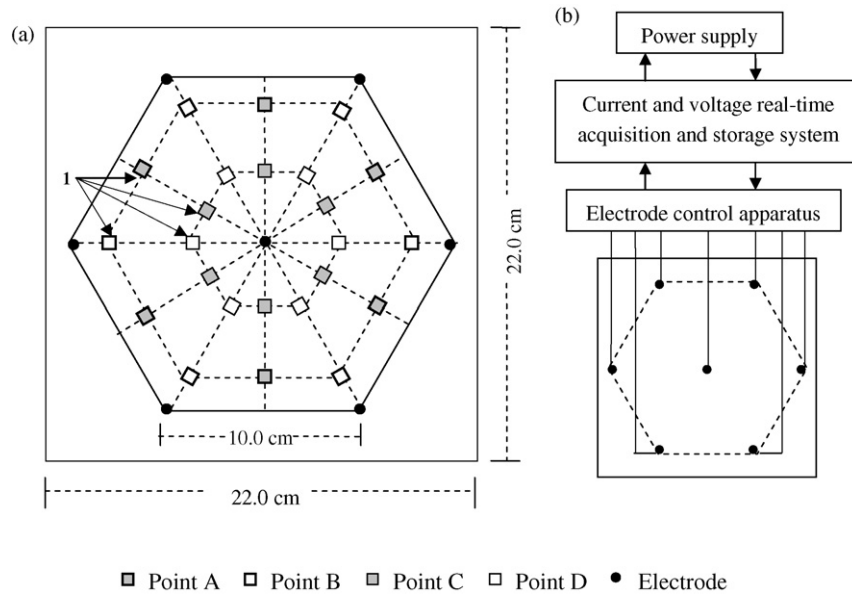


Fig. 1. Schematic of experimental set-up (a) and sampling points (b) in the square reactor.

2.2. Experimental system

Two sets of electrokinetic systems were used in the tests. Each consisted of a soil cell, inert graphite electrodes, an electrode control system, an electric current and voltage real-time monitoring system and a dc power supply. The first set of system was made of a rectangle soil cell in a size of length 24 cm \times width 12 cm \times height 7 cm, as described by Luo et al. [16]. The second one was made of perspex, with an inner effective size of length 22 cm \times width 22 cm \times height 10 cm, as shown in Fig. 1a. Column-shaped graphite electrodes, length 6 cm \times diameter 0.5 cm, were used to generate the non-uniform electric field. The electrode control apparatus (Omron, Japan) was capable of switching the polarity of electric field, and thus allowing a change in operational modes (i.e. unidirectional, bidirectional or rotational) for tests. The monitoring system could monitor electric current and voltage on-line and store them into a personal computer for later analysis. The power supply could provide a constant direct current electric voltage in a range from 0 to 60 V for the electrokinetic tests.

2.3. Experimental procedures

During experimental preparation, the soils of different types and weights were blended with either deionized water or bacterial suspensions (about 1.0×10^9 CFU/ml) thoroughly to obtain target moisture (shown in Table 2). The wet soils were tamped into the soil cell in layers, vibrated for 5 min and then compacted for 12 h at a pressure of 0.1 kg/cm² so as to minimize the void space. The extruded pore fluids from the top layer was removed with bibulous paper. The soil beds with the volume of length 24 cm \times width 12 cm \times height 5 cm and length 22 cm \times width 22 cm \times height 3.5 cm were obtained in rectangle and square reactors, respectively. The soil beds were then sampled to determine initial soil pH, water content and 2,4-DCP content.

For the rectangle reactors, a couple of electrodes were oppositely installed into the wet soil specimen with a distance of 20 cm and then connected with two poles of power supply through electrode control apparatus and monitoring equipment. When bidirectional operation was applied, two electrodes exchanged polarity periodically.

In the square reactors, six electrodes were arranged in a hexagonal configuration, and the seventh electrode was located in the center of hexagon, as shown in Fig. 1a. The distance between central electrode and peripheral electrode was 10 cm. All the electrodes were then connected with power supply according to Fig. 1b. Under bidirectional operation, central and peripheral electrodes exchanged polarity periodically, as shown in Fig. 2a. In contrast, rotational operation mode was more complicated, with the whole process shown in Fig. 2b. Under this mode, the peripheral electrodes were electrified one by one clockwise, while the central electrode was electrified all along. Moreover, electrodes reversed polarity once every rotational cycle, with the same reversal interval as bidirectional mode. Whenever bidirectional or rotational mode was used, the initial polarity of central electrode was anodic so as to prevent water accumulation and weaken electrolysis reaction therein.

Table 2
Variables in different groups of tests

Group number	1	2	3	4
Soil bed	Rectangle	Square	Square	Square
2,4-DCP content (mg/kg soil)	100	0	100	100
Dry soil weight (kg)	2.2	2.8	2.8	2.8
Moisture (%)	17.5	20.8	20.8	20.8
Bacterial content (CFU/g soil)	N/A	N/A	2.3×10^8	2.3×10^8
Operational mode	U and B	U and B	B	R
Operational time (days)	10	4	15	15
Number of duplicate tests	2	2	2	2

Where U, B and R refer to unidirectional, bidirectional and rotational operation, respectively.

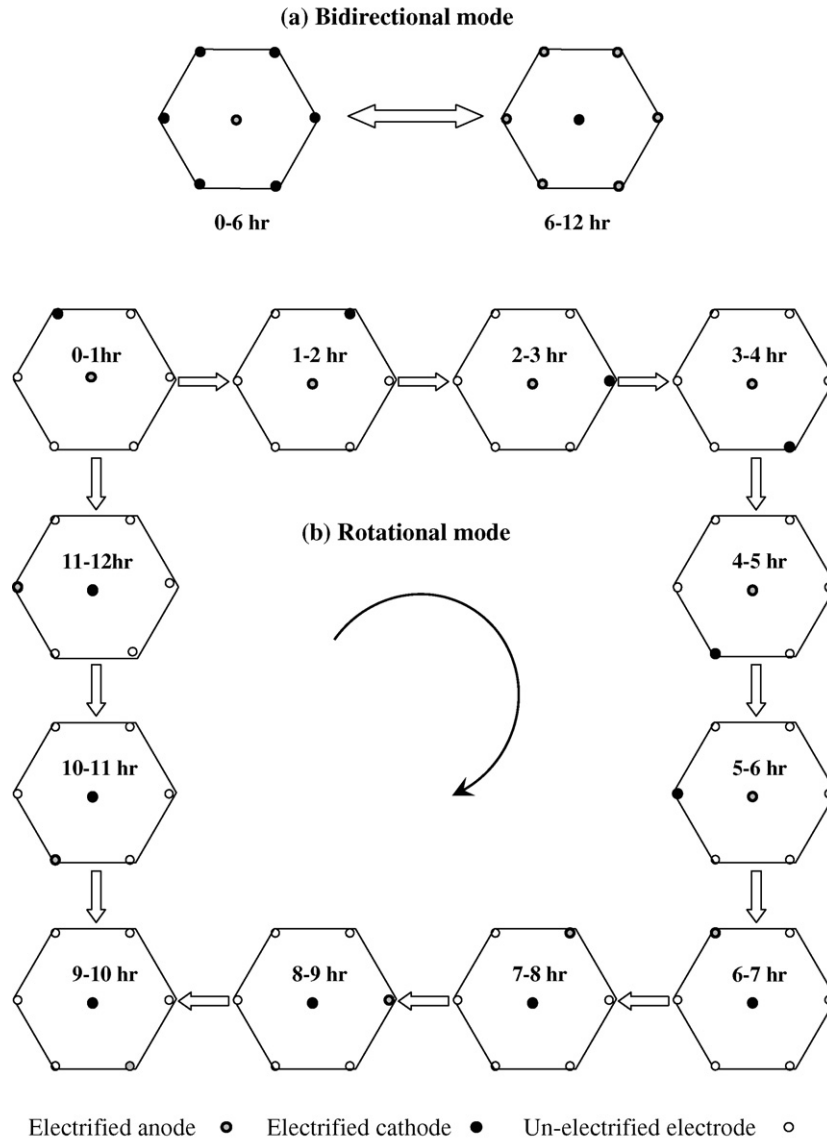


Fig. 2. Schematic of bidirectional (a) and rotational (b) mode for an operation cycle by use of a hexagonal electrode matrix.

Four separate groups of tests were conducted, with basic variables listed in Table 2. The first group was to investigate 2,4-DCP desorption and migration under non-uniform electric field. The second group was to study the change of soil characteristics under 2D electric field and the results were used to determine a proper polarity-reversal interval for bidirectional operation. The third and fourth group were to study in situ electrokinetic biodegradation of 2,4-DCP at bidirectional and rotational modes, respectively. In last two bioremediation tests, water content was increased to 21% so as to prevent moisture from being limiting factor of biodegradation. Each test was run at a constant voltage gradient of 1.0 V/cm in the soil cell while the current and voltage across the soil specimen were automatically measured every 15 min. A control experiment with no electric field applied was conducted in parallel.

At the end of tests, a fraction of the soil specimen (length 1 cm × width 1 cm × height 3.5–5 cm) was taken using a U-shaped sampler and a spartula to determine the soil pH, water

content and the residual 2,4-DCP content. In the rectangle soil cells, the soil samples were taken along the line on which the two electrodes were located. Seven sampling points were distributed in each line, with a space of 3 cm between neighboring locations. For the square soil cells, the specimens were sampled clockwise from the initial location labeled “1” to the final location labeled “6” (Fig. 1a). For the purpose of reflecting spatial variation, specimens were sampled at six sorts of points indicated by A, B, C, D, Op and Oc, respectively. Points B and D referred to the points in bisector of hexagonal configuration, with the distance of 8 and 4 cm from the central electrode, respectively (Fig. 1a). Point A was the midpoint of adjacent point B and point C was in the middle of adjacent point D (Fig. 1a). In order to monitor soil characteristics around electrodes, soil bed was sampled at point Op and Oc which were located in hexagonal bisector and 1.0 cm away from the peripheral and central electrodes, respectively.

Acetonitrile was used to extract 2,4-DCP from 1.0 to 1.5 g of soil samples. After ultrasonic extraction for three times (with

an extraction efficiency of 94.8%), the extractant was filtered through 0.45 μm Teflon membrane and then analyzed on a high performance liquid chromatograph (HPLC, Hewlett Packard 1050) at 284 nm equipped with a reverse-phase C18 column (Agilent, USA) and a mobile phase containing methanol and 5% acetic acid (67/53, v/v). HPLC was calibrated using four external standards prior to performing chemical analysis and using standard 2,4-DCP during analysis to ensure that the system remained good performance and to certify a consistent response. In addition, the syringe for sample injection was rinsed three times between each injection to eliminate cross-contamination.

Soil pH was determined using a soil to water ratio of 1:2.5 and water content of the soil samples was determined using the standard methods [25]. All the analysis was performed in duplicate and the average value was presented for the testing result.

3. Result and discussion

3.1. The mobilization of 2,4-DCP under non-uniform electric field

In this study, the initial content of 2,4-DCP and water in tested soil was about 100 mg/kg and 17.5%, respectively. Based on the sorption study for 2,4-DCP on the natural soil by Luo et al. [8], about 78 mg/l of 2,4-DCP was in porous water and 86.4% of the total 2,4-DCP was sorbed on soil particles. Therefore, the migration for the most of 2,4-DCP at this content would require 2,4-DCP desorption from soil particle surface. At the beginning of the test, 2,4-DCP was evenly distributed in soil cell, with the homogeneous pH and water content. Under a constant electric gradient of 1.0 V/cm at unidirectional operation, however, the 2,4-DCP was concentrated to a specific region depending on the operation time as shown in Fig. 3. These results suggested that the 2,4-DCP could be desorbed and mobilized through soil matrix in the applied non-uniform electric field.

In the process of 10-day unidirectional operation, the 2,4-DCP dropped gradually in the cathode region, while increased slightly or remained unchanged in the anode region at the early stage, as shown in Fig. 3, demonstrating the bulk 2,4-DCP was

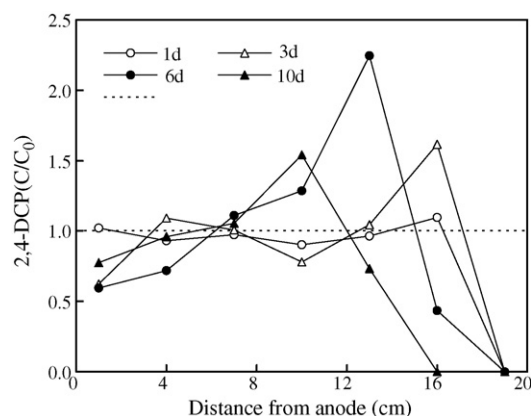


Fig. 3. The change of 2,4-DCP distribution in soil at unidirectional mode over 10 days.

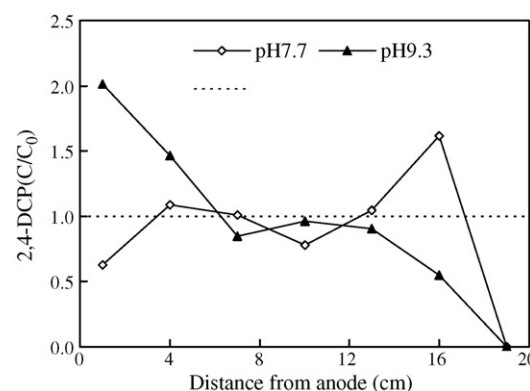


Fig. 4. The distribution of 2,4-DCP in soil under different pH conditions at unidirectional mode (3 days).

mobilized to the anode region over this period. At the initial stage of test, the migration of 2,4-DCP was only remarkable in cathode region. After 1-day operation, the 2,4-DCP content at a distance of 1 cm from the cathode was decreased to zero, whereas in the region 4 cm from the cathode improved by 10% and at other positions kept almost unchanged (Fig. 3). After 6 days, the peak 2,4-DCP was observed at 10–14 cm away from the anode. At the end of 10 days, the peak content of 2,4-DCP was observed at 10 cm from the anode. This could infer that the 2,4-DCP was mobilized through soil media towards the anode at an average rate of about 1.0 cm d⁻¹ V⁻¹. With treatment time increased, the soil pH near the cathode increased (data not shown) [21]. As an ionizable organics at high pH, 2,4-DCP at the cathode in soil moving toward anode in electric field in later stage might rely on electromigration as the main mechanism of its electrokinetic transport due to its higher efficiency. Furthermore, 2,4-DCP in anode region was reduced to some extent after 3-day operation. This might result from the migration of neutral 2,4-DCP to cathode through electroosmosis.

Because pH changed in the soil during the treatment time period, the effect of pH variation on 2,4-DCP migration was also examined in this study. pH 7.7 and 9.3 were chosen to represent neutral and alkaline soil conditions, respectively. Our results showed that under initial pH 7.7, the peak 2,4-DCP was at a distance of 4 cm away from the cathode after 3-day unidirectional operation, whereas, with pH 9.3, the peak 2,3-DCP was at 19 cm, and the peak content was over 1.24 times of that under pH 7.7 (Fig. 4). These indicated that the 2,4-DCP in soil moved mainly towards the anode region under pH 9.3, and its migration rate was five times greater than that under pH 7.7. Natural soil had an average pH of 7.7, close to the 2,4-DCP pK_a value of 7.85. The slight increase of pH in soil could induce dramatic dissociation of neutral 2,4-DCP, based on the dissociation equilibrium [17]. The electrolysis reaction could change the soil pH conditions with treatment time and thus might influence 2,4-DCP migration in soil bed, especially cathode region.

At bidirectional modes with polarity-reversal intervals of 6 and 12 h under the application of 1D electric field, there was no significant accumulation of 2,4-DCP observed in the electrokinetic cells over 6-day period in spite of the slight decrease at the electrodes region (Fig. 5), indicating that bidirectional operation

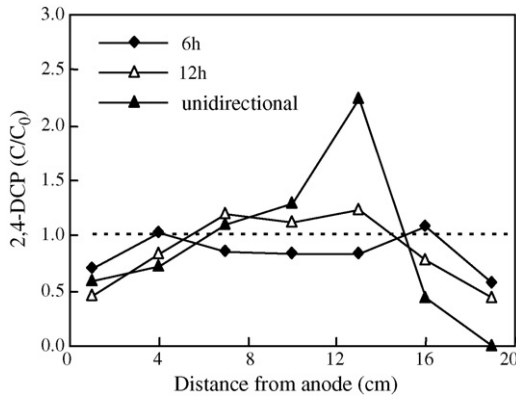


Fig. 5. Effect of polarity-reversal of non-uniform electric field on 2,4-DCP distribution in soil bed (6 days).

could keep 2,4-DCP uniformity in the soil bed. Reversing the polarity of electric field can change 2,4-DCP movement direction periodically and hence may result in 2,4-DCP to move back and forth through the soil. As a result, no significant net effect on the distribution of contaminant was observed.

The studies above demonstrated 2,4-DCP could be desorbed and migrated in soil matrix under the application of non-uniform electric field and the bidirectional operation might provide the possibility to enhance in situ biodegradation of 2,4-DCP in soil matrix by improving the transport of 2,4-DCP to degrading bacteria without changing contaminant distribution in the soil.

3.2. The changes of soil characteristics under different operation modes

The clean natural soil was used in hexagonal configuration to examine the effects of applying 2D electric field on soil properties. The experimental results showed the soil water content and soil pH varied with operation mode and treatment time (Figs. 6 and 7). Unidirectional operation induced the extreme soil pH and the remarkable change of water content in the electrode region under hexagonal configuration.

After 4-day operation, the soil pH near the cathode increase from initial 7.7–9.5, while near the anode dropped sharply to about 0.7 (Fig. 6a). This indicated that soil pH around the central electrode changed more dramatically than that near the peripheral electrodes. The rapid acidification in the central region was induced by the intense electrolysis reaction around the central electrode. Theoretically, the current through central electrode was six times as large as that passing individual peripheral electrode. In the other part of the cell, soil pH kept almost unchanged. This might be attributed from the high buffering capacity of natural soil. The previous study has demonstrated the acid–base buffering capacity of natural soil tested was much greater than other types of soil, such as kaolin soil [8]. Generally, electrolysis reaction caused less soil pH change in the soil with the greater acid–base capacity.

In addition, the soil moisture near the anode reduced by 24.3% while near the cathode increased by 18.0% (Fig. 6b), which might result from radial electroosmotic flow directing to cathode. Due to the extreme pH and moisture variation in the

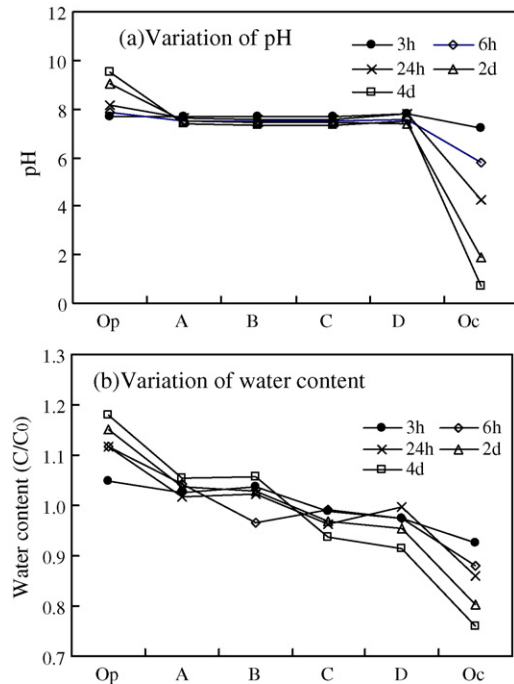


Fig. 6. The change of soil pH (a) and water content (b) at unidirectional mode over 4 days.

central region after a short-term operation, unidirectional mode seemed to be unsuited with biodegradation. Therefore, when 2D configuration was adopted, bidirectional operation was carefully investigated to control the variations of pH and moisture near the central electrode.

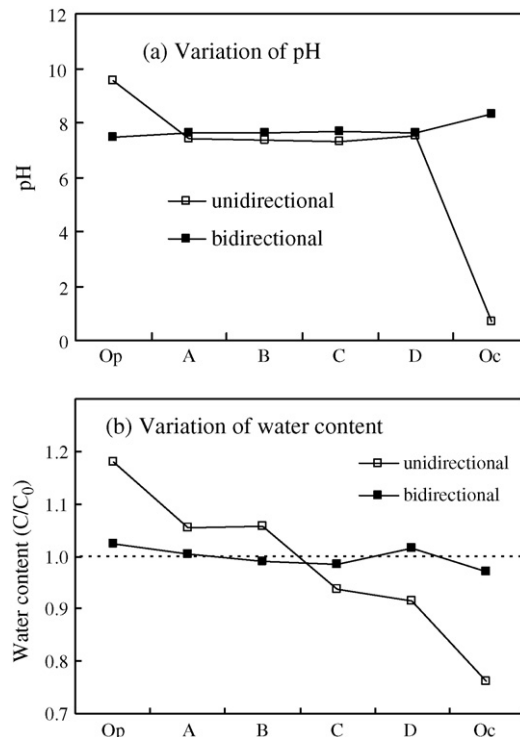


Fig. 7. Effect of polarity-reversal of non-uniform electric field on soil pH (a) and water content (b) at the operation of 6 h interval for 4 days.

Generally, soil pH with a range from 5.5 to 8.5 was considered as a favorable condition for bioremediation [27]. The results with unidirectional mode showed that, after 6 h unidirectional operation, pH near the central electrode dropped to 5.8, close to the lower limit of the favorable range for bioremediation (Fig. 6a). It suggested the polarity of electric field should be reversed in time so as to prevent further acidification. The extreme pH conditions could be adequately avoided if the reversal occurred earlier, e.g. after unidirectional operation for 3 h. Unfortunately, the reversal in advance might induce more energy to be consumed on the basis of the previous finding that the faster polarity reversal, the greater the electricity consumption [21]. Thus, 6 h seemed to be a better interval for bidirectional operation to keep proper soil pH condition and to save energy at the same time.

Under bidirectional operation with an interval of 6 h, the dramatic changes in the soil pH and water content could be effectively controlled in the electrode region, as shown in Fig. 7. At the end of 4 days, the soil pH was maintained in a range from 7.0 to 7.7 (Fig. 7a) while the soil moisture changed less than 5% (Fig. 7b) all over the sampling locations in the cell. It was concluded from these results that, bidirectional operation could overcome the rapid acidification and water draining in central region associated with unidirectional application of electric field. As a result, bidirectional operation with a polarity-reversal interval of 6 h was chosen as an optimized operation mode for later electrokinetic bioremediation.

3.3. The *in situ* biodegradation of 2,4-DCP under bidirectional operation

The test cells were prepared as listed in the group 3 of Table 2. At the beginning of test, the degrading bacteria and 2,4-DCP were completely mixed and evenly distributed in the tested soil. In the control tests which were uncoupled with electric field, 82.9% of 2,4-DCP was found still remained in the soil after 15 days at moisture of 20.8% regardless the locations of sampling (Fig. 8). This indicated that *in situ* biodegradation without an imposed electric field was not sufficient enough. Slow biodegradation with the favorable distribution form of contaminant and degrading bacteria implied that an adequate mass-transfer might be required for the effective biodegradation of 2,4-DCP in the soil matrix.

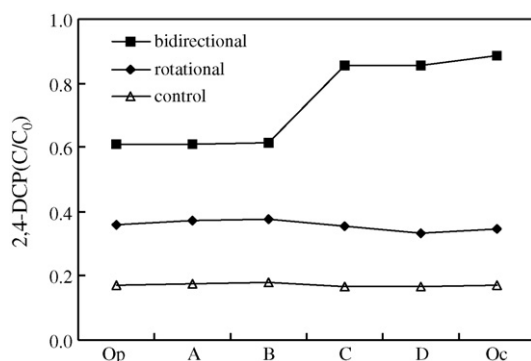


Fig. 8. The average removal rate of 2,4-DCP at different positions under bidirectional and rotational operation (15 days).

When a constant voltage gradient of 1.0 V/cm was applied in a bidirectional mode for 15 days, 73.4% of 2,4-DCP in the soil was reduced on average of over all sampling locations (shown in Fig. 8), more than three times removal as in the control tests. This indicated that the applied electric field could significantly improve the biodegradation of 2,4-DCP in the soil. The results also showed that although the same biodegradation rate was observed at identical geometrical locations, the efficiency of biodegradation of 2,4-DCP in the hexagonal treatment area varied spatially. After 15 days, the 2,4-DCP at point A and B in the outer sampling circle decreased on average by 61.0 and 60.7%, respectively, whereas at point C and D decreased by 85.4 and 85.5%, respectively, suggesting a more rapid removal of 2,4-DCP in inner circle (shown in Fig. 8). The maximum removal of 2,4-DCP with 88.4% was observed at point Oc. Unevenness in remediation might be attributed to the unique radial distribution of 2D electric field. The closer to the center electrode, the higher the density of electric field was. The density of electric field is believed a driving force for mass transfer in the electric field [16,21], thus greater mass transfer in the region close to the central electrode resulted in rapider remediation of 2,4-DCP.

3.4. The *in situ* biodegradation of 2,4-DCP under rotational operation

The extent of remediation uniformity was usually considered as one of important parameters for evaluating good remediation methods. As shown previously, bidirectional operation induced uneven bioremediation under hexagonal configuration. The dynamic mechanism of the process might be continuous linear movement of contaminants and bacteria induced by bidirectional electric field. In contrast, rotational electric field possesses a potential to producing a more complex mechanism, i.e. the multidirectional movement of contaminants and bacteria. To study the characteristics of rotational electric field, rotational operation was adopted in the test for enhancing biodegradation of 2,4-DCP in soil.

As shown in Fig. 8, after rotational operation for 15 days, 2,4-DCP at all the sampling points decreased on average by 34.8%, about one time greater than removal in control tests without applied electric field. This demonstrated that rotational electric field could enhance the biodegradation of 2,4-DCP in tested soil. Moreover, after 15-day operation, the 2,4-DCP at the points A, B, C and D dropped similarly, on the average by 37.4, 37.5, 35.4 and 33.4%, respectively; while 34.9 and 36.2% of 2,4-DCP were removed at the points Oc and Op, respectively. These results revealed that rotational operation could induce 2,4-DCP removal in the soil cell more uniform than bidirectional operation. In addition, soil pH in all sampling points remained in a narrower range from 7.4 to 7.6 after 15-day rotational operation, especially even in the region around the central and peripheral electrode (Fig. 9). In contrast, under bidirectional operation, a high pH value of 8.8 at point Oc was observed, though soil pH at the rest of the sampling points was kept within favorable range (Fig. 9). Our results demonstrated that both bidirectional and rotational operation could be useful in the control of pH variation of bulk soil in the process of remediation, but rotational

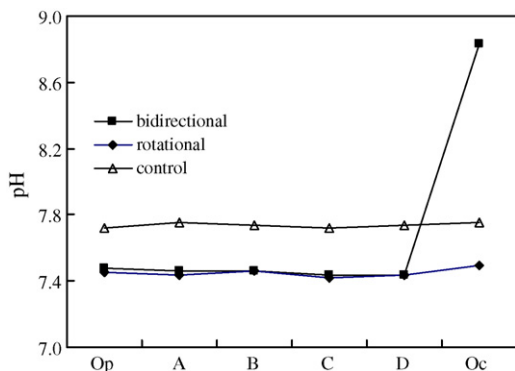


Fig. 9. The change of soil pH in the process of electrokinetic bioremediation at different modes (15 days).

mode showed more effective in maintaining the pH stability of the central region.

The uniformity of 2,4-DCP removal and the stability of soil pH with rotational mode in the tests may be attributed to the identical current and approximately linear electric field through central and peripheral electrode due to only one couple of electrode used at each interval in the rotational process. Rotational operation mode included the advantages of bidirectional operation that moved pollutants and degrading bacteria forth and back in soil, but effectively reduced the electrolysis reaction occurring around the central electrode and avoid radial electric field under bidirectional operation. Since the density of electric field strongly influenced mass transfer and biodegradation of pollutants, linear electric field might induce comparatively uniform removal in contrast with radial electric field.

The bioremediation efficiency under rotational operation was lower than that under bidirectional operation in the same electrode configuration. Nevertheless, it might still be considered as a better mode due to its unique advantages in holding uniformity of bioremediation and stabilizing soil pH.

3.5. The current and electricity consumption

Current and electricity consumption were depending upon the operation modes. Whether bidirectional or rotational operation was adopted, the current dropped slightly with the treatment time. After 15-day bidirectional and rotational operation, the average current of each day decreased from the initial 21.3 and 7.5 mA to final 15.8 and 5.7 mA, respectively (Fig. 10). In contrast, the current dropped by the same extent within only 3 days under the unidirectional operation (data not given here), indicating polarity reversal adopted in bidirectional and rotational mode could effectively prevent the current drop. At a stable voltage gradient of 1 V/cm, current variations reflected the changes of soil conductance, which was closely related with soil characteristics. Constant soil conductance might be attributed to automatic neutralization of H^+ and OH^- around electrodes, to-and-fro movement of pore water (ions) in soil bed and alternation of the double electric layer discharging and recharging on soil surface, which were related with polarity reversal [21].

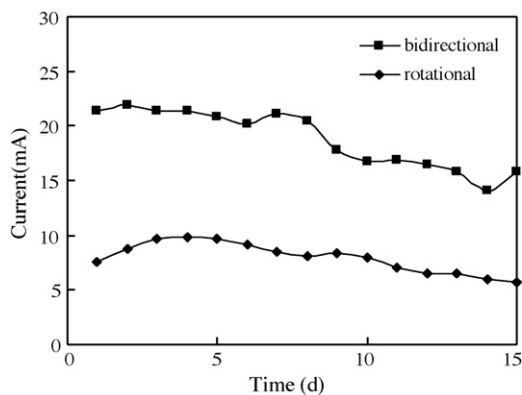


Fig. 10. The change of current in the process of bioremediation at different modes over 15 days.

The electricity consumption per unit volume of soil was calculated by the following equation [28]:

$$E_u = \frac{1}{V_s} \int_0^t UI dt$$

where E_u is the electricity expenditure per unit volume of soil (kWh/m^3), V_s the soil volume (m^3), U the electric potential difference across the electrodes (V), I the electric current (A) and t is the treatment time (h).

The results showed that, under bidirectional rotational mode, the total electricity consumption in 15 days was $38.7 kWh/m^3$, whereas, rotational mode consumed $16.8 kWh/m^3$, in the same time period. If correlated with the efficiency of 2,4-DCP removal, every kWh of electricity consumption enhanced the removal of 2,4-DCP in tested soil by a mass of 2.18g for bidirectional mode and 1.65 g for rotational mode, which was calculated on the basis of 2,4-DCP average removal in all the sampling points. This implied that bidirectional mode was more cost-efficient than rotational mode in accelerating the biodegradation of 2,4-DCP. Theoretically, rotational operation induces complicated multidirectional migration while bidirectional mode produces simple to-and-fro movement, inferring that the efficiency of electrokinetic mass transfer in soil matrix might be determined by the density but not direction of electric field applied. In conclusion, bidirectional operation should be adopted if saving time and energy was emphasized.

4. Conclusion

Non-uniform electrokinetic process can effectively accelerate the desorption and movement of 2,4-DCP in unsaturated sandy loam, primarily depending on treatment time and operation mode. In tested soil, 2,4-DCP was gradually migrated toward anode and accumulated to specific region at unidirectional mode. Polarity reversal of electric field produced an uniform distribution of 2,4-DCP throughout the soil. A high pH could induce more dissociation of 2,4-DCP, which was favorable for electromigration through soil matrix.

2D electric field can effectively enhance in situ biodegradation of 2,4-DCP in unsaturated sandy loam depending upon the operation mode. Despite of higher remediation efficiency,

bidirectional operation induced uneven distribution for 2,4-DCP removal that the closer to the central electrode, the greater the degradation rate of 2,4-DCP. As contrast, the rotational mode kept uniformity of bioremediation in soil, but produced lower remediation efficiency.

Current, energy consumption and soil properties strongly depended upon operation modes of 2D electrokinetics. Current dropped sharply under unidirectional operation, whereas bidirectional and rotational modes counteracted the fall of current to a great extent. Bidirectional mode seemed more cost-efficient than rotational mode in accelerating the biodegradation of 2,4-DCP. Hexagonal electrode configuration easily induced remarkable change of soil pH around the central electrode, which could be effectively mitigated by periodical polarity reversal at a proper interval.

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