Remediation of a hexachlorobenzene-contaminated soil by surfactant-enhanced electrokinetics coupled with microscale Pd/Fe PRB

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ABSTRACT

Treatment of soils contaminated with chlorinated hydrophobic organic compounds (CHOCs) remains a challenge for environmental scientists worldwide. In this study surfactant-enhanced electrokinetics (SEEK) was coupled with permeable reactive barrier (PRB) composed of microscale Pd/Fe to treat a hexachlorobenzene (HCB)-contaminated soil. A nonionic surfactant, Triton X-100 (TX-100), was selected as the solubility-enhancing agent. Five bench-scale tests were conducted to investigate the performance of EK–PRB on HCB removal from soils. Results showed that the HCB removal was generally increased by a factor of 4 by EK coupled with PRB compared with EK alone (60% versus 13%). In the EK–PRB system, HCB was removed from soil through several sequential processes: the movement driven by electroosmotic flow (EOF) in the anode column, the complete adsorption/degradation by the reactive Pd/Fe particles in PRB, and the consequent movement by EOF and probable electrochemical reactions in the cathode column. TX-100 was supposed to be a superior enhancement agent for HCB removal, not only in the EOF movement process but also in the Pd/Fe degradation process. This study indicates that the combination of SEEK and Pd/Fe PRB is efficient and promising to remove CHOCs from contaminated soils.

1. Introduction

Soil contamination that associated with chlorinated hydrophobic organic compounds (CHOCs) such as hexachlorobenzene (HCB), pentachlorophenol (PCP), and polychlorinated biphenyls (PCBs) has aroused intensive concerns [1]. Various biologic, physical and chemical techniques have been initiated to decontaminate these soils [2–4]. Among which electrokinetic (EK) remediation is considered as an emerging alternative especially for low permeable soils [2,5–7]. However, our recent bench- and pilot-scale EK tests revealed that although surfactant/cyclodextrin-enhanced EK showed certain potential in transporting HCB in soils, in most cases it could only remove HCB in anode regions to a considerable extent, with significant contaminants accumulation in central and cathode regions [8–10]. As a consequence, the overall removal of CHOCs from soils by EK was very low. Similar observations were also found by several other researchers [11]. It is suggested that long distance movement of CHOCs in soil is rather difficult by EK technique, which limits the removal efficiency of CHOCs and constrains the field application of EK.

Fortunately, the integration of EK with permeable reactive barrier (PRB) was supposed to overcome the aforementioned deficiency. Researchers have reported that coupling EK with various PRB could greatly enhance the overall removal of contaminants from soils [12–15]. In these processes, the PRB was generally installed between the anode and cathode, and functioned as a disposal unit to remove the contaminants (organics or heavy metals) passing by via adsorption, precipitation or even degradation. For instance, PRB composed of zero valent iron (ZVI), an extensively used reductant that could treat a series of chlorinated organics or heavy metals, can be successfully coupled to EK [13,16,17]. Yuan [17] found that EK–ZVI-PRB removed 2.4 times higher of PCE from soil than that by EK only, and a high removal efficiency of 90.4% was reached. Similar results were also evidenced by Chang and Cheng [13], wherein the combination of EK and zero valent metal (Fe and Zn) exhibited a 99% removal of PCE from a field sandy soil, much higher than that by EK alone.

However, till now information concerning the removal of CHOCs by EK–ZVI-PRB remains unknown. The challenge may lie in the facts that CHOCs are poorly dissoluble and hardly mobile by electroosmotic flow (EOF), and furthermore, their reductive gradation by commercial ZVI is very difficult. Our previous SEEK studies have revealed a significant movement of HCB in soils/sediments in anode regions [8–10]. Very recently, the reductive dechlorination of HCB by microscale Fe/Cu particles was also revealed, the dechlorination was rapid but not complete [18]. Given background and results

Table 1
Main physical–chemical properties associated with soils collected.

Main properties		Value	Method or instrument
Particle size (mm)	0.25–0.10 (%)	5.6	TM-85 soil densimeter
	0.10–0.05 (%)	3.2	
	0.05–0.005 (%)	32.1	
	0.005–0.001(%)	17.1	
	<0.001 (%)	42.0	
	Special gravity	2.71	Pycnometer method
	Organic content (%)	4.4	Potassium dichromate digestion method
	Porosity	0.42	–
	pH	7.8	pH meter
	Cation exchange capacity (meq/100 g)	8.5	Ca(OAc)$_2$ method
	Zero point of charge	2.4	Potentiometric titration
	Major elements (wt.%)	Al (15.6)	X-Ray Fluorescence, Eagle III, EDAX, Inc.
		Si (60.3)	
		Fe (18.2)	
		K (2.5)	
		Ti (2.3)	
		Mn (1.1)	
	USCS classification	Clay	

aforementioned, in present study we integrated SEEK with Pd/Fe particles to remove HCB from a clayed soil. Pd/Fe reductant was selected due to its superior reactivity toward chlorinated organics especially CHOCs [19,20]. Particularly, Shih et al. [21] recently reported an efficient reduction of HCB by nanoscale Pd/Fe particles. Less chlorinated species from the degradation of HCB by nanoscale Pd/Fe particles were recorded compared to those by nanoscale Fe particles due to the catalytic effect of Pd on iron surface [21]. Triton X-100 (TX-100) was chosen as the enhancement agent because of its solubility-enhancing capacity for HCB and possible promotion in ZVI reactivity toward HCB [18]. Our primary objective was to evaluate the enhancement of EK–PRB in CHOCs removal from soils compared with EK alone in the presence of surfactants. Results of this study are supposed to provide a solution to the low efficiency of EK on CHOCs removal in soils.

2. Materials and methods

2.1. Chemicals and soils

HCB (99.0%) was purchased from Shanghai General Reagent Factory, China. TX-100 (>99.0%) was from Aldrich and used as received. Microscaled iron (>98%) was from Tianjing Dengfeng Chemical Reagent Factory, China, and palladium acetate (Pd > 47.4%) was from Shanxi Kaida Chemical Ltd. Co., China.

The model soil used in this study was one deep turf soil, collected from the campus of Huazhong University of Science and Technology, Wuhan, China (longitude of 114.40° and latitude of 30.52°). The soils were air-dried, ground and passed through a No. 50 (0.355 mm) sieve, then storied in dark for use. The physical–chemical properties of soil are listed in Table 1. It is obvious that the soil is highly clayed, and is rich in metallic elements like Fe, Al and Mn.

2.2. Aqueous degradation experiment

Prior to the EK experiment, degradation of HCB by Pd/Fe particles in aqueous solution was investigated, and the effects of TX-100 concentration and solution pH on HCB degradation by Pd/Fe were also studied, given the presence of TX-100 and the dramatic variation of pH in our EK–PRB tests. The procedures of Pd/Fe preparation and HCB degradation were the same as previously reported [18]. In brief, 0.2 g of microscale iron was acid-washed and purged with water, then palladium acetate dissolved in acetone was added at a theoretical Pd loading of 0.5%. The purged reductant was promptly mixed with 5 mL of HCB solutions in the presence or absence of

TX-100, and incubated in a reciprocating shaker for certain period. Once sampled, the mixture of Pd/Fe particles and solution was extracted immediately by hexane and centrifugated at 4000 rpm, then HCB and chlorinated intermediates in the supernatant were subjected to gas chromatography (GC) analysis.

2.3. EK–PRB experiment

Bench-scale EK–PRB experiments were conducted on a setup as shown in Fig. 1. The setup comprised two plexiglass soil columns (i.d. 5 cm × 4.5 cm), two perforated graphite electrodes (Φ 6 cm × 1 cm), one PRB compartment (i.d. 4.5 cm × 1 cm), two pairs of electrolyte compartment (i.d. 6 cm × 5 cm), two reservoirs, one direct current power supply and one multimeter. Each electrode was inserted and clamped by the two parts of the electrolyte compartment. All the compartments along with the electrodes and the soil columns were assembled and clamped firmly with three screw and nut units. A two-channel peristaltic pump was used to circulate the anolyte or cathode between the respective compartment and reservoir, to better condition the electrolyte pH and record the cumulative electroosmotic flow (EOF).

The preparation of HCB-spiked soil was reported elsewhere [8]. Pd/Fe particles for PRB material were synthesized according to methods aforementioned in Section 2.2. The particles were then blended with acid-washed quartz sands (with the initial mass to mass of 1:1) to ensure even dispersion and impede clogging by iron precipitation. The spiked soil was mixed manually with deionized water at a ratio of 2:1 (m/v). About 180 g of the slurry was loaded into each soil column fractions by fractions. Filter paper and nylon cloth (No. 100 mesh) were sequentially attached to each end of the column to prevent any leakage of soil particles. The columns were weighted and assembled with the electrodes and compartments, meanwhile approximately 50 g of PRB materials was loaded into the PRB compartment. Working solutions were pumped into the compartments and reservoirs. A total voltage of 30 V was applied. Electrical current and cumulative EOF were measured every 12 h during the run.

Five EK tests were carried out with parameters as listed in Table 2. For all tests, TX-100 solution at 10 mmol/L (50 cmc) was used as the anode flushing solution. The TX-100 concentration was based on our preliminary batch desorption tests, wherein TX-100 of 10 mmol/L was supposed to be required for desorbing over 85% of HCB from target soil. Furthermore, 0.025 mol/L Na$_2$CO$_3$ was contained as a buffer of anolyte, and Na$_2$SO$_4$ solution at 0.025 mol/L was used as the catholyte. As shown in Table 2, T2 was set as the typical EK–PRB test, and T1 was as the blank, since our pri-
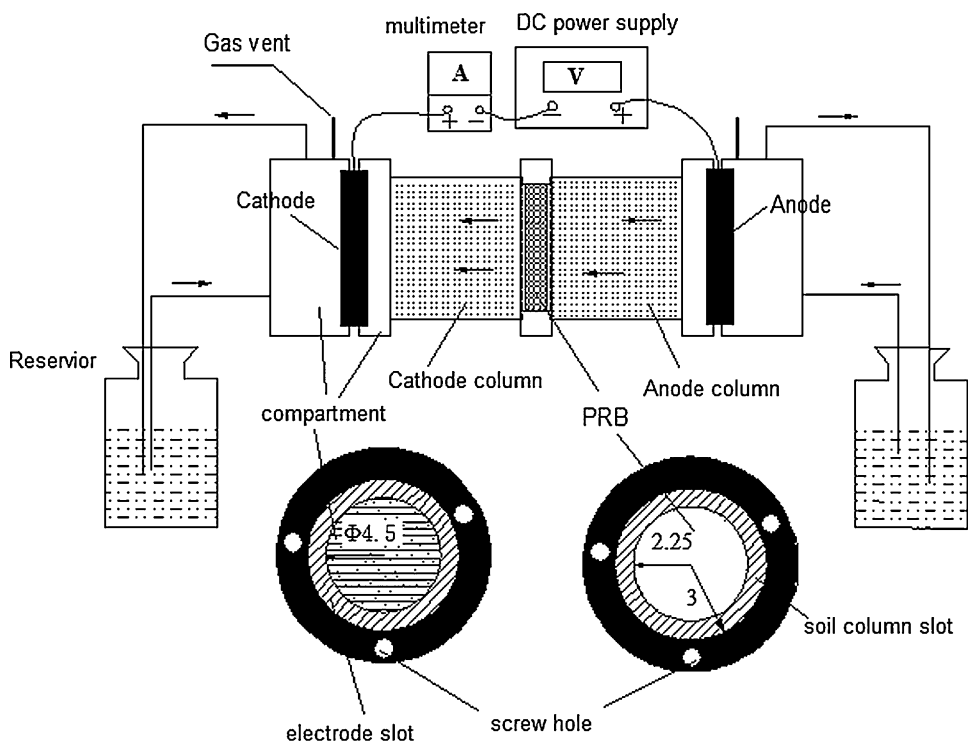
Fig. 1. Schematic diagram of EK–PRB setup.

mary objective was to evaluate the enhancing role of PRB in HCB movement and removal compared to our previous conventional EK experiments. T3–5 were conducted for the comparative purpose, wherein T4 was supposed to verify the removal of HCB by Pd/Fe when passing through PRB. In T5 the anode and cathode, together with respective electrolyte, were reserved after 5 d, with the intention to remove HCB once in the cathode column by Pd/Fe PRB. Note that for all EK–PRB tests, the PRB was set in the middle of the soil matrix, the reason was that our purpose of utilizing PRB was to enhance the removal of HOCs from soils by lowering the distance, as stated in Section 1.

2.4. Chemical analysis

Upon the completion of the EK process, the soils were extruded from each column and separated equally into two sections. The four sections were denoted as Sections 1–4 from anode to cathode. After air-dried, the soils were ground and passed through a 0.335 mm sieve. The samples were analyzed for pH value and HCB (as well as chlorinated intermediates) concentration. For the pH measurement, soil was mixed with deionized water at a solid–liquid ratio of 1:2.5, and pH of the slurry was measured by a pHS-3C meter (Shanghai Jinmai, China). To determine HCB and other chlorinated

intermediates in soils or PRB, 0.5 g of dry soil or 5 g of PRB composite was extracted with 5 mL of 1:1 acetone and hexane under the assistance of ultrasonication (20 kHz) for 30 min. The pollutants in the electrolytes were extracted by hexane, then concentrated under a gentle nitrogen-blowing and kept at a constant volume of 1 mL before determination.

HCB and possible intermediates were analyzed by a Hewlett-Packard 6890 GC equipped with an electron capture detector and a ZB-5 capillary column (Phenomenex, USA). The oven procedure was set as following: the temperature was first increased from 120 to 180 °C at a rate of 20 °C/min, followed by a rate of 40 °C/min to 190 °C, and finally increased to 240 °C at 10 °C/min then kept for 0.75 min. The flow rate of carrier gas (nitrogen 99.999%) was 2 mL/min. The inlet and detector temperature were 250 and 300 °C, respectively. The split ratio was 2 and the injection volume was 1 μL.

3. Results and discussion

3.1. Reductive degradation of HCB by Pd/Fe particles in aqueous solutions

The degradation rate of HCB by microscale Pd/Fe particles, and the effects of TX-100 concentration and solution pH on the degradation are plotted as shown in Fig. 2a–c. The initial concentration of HCB was 0.5 mg L^{-1}. Inspection of Fig. 2a reveals that Pd/Fe particles had a rather high reactivity toward HCB, approximately 80% of the initial HCB was degraded within 1 h, and the removal reached nearly 100% after 24 h treatment. The removal fits well with two-stage linear relationship. There was a prompt increase in HCB degradation in the first stage (0–1 h), followed by an obviously slower stage during 3–24 h. Correlating −ln(C/C0) with elapsed time also gives a two-stage pseudo-first-order kinetic for HCB degradation, and the k_{obs} are deduced as 1.5 and 0.15 h^{-1}, respectively, much higher than that of the degradation by Cu/Fe particles [18].

Table 2
Associated parameters with EK–PRB tests.

No.	PRB	Anode column	Cathode column	Reverse	Duration (d)
T1	No[a]	Spiked soil	Spiked soil	No[b]	10
T2	Yes	Spiked soil	Spiked soil	No	10
T3	Yes	Spiked soil	Spiked soil	No	5
T4	Yes	Spiked soil	Clear soil	No	10
T5	Yes	Spiked soil	Spiked soil	From 6 d	10

[a] For T1 no PRB was installed, and only one soil column (Φ 5 cm × 10 cm) was used.
[b] For T5 the electrodes (along with the electrolytes and the reservoirs) were reversed on 6th d to move and degrade HCB in the cathode column.
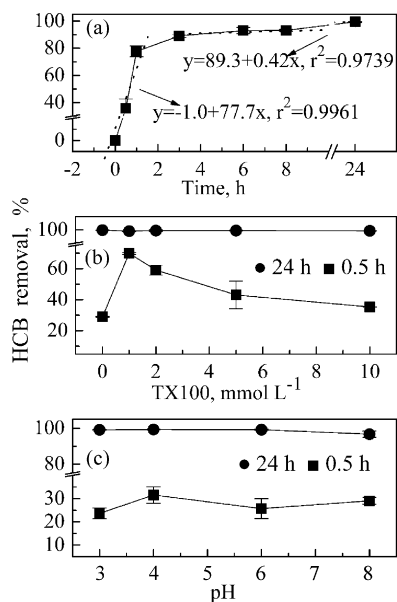
Fig. 2. (a) Degradation kinetics of aqueous HCB by Pd/Fe (without TX-100, pH 6–7), (b) effect of TX-100 concentration and (c) effect of initial solution pH (without TX-100).

Fig. 3. Variation of (a) electrical current and (b) cumulative EOF in EK tests.

It can be found from Fig. 2b that within 0.5 h the presence of TX-100 showed a repeatable enhancement in HCB degradation for the concentration range of 1–10 mmol/L. Particularly, when 1 and 2 mmol/L TX-100 were present, HCB removal was increased by a factor of 2.4 and 2.0, respectively. An increased HCB degradation kinetics by Cu/Fe particles due to the presence of TX-100 was also observed in our previous study [18]. Furthermore, the promotion caused by TX-100 decreased as the TX-100 concentration increased above 1 mmol/L, similar to the observations in the literature [18,22]. It is established that the dechlorinaition of CHOCs on ZVI surfaces involves a series of adsorption and degradation reactions. The presence of surfactants further complicates the process, since lower surfactant concentration would favor the mobilization and adsorption of HCB molecule to Pd/Fe surface and promote the reduction process, while higher surfactant concentration would impede the dechlorination due to its coverage on reductant surface and remarkable partition capacity for HCB in aqueous phase, therefore hindering the interaction between HCB and Pd/Fe catalyst [22]. However, the degradation of HCB by Pd/Fe for 24 h seems independent of TX-100 concentration, and nearly complete disappearance of HCB was recorded for all sets of experiments. Fig. 2c illustrates the effect of solution pH on HCB degradation by Pd/Fe particles. It is suggested that the pH range of 3–8 leads to no appreciable difference in HCB degradation. Furthermore, no detectable chlorinated intermediates were found for all the aqueous degradation experiments, suggesting a complete dechlorination of HCB by Pd/Fe reductant. So the Pd/Fe particles synthesized was expected to show a promising potential in the following EK–PRB tests.

3.2. Electrical current and cumulative EOF

Fig. 3a and b displays the variations of electrical current and cumulative EOF versus the elapsed time for all five EK tests. As shown in Fig. 3a, the current decreased almost linearly from approximately 25 to 5–10 mA within 5 d, then was maintained at about 5 mA. Comparison of the electrical current during 2–10 d indicates that tests with PRB had higher currents than test without (T1), suggesting a slight promotion on the electrical current by the presence of PRB. This is in agreement with that reported by Cha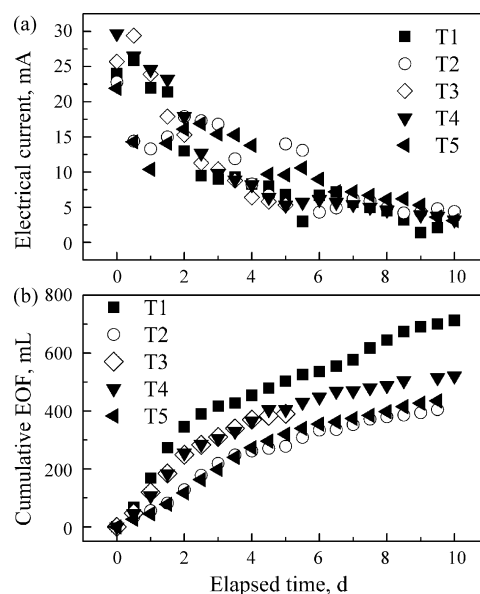ng and Cheng [13], wherein the EK-ZVM test had a higher electrical current than EK test, due to the higher conductivity of pore solution and the lower resistance of high electric conductive ZVM.

Inspection of Fig. 3b reveals that the cumulative EOF collected at cathode varied from test to test. The cumulative EOF of T2 and T5 was slightly lower than that of T3 and T4, probably due to the lower electrical current for T2 and T5 in the first 2 d which resulted in less EOF being generated. In addition, test without PRB (T1) exhibited the highest EOF generation, and the cumulative EOF in T1 was 1.8 times larger than in T2 (713 versus 405 mL). According to the Helmholtz–Smoluchowski equation, the EO velocity (u_{EO}) is directly proportional to the zeta potential of soil (ζ) and the dielectric constant of pore fluid (ε) [2,5]. Herein the lower EOF associated with PRB can be mainly ascribed to two factors. One is the decrease in ε in the EK–PRB process. As known, considerable H_2 can be generated by the ZVI system, due to the decomposition of H_2O by Fe(0) especially under the catalytic effect of Pd [19,23]. So there would be an accumulation of gaseous H_2 in the PRB compartment, which dramatically decrease ε of the system. Furthermore, the presence of quartz sand could further contribute to the decrease of ε, considering its poor conductivity compared with water or even soil. The other factor should be noted is the lower permeability of soil in cathode regions, which was caused by the block of Fe oxides formed due to the very alkali circumstance near cathode. This was indicated by an increasing dark-green color in the cathode regions during EK–PRB process. In addition, a higher ion strength of the pore solution due to the dissolution of ZVI is also expected to impede the EOF by compressing the thickness of diffusive double layer [2].

Furthermore, it is suggested that EOF rate is directly related with the retention time that contaminants passed through the PRB, thereby influencing the removal efficiency of contaminants by PRB [12]. In this sense, lower EOF implies longer treatment duration and consequently, better HCB removal in PRB. The EOF rate and corresponding retention time in four EK–PRB tests was therefore estimated. It can be found from Table 3 that the average retention time for T2–5 was in the range of 4–7 h, and the minimal retention time generally fell into 2–3 h. So correlating the retention time with the kinetic plot of aqueous HCB degradation experiment (Fig. 2a), it is suggested that the EOF rate and the thickness of PRB of 1 cm can guarantee a nearly complete degradation of HCB in our EK–PRB tests [12].

Table 3
EOF rate and retention time of HCB in PRB for each test.

Test No.	T1	T2	T3	T4	T5
v_{ave}[a] (mL d^{-1})	71	43	78	52	46
t_{ave}[b] (h)	–	7.1	3.9	5.8	6.6
v_{max} (mL d^{-1})	200	100	144	152	92
t_{min} (h)	–	3.0	2.1	2.0	3.3

[a] Average EOF rate, the total cumulative EOF divided by total running days.

[b] Average retention time, calculated by $D \times A/v_{ave}$, where D and A are the thickness and cross-sectional area of the PRB layer, respectively.
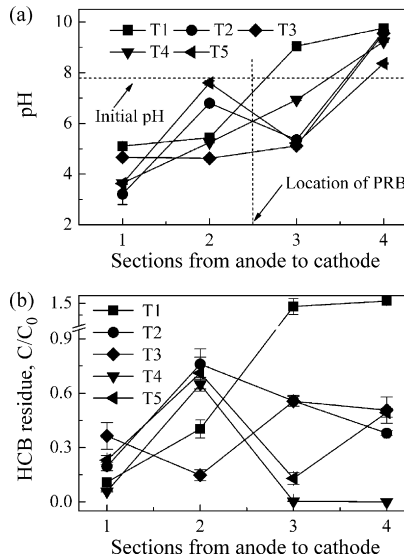

Fig. 4. Distribution of (a) soil pH and (b) HCB residue upon the completion of EK tests.

3.3. pH distribution

The soil pH values across the columns upon the completion of EK tests are plotted in Fig. 4a. Generally, the pH increased from anode to cathode, with the anode region acidified to 3–5 and the cathode region alkalified to 8–10, respectively. For the five tests the soil pH in most sections was below the initial value of 7.76. In comparison, test without PRB (T1) showed a higher soil pH distribution, which may be attributed to the less H$^+$ generation at anode due to the lower electrical current [10]. Furthermore, it can be found that tests with PRB (except for T2 and T4) exhibited a more fluctuant distribution of soil pH compared with test without (T1). Particularly, unexpected lower pH at Section 3 was recorded for most EK–PRB tests (T2, T3 and T5). It is suggested that in the presence of PRB, reactions between Pd/Fe particles and the contaminants, the corrosion and transformation of Fe and its oxides, as well as reactions associated with quartz sand may all affect the variation of soil pH.

Note that for EK–PRB tests, the pH for both Section 2 and Section 3 was in the range of 4–8. In addition, pH of the pore solution that sampled from the PRB compartment during the process, as well as pH of the PRB materials after the remediation were both measured. The values were ranged from 7.5 to 8.1, slightly higher than those of the soil adjacent. This may be caused by the reductive reaction of Pd/Fe, since it is known that in the ZVI remediation a slightly increased pH can be achieved [21]. Nevertheless, the pH of PRB materials was supposed to have little impeditive effect on HCB degradation by Pd/Fe particles, as indicated in Fig. 2c.

3.4. HCB distribution

Fig. 4b illustrates the distribution of residual HCB in soils for the five tests upon the completion of remediation. In addition, the mass of HCB in each column and in cumulative EOF was calculated and listed in Table 4. Comparison of HCB residue in each column (Table 4) reveals that test with PRB generally obtained an overall HCB removal of about 60%, which was nearly 40–50% higher than that by EK alone. This reliable promotion in contaminants removal by the combination of EK and ZVI-PRB has also been reported in the literature [16,17]. In detail, T1 exhibited a drastic increase in HCB residue toward cathode, and the relative HCB contents in the anode and cathode column were 0.24 and 1.50 (Fig. 4b), respectively. The observation confirms the fact that EK alone can only reach a reliable removal of HOCs in anode regions, as found in several previous studies [9,10]. However, in the typical EK–PRB test of T2, the increased HCB residue in anode column was followed by a sharp decrease in the cathode column. Correspondingly, the overall HCB removal in the cathode column in T2 was much higher than that in T1, while in anode column the opposite result was recorded. For T4 and T5, HCB distribution in the anode column was higher than T2, and in the cathode column the residue was lower than in T2. Particularly, no detectable HCB was recorded in the cathode regions in T4, suggesting that no HCB from the anode column moved into these regions. Furthermore, comparison of overall HCB removal between T2 and T3 indicates that longer running time than 5 d had no repeatable increase in contaminant removal. It was also suggested that reversing the anode and cathode could further promote the removal of HCB once in the cathode column by about 10% with respect to T2, thus the highest HCB removal of 85% from the cathode column was recorded in T5 compared with other EK–PRB tests.

In the EK–PRB process, there are two main approaches that contribute to the removal of HCB from soils. One is electroosmotic (EO) movement of contaminants across soil matrix from anode to cathode, which plays a primary role in HOCs removal in conventional EK remediation [2,5]. The other is the adsorption/degradation of HCB by Pd/Fe particles in the PRB compartment. Generally, EO functioned as the predominant approach to move HCB in the anode column, and ZVI-PRB functioned as a unit to remove HCB that was moved by EOF from the anode. On one hand, the efficiency of EO

Table 4
Mass balance of HCB for five EK tests.

Test No.	Initial mass[a] (µg)	Soil column (µg)			Catholyte (µg)	Removal from soil[b] (%)	Mass balance[c] (%)
		Anode	Cathode	Total			
T1	1341.9	160.0 (23.8%[d])	1004.9 (149.8%)	1164.9	7.6	13.4	87.4
T2	1693.4	387.9 (45.8%)	402.4 (47.8%)	790.3	0.9	53.3	46.7
T3	1319.3	171.9 (26.1%)	358.2 (54.3%)	530.1	1.1	59.8	40.3
T4	666.0	238.3 (35.8%)	0.4 (0)	238.7	Undetectable	64.2	35.8
T5	1728.4	422.7 (48.9%)	266.2 (30.8%)	688.9	17.1	60.1	40.8

[a] Total mass of HCB that added in anode and cathode columns.

[b] Percentage of HCB removal of soil, by subtracting the percentage of HCB remained in soil matrix (i.e., the anode and cathode column while except the catholyte).

[c] Sum of percentage of HCB in soil matrix and catholyte.

[d] Percentage of HCB remained with respective to the initial value in each column, same for other data in the brackets.

movement of HCB was controlled by both the solubility-enhancing capacity of the pore solution and the quantity of EOF generated in the EK process [9]. So the higher HCB removal in anode column for T1 and T3 could be mainly associated with higher cumulative EOF, as displayed by Fig. 3b. Furthermore, the relatively higher HCB content in Section 2 in the other three tests (T2, T4 and T5) also suggests that more abundant EOF was required to obtain a reliable HCB removal from anode regions.

The efficiency of ZVI-PRB in the removal of HCB, on the other hand, is affected by a number of factors, including the concentration of TX-100, the pH value of the pore solution, and the retention time of EOF passing by. Fortunately, as stated in Sections 3.1 and 3.2, the retention time of HCB in PRB was above 2 h, long enough to reach a reliably complete contaminant removal by Pd/Fe particles (Fig. 2a and Table 3). Furthermore, the performance of HCB removal by Pd/Fe was found independent of pH in the range of 3–8 which accorded with the range of soil pH obtained in EK tests. In addition, the presence of TX-100 at the concentration applied (1–10 mmol/L) can further facilitate the HCB removal (Fig. 2b and c). Theses observations lead to a reasonable conclusion that HCB passing through the PRB compartment can be completely removed by Pd/Fe particles. It is noted that no detectable HCB was recorded in the cathode clean soils of T4, or in the PRB materials of T2–5, indicating that HCB transported by EO from anode column had been completely removed in the ZVI-PRB. The same reason may also be used to explain the fact that no HCB accumulation in the cathode column was recorded for other EK–PRB tests (T2, T3 and T5).

It should be also addressed that the complete removal of HCB in PRB compartment implied an in situ recycling of the TX-100 contained in the EOF, which could further contribute to transporting HCB in the cathode column effectively. Inspection of Fig. 4b and Table 4 reveals that for tests with ZVI-PRB the HCB removal from cathode column was generally comparable with that from anode column. Surprisingly, negligible HCB accumulation was detected in catholyte for all tests, suggesting the repeatable disappearance of HCB in the cathode column was not solely resulted from the movement by EOF. Note that even in test without PRB (T1) a mass loss of 13.4% for HCB was recorded. Our previous SEEK study of HCB-contaminated soils/sediments have also evidenced an appreciable disappearance of HCB at the cathode region, and we ascribed it to possible electrochemical reactions near the cathode [8,10,24]. Furthermore, the mass balance of HCB for all EK–PRB tests also suggests that the degradation played a predominant role in the removal of HCB for all EK–PRB tests, agreeing with the results of Chang and Cheng [13], who found that the degradation by ZVM (Fe or Zn) at PRB accounted for 60% of the total PCE removal from soils.

4. Conclusions

In this study we investigated the performance of SEEK–PRB technique to remediate HCB, a typical CHOC, in contaminated soils. TX-100 was selected as a solubility-enhanced agent and microscale Pd/Fe bimetal particles were used as a PRB material. The results showed that EK–PRB could greatly enhance the removal of target contaminants in soils. Major conclusions can be summed up as follows:

(1) The combination of EK and Pd/Fe PRB could increase the overall HCB removal from soils by 40–50% compared with EK alone, with general efficiencies of about 60%. The results also suggest that TX-100 is a superior enhancement agent for HCB removal, both in the EOF movement process and in the Pd/Fe degradation process.
(2) Mass balance of HCB revealed that in the EK–PRB system HCB could be removed from soil through several sequential pro-

cesses: the movement driven by EOF in the anode column, the complete adsorption/degradation by the Pd/Fe PRB, and the consequent movement by EOF and probable degradation by electrochemical reactions in the cathode column. Overall, the degradation rather than movement by EO plays a predominant role in HCB removal.
(3) Our results suggest that SEEK–Pd/Fe PRB showed superior performance in the remediation of CHOCs-contaminated soils. However, further studies are still needed to investigate and optimize the parameters associated with this technique, such as the position of PRB, the amount of Pd/Fe used and more efficient solubility-enhancing agents.

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