The remediation performance of a specific electrokinetics integrated with zero-valent metals for perchloroethylene contaminated soils

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Abstract

This research was conducted to evaluate an integrated technique, combination of the electrokinetics (EK) and zero-valent metal (ZVM), for remediation of the perchloroethylene (PCE) contaminated soils. Various experimental conditions were controlled such as different voltage gradients, the position of ZVM, and ZVM species. The appropriate operational parameters are concluded as follows: (1) 0.01 M sodium carbonate serves as the working solution; (2) the voltage gradient is controlled at 1.0 V/cm; (3) ZVM wall is settled close to the anode. Based on the above operation conditions, the pH value of working solution can maintain at neutral range for avoiding the soil acidification. Neutral pH also causes the system to stay at a stable status of electricity consumption. The removal efficiency reaches 99% and 90% for decontaminating the PCE in the pore-water and the soil, respectively, after a 10-day treatment. The zero-valent zinc performs better PCE degradation than zero-valent iron. Moreover, the soils treated by EK + ZVM still possess their original properties.
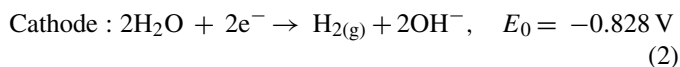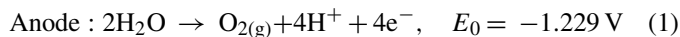
1. Introduction

The environmental concern of the soil and groundwater contaminated by chlorinated organic solvents has been paid for years. Since the densities of chlorinated solvents are higher than that of water, these organics are denoted as DNAPLs (dense non-aqueous phase liquids). Due to this feature, DNAPLs will broadly pass through the soil surface to contaminate soils and groundwater. Moreover, DNAPLs pose high adsorption capacity in soils and low aqueous solubility, which result in extremely difficult remediation [1]. Many remediation techniques have been developed and received some advances [2–4]. Among those techniques, the ZVM has been considered as a promising technique to clean DNAPLs in groundwater because of its advantages of in situ applicability, low cost, and effectiveness. The ZVM always is constructed as a treatment wall (i.e., permeable reactive barrier); the DNAPLs in groundwater can be degraded when they pass through the ZVM wall [5]. However,

the DNAPLs in the vadose zone of soil layer without appropriate treatment usually become a pollution source (i.e., hot spot) to continuously contaminate the groundwater. Thus, it is essential to clean up the DNAPLs contaminated soils in addition to treating the groundwater. For the soil remediation, the EK process has been considered as a feasible in situ technique. One of special features of EK technique is that can be integrated with other chemical- or bio-techniques to achieve more effective treatment [6,7]. In this study, an EK + ZVM integration technique was developed and its remediation performance was investigated under different operational conditions.

An EK system is basically composed of one pair of electrodes and applied by the direct-current power [8]. When the EK system is employed in the contaminated soils, several transport mechanisms (e.g., electroosmosis and ion migration) and electrochemical reactions (such as electrolysis and electrodeposition) will be induced [9]. Since excess positive ions possess in the double layer on the surface of soil particles, the ions hydrated with water molecule will migrate under the electrical field. The pore-water in the soil (similar to that in a capillary) can be driven to pass through the soils. This phenomenon is called the electroosmosis, which can flush contaminants throughout the soil
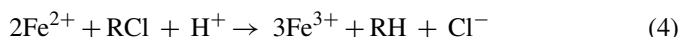
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layer. Simultaneously, the ions in the pore-water driven by electrical field will move to electrodes directly (i.e., ion migration). Besides, water electrolysis will produce H^+ at the anode and OH^- at the cathode due to redox reactions, which influence the pH value of the whole system significantly. The following equations show the water electrolysis:

$$\text{Anode}: 2H_2O \rightarrow O_{2(g)} + 4H^+ + 4e^-, \quad E_0 = -1.229\,V \quad (1)$$

$$\text{Cathode}: 2H_2O + 2e^- \rightarrow H_{2(g)} + 2OH^-, \quad E_0 = -0.828\,V \quad (2)$$

A circulation EK system (CEEK) has been developed in our previous study, which can maintain the neutral pH circumstance (the working solution and treated soils) to avoid the pH variation and other drawbacks of EK [10]. Constructed on the CEEK process in this research, a ZVM treatment plate was installed in the PCE contaminated soil (in terms of EK + ZVM) to degrade chlorinated organic contaminants in the vadose zone.

The fundamental reaction mechanisms and kinetics of ZVM with chlorinated organic pollutants including PCE, TCE, DCE have been studied thoroughly [11–13]. Among many ZVM like iron, zinc, nickel, and other transition metals, the iron is one of the most popular ZVM because of its low cost. For the consideration of iron, the zero-valent iron (ZVI) can cause chlorinated organics being reduced under certain pH and pE conditions [14]. In general, there exit three dechloronization reactions in the ZVI–water system shown in the following equations [15]:

$$Fe^0 + RCl + H^+ \rightarrow Fe^{2+} + RH + Cl^- \quad (3)$$

$$2Fe^{2+} + RCl + H^+ \rightarrow 3Fe^{3+} + RH + Cl^- \quad (4)$$

$$H_2 + RCl \xrightarrow{\text{catalyst}} RH + H^+ + Cl^- \quad (5)$$

According to Eq. (3), the ZVI will be oxidized to be Fe(II) ions as degrading the chlorinated organics. Subsequently, the Fe(II) ions reacts with other chlorinated organics to be Fe(III) ions and produce the ferric oxide. In fact, the ferric oxide will cover the ZVI surface to decrease the activity of ZVI, which results in the limited operational life of ZVI [16,17]. As a consequence, the proton (H^+) is not only beneficial to the dechloronization reactions shown in Eqs. (3) and (4) but also to eliminate the ferric oxide to maintain the ZVI activity. Based on Eq. (1), the EK system may play the role of H^+ provider as integrating the ZVM technique.

The remediation limitation of EK system is that it can only remove the organic pollutants from the soil phase to other phases, which still need other treatment facility to degrade the pollutants. In contrast, the ZVM technique can only passively applied to degrade organic contaminants in the groundwater. Accordingly, the integration of above two technologies is expected to couple EK and ZVM advantages, that is, the chlorinated-organics contaminated sites can be in situ remediated (remove and degrade). In this research, we investigate the remediation performance of a specific electrokinetics (CEEK) integrated with zero-valent metals for treating perchloroethylene-contaminated soils under various operational parameters such as voltage gradients, ZVM species, and installation positions of ZVM. In addition, the soil characteristics such as pH, water content and organic matters at the completion of treatment are also measured for understanding the side impacts of the innovative technique.

2. Materials and methods

Soil samples were collected from the sites near Chaoyang University of Technology located in Taichung County, Taiwan. The basic characteristics of soil including soil texture, specific gravity, pH, water content of soil, and organic content were determined. Table 1 lists the results and their analytical methods. According to Table 1, the soil samples could be categorized as sandy soils with neutral pH. In comparison with other soil remediation technologies such as soil washing and flushing, the EK's advantages include: in situ applicability, suitable to a variety of soils, simple installation, easy operation, and little impact on the surroundings. Thus, the EK process applied to sandy soils is still with commercial potential; even the EK process has been considered as a promising technology in remediating low permeability soils. The extent of water content and organic matter was 1.9% and 2.2%, respectively. The soil specimen was spiked with PCE solution and equilibrated for 3 days which concentration was measured around 60 mg/kg. During the preparation of soil specimen, the electrolyte of sodium carbonate in 0.01 M was mixed in PCE solution and the water content of soil matrix was around 20%.

Fig. 1 shows the integration system of EK and ZVM. The system was composed of one pair electrodes, one soil storage zone, working solution reservoir, one circulation pump, and one dc power supplier. To avoid the soil leakage, a pair of nylon meshes (Spectrum model PP, mesh opening 149 μm) and a filter paper (Whatman No. 1) were placed between the soil sample and electrodes. A dc power supplier (IP 200-21 DS) was applied to the EK system at certain constant voltage gradient. Graphite plates served as the electrodes and placed at each electrolytic compartment right behind the membranes. A circulation pump was used to carry the working solution from the cathode to anode for neutralizing pH of working solution.

Experiments were conducted in a batch mode. The control factors listed in Table 2 include various electric field gradients (0.5, 1.0, and 2.0 V/cm), ZVM species (iron and zinc), and ZVM installed positions (close to anode-around 5.0 cm away from the anode, in middle area, and close to cathode-around 5.0 cm away from the cathode). One set of experiment without EK and ZVM application served as a blank set. Each experiment was preceded for a selected period of time; the pH and conductivity of working solution, and the system current were monitored

Table 1
Basic physical–chemical properties of the soil

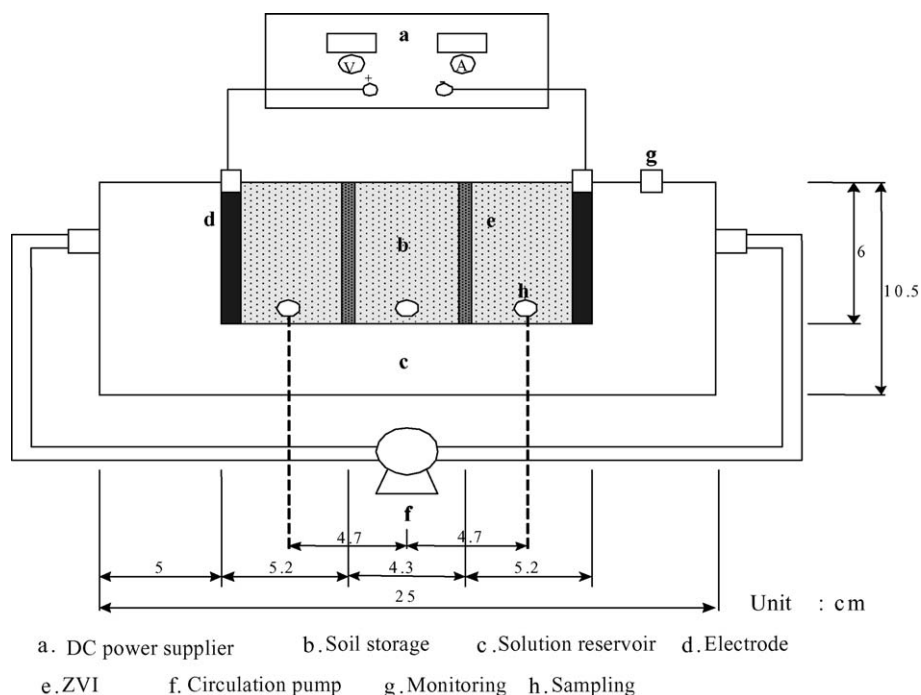| Physical–chemical property	Result	Analytical method
Soil texture	Sandy soil	ASTM D 422–463, 1963
Gravity (g cm^{-3})	2.1	ASTM D 854–883, 1963
pH	7.0	NIEA S10.60T, 1997
Water content (%)	1.9	NIEA S280.60T, 1997
Organic matter (%)	2.2	[18]

Fig. 1. The schematic diagram of EK and ZVM system.

throughout all experiments to evaluate the stability of the integrated system. The pH and ORP of pore-water collected from the sampling hole of the reactor were measured to obtain the pH and pE status for understanding the ZVM reduction activity. The pH and conductance of solution were monitored by a pH/conductivity meter (Hettich Zentrifugen Co., model EBA12). The ORP of solution was determined by an ORP meter (Suntex, SC-170). Moreover, the pH, water content, and organic matter of treated soils were measured to observe the treatment impacts on the soil specimen. During the experiment period, the concentration of chlorinated organics in pore-water and that in the soil matrix is determined, respectively. The PCE in pore-water was extracted by hexane. The average value of PCE and TCE in the soil was determined by three soil samples, which collected at the position close to anodic, in the middle, and close to cathodic compartment. In order to extract the target organics from the soil, 2 g of the treated soil sample was mixed with 2 mL 0.1 M sulfuric acid and 5 mL hexane for shaking 24 h. The chlorinated organics in the extractor were determined by gas chromatography equipped with an electron capture detector (GC/ECD, Varian CP3800). After analyzing experimental data, the removal efficiency of PCE under different experimental conditions could be obtained. All chemicals were purchased from Fluka Co and the purity is greater than 97.0%.

Table 2
Control factors for conducting EK + ZVM experiments

Voltage gradient (V/cm)	ZVM species	ZVM installed positions
0	None	Blank test
0.5	Iron	Close to anode
1.0	Zinc	In middle area
2.0		Close to cathode

3. Results and discussion

In order to evaluate the remediation performance of the EK + ZVM system under different operational conditions, the relationship between pH and conductivity of working solution, the varying trend of system current, and the PCE removal efficiency during treatment are elucidated as follows.

3.1. pH, conductivity of working solution and system current variation

Figs. 2–4 shows the pH and conductivity of working solution, and system current variation versus different ZVM and electric field gradients, respectively. In Fig. 2(a) and (b), results present the similar pH variation regardless of ZVM species, which decreases fast initially and approaches a stable value (around 7.2). When the water molecule is electrolyzed to be H^+ and OH^- continuously at electrodes according to Eqs. (1) and (2), the pH of working solution will be influenced by these acid and base. Since the electrolyte of carbonate and soil both are with high buffering capacity and the EK system equipped with a circulation pump to neutralize the working solution, the pH can be controlled at a neutral range. Even so, the pH of working solution decreases to an acidic level as the system applied by 2.0 V/cm shown in Fig. 2(c). This indicates that more protons produced by 2.0 V/cm application exceed the buffering capacity of the system. In comparison with pH data based on different ZVM conditions, the system with ZVM performs slightly higher pH than that without ZVM. The higher pH value implies that the protons consumed to couple with ZVM for degrading PCE as shown in Eq. (3).
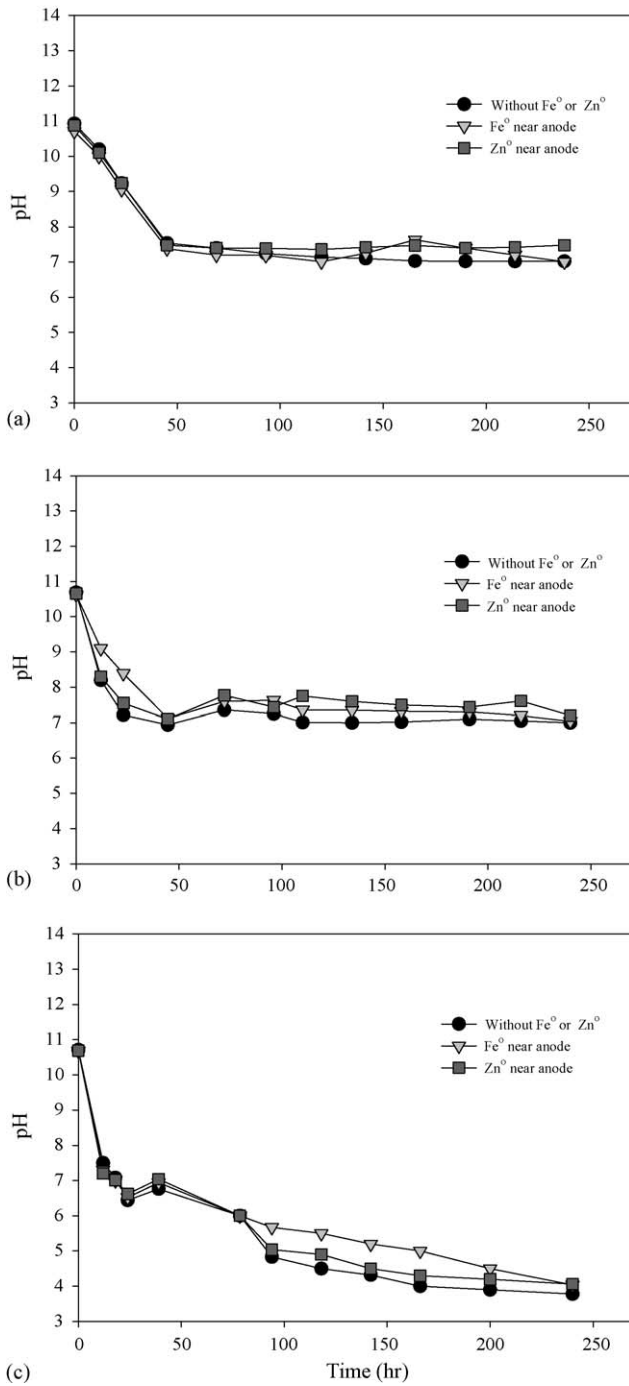
Fig. 2. The pH variation of working solution vs. different ZVM and voltage gradients: (a) 0.5 V/cm, (b) 1 V/cm, (c) 2 V/cm.

Fig. 3. The conductivity variation of working solution vs. different ZVM and voltage gradients: (a) 0.5 V/cm, (b) 1 V/cm, (c) 2 V/cm.

According to Fig. 3, the conductivity of working solution has a similar trend as pH variation, which decreases initially and approaches a stable value. Additionally, it is seen that the system without ZVM performs higher conductivity of working solution. Since the conductivity relates to the total amount of ions in the solution, the low pH with high proton concentration can induce high conductivity. Therefore, the working solution of system without ZVM possesses higher conductivity due to its lower pH (more H$^+$ ions) shown in Fig. 2. Like-
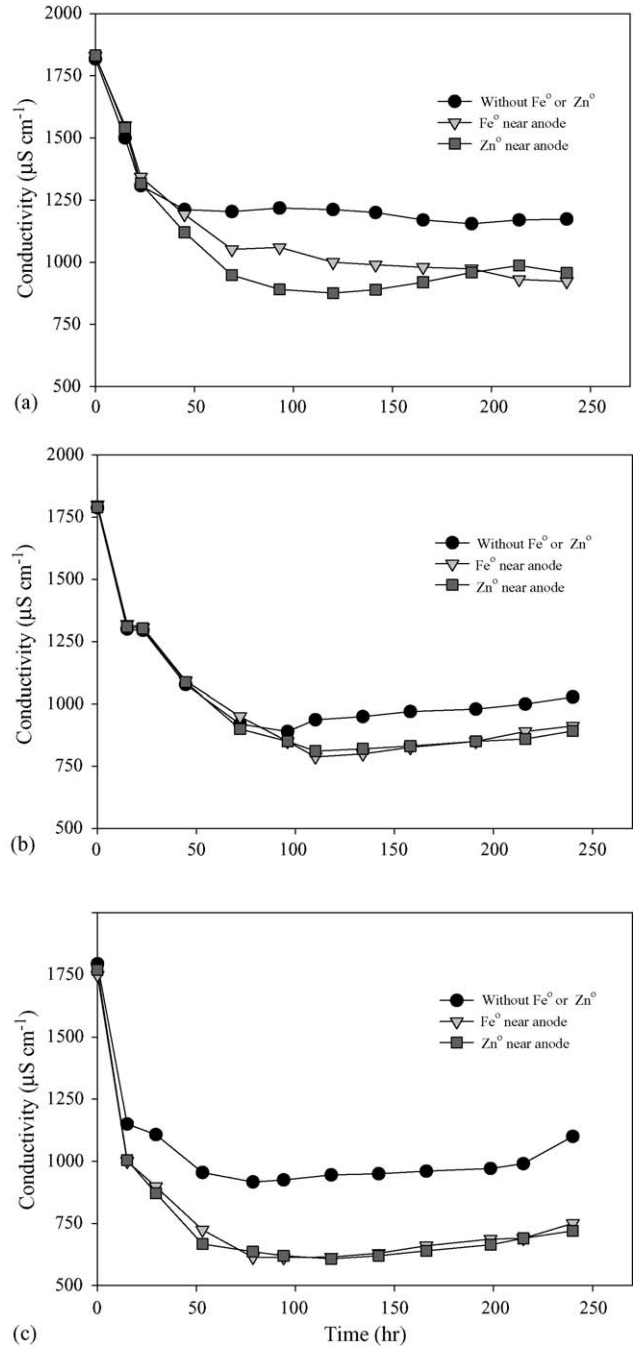
wise, the decrease rate of conductivity follows the order of 2.0 > 1.0 > 0.5 V/cm, which is also similar to the decrease rate of pH.

From Fig. 4, the system current also has a similar decreasing trend as pH variation. Since the system current is composed of many factors such as liquid conductivity, water content of soils, electrode characteristics, and electric field, the current reflects the electron flux through the complex system. However, the electric field seems to play the major role on controlling current in our system. According to results, the current magnitude is
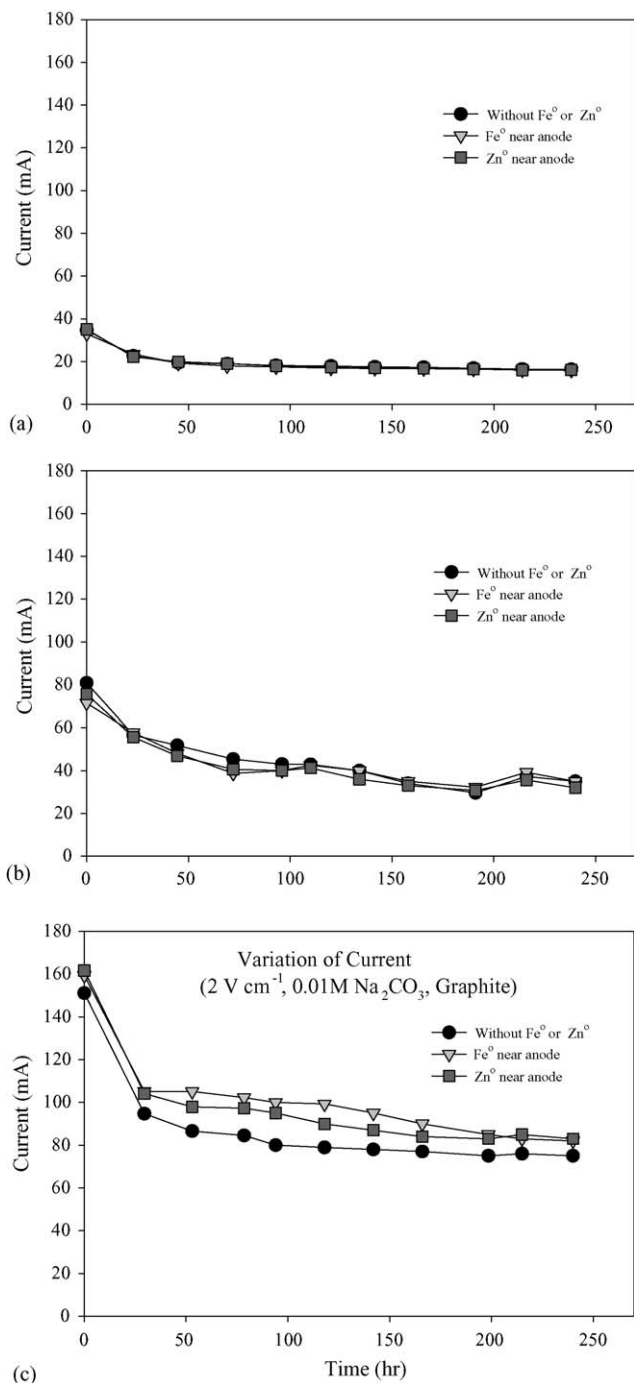
(a)

(b)

(c)

Fig. 4. The system current variation vs. different ZVM and voltage gradients: (a) 0.5 V/cm, (b) 1 V/cm, (c) 2 V/cm.

Fig. 5. The PCE concentration in the pore-water vs. operation time.

3.2. Degradation efficiency of PCE in pore-water and soils

Fig. 5 is the PCE concentration in pore-water versus operation time under different ZVI positions. The PCE concentration is averagely determined by three solution samples and the PCE initial concentration, C_0, is around 10–15 mg/L. Results show that the PCE concentration in pore-water under EK process decreases slightly faster than that of blank (without ZVI and EK). The decrease of PCE in the system without ZVI and EK can be attributed to the evaporation mechanism due to the volatilization of PCE volatility. After the ZVI plate installed, the PCE decreases dramatically in the beginning of the test and then gradually decays. This indicates that EK + ZVM can significantly enhance PCE removal efficiency in comparison with EK process. It can be seen that the set of ZVI close to the anode performs better PCE removal than that close to the cathode. After 240 h treatment, the former one almost removes 100% PCE in the pore-water. That the H^+ is produced at the anode can promptly react with ZVI to degrade PCE as expected from Eq. (3). Furthermore, this close-anode position can avoid the metal surface to be covered by some oxides that reduce the reaction activity of ZVI. On the contrary, as ZVI installed close to the cathode where few H^+ can react with ZVI and OH^- will results in the iron precipitates on the metal surface. Consequently, the ZVM installed close to anode is the relatively valid position for this integration system.

Fig. 6 shows the PCE concentration in the pore-water versus operation time under different ZVM (installed close to anode) and voltage gradients. The system without EK + ZVM serves as a blank reference to obtain the evaporation effect. From Fig. 6, the EK + iron and EK + zinc processes present more distinguished PCE removal than EK process for all voltage applications. That means the ZVM possesses dramatic degradation ability for decontaminating the PCE in the pore-water. It can be seen that PCE in the pore-water decreases dramatically in the beginning of experiments, then, gradually presents almost parallel decrease curve as EK process does. Furthermore, the degradation kinetics of PCE seems to be suitably described by the pseudo-first-order reaction equation (i.e., $\ln C/C_0$

proportional to the electric field, i.e., the current of 20, 40, and 80 mA for 0.5, 1.0, and 2.0 V/cm, respectively. In addition, the EK + ZVM possesses higher current than EK process. Because not only the solution conductivity but also the electric resistance of the soil specimen influences the current variation, the higher current can be attributed to the soil in the presence of high electric conductance of ZVM. It can be noticed that the current behavior demonstrates a stable energy consumption status of EK + ZVM technique.
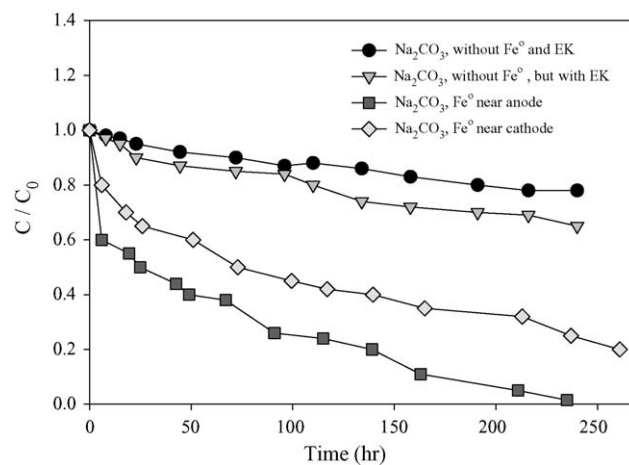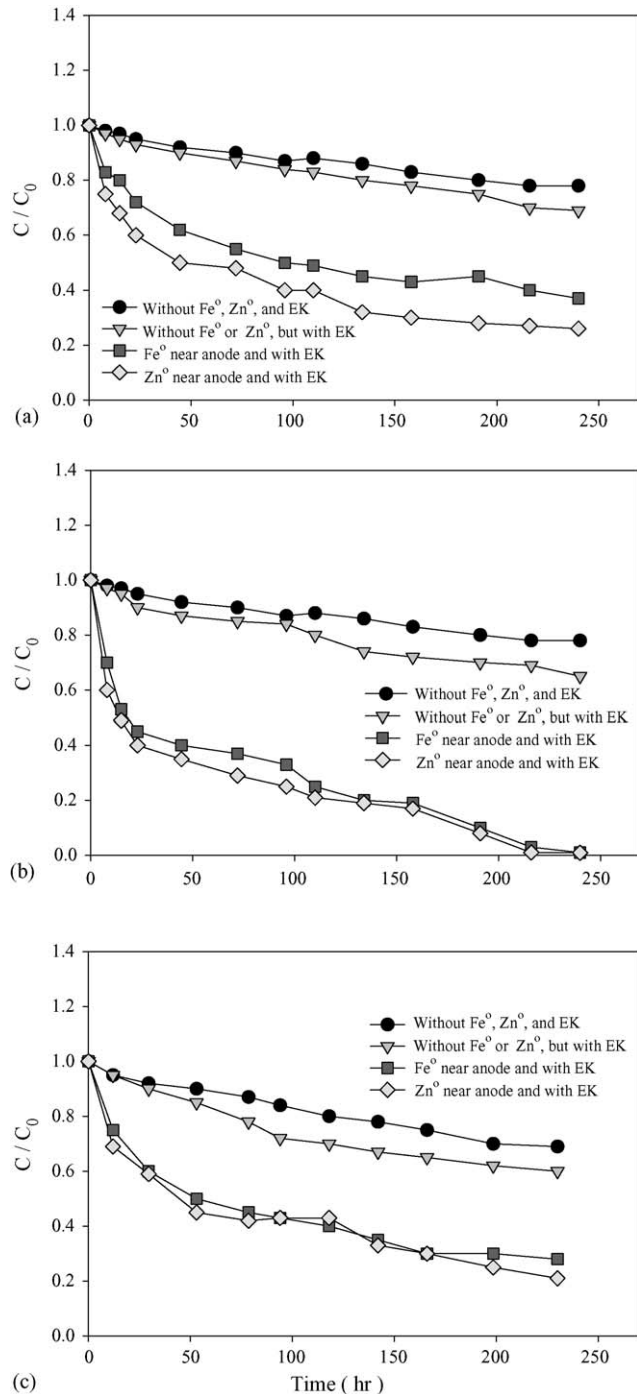
(a)

(b)

(c)

Fig. 6. The PCE concentration in the pore-water vs. operation time under different ZVM and voltage gradients: (a) 0.5 V/cm, (b) 1 V/cm, (c) 2 V/cm.
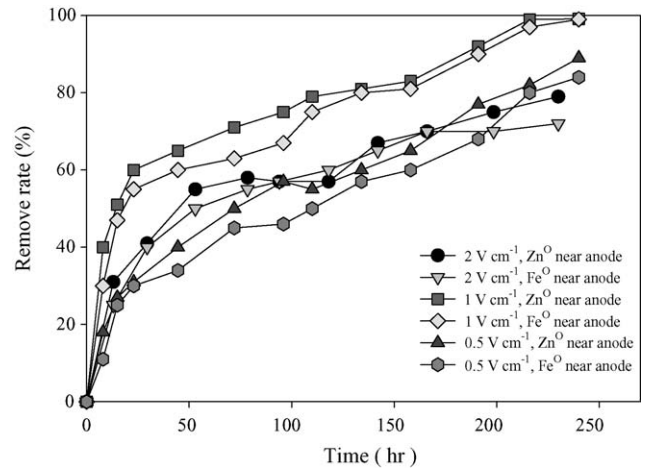

Fig. 7. The PCE removal efficiency in the pore-water vs. operation time under different ZVM and voltage gradients.

the dehalogenation rate. The zero-valent zinc with lower redox potential (-0.7628 V versus SHE) than the zero-valent iron (-0.409 V versus SHE) may be one major reason. Additionally, the specific surface area of zinc may be higher than that of iron, or the oxide produced on the zinc is less than that on the iron, therefore, the zinc behaves higher PCE dehalogenation ability.

Fig. 7 shows the PCE removal efficiency in the pore-water versus operation time under different ZVM and voltage gradients. Based on Fig. 7, the removal efficiency of PCE in pore-water approaches to 70% regardless of operational conditions after the 10-day treatment. Results present EK + zinc and EK + iron under 1.0 V/cm operation obtains highest removal efficiency of 99%; the residual concentration of PCE is down to 0.05 mg/L. The voltage gradient of 2.0 V/cm can remove around 85% PCE in the pore-water. In fact, the removal efficiency of PCE under EK + ZVM process comprises three removal mechanisms including evaporation, EK removal, and ZVM degradation. If the ZVM degradation can be independent of EK removal efficiency, the computation on the basis of experimental data can be roughly conducted. The removal efficiency of evaporation can be obtained from the blank test (without EK + ZVM). The EK removal efficiency of PCE can be obtained by comparing the difference between EK test (without ZVM) and blank test. Likewise, the ZVM degradation efficiency can be obtained. After a 10-day run, the evaporation efficiency is around 20%. The EK removal efficiency is around 31%, 35%, and 40% for EK process under 0.5, 1.0, and 2.0 V/cm, respectively. The degradation efficiency of ZVM is around 37%, 61%, and 38% under 0.5, 1.0, and 2.0 V/cm, respectively.

Fig. 8 shows the PCE concentration in soils versus operation time under different ZVM and voltage gradients. The EK + iron and EK + zinc processes present fast degradation reactions and follow the order of 2.0 > 1.0 > 0.5 V/cm. It can be seen that PCE decrease in soils presents a similar trend as that in pore-water. The PCE concentration in soils decreases fast initially, then, presents parallel decrease curve as EK process. The removal curve also seems to fit the psuedo-first-order reaction and the EK + zinc still has best performance. Fig. 9 shows the PCE

is proportional to time; data not shown). This degradation kinetics of PCE agrees with results of some researches about halogenated organics treated by ZVI [12,19]. Their reports indicate that desorption and diffusion mechanisms are the major factors for controlling the degradation kinetics. According to Fig. 6, the zero-valent zinc performs better PCE degradation ability than the zero-valent iron. Many ZVM characteristics such as the redox potential, the specific surface area, material purity, and the amount of oxides on the ZVM surface control

Fig. 9. The PCE removal efficiency in the soils vs. operation time under different ZVM and voltage gradients.
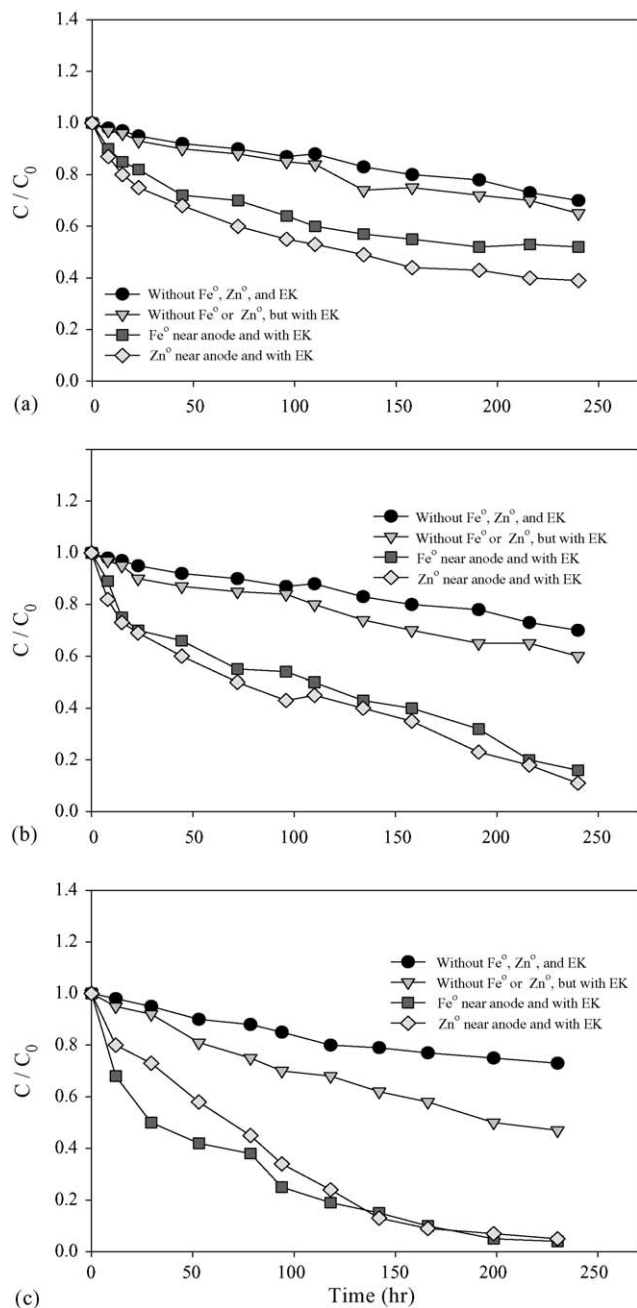

Fig. 8. The PCE concentration in the soils vs. operation time under different ZVM and voltage gradients: (a) 0.5 V/cm, (b) 1 V/cm, (c) 2 V/cm.

removal efficiency in the soils versus operation time. Results present that the PCE removal efficiency can reach 99% under 2.0 V/cm with EK + ZVM operation. However, there is around 85% PCE removal efficiency in pore-water under the same operation. Since PCE is dehalogenized on the ZVM surface and in the aqueous phase according to Eqs. (3) and (4), PCE in the soil should be desorbed from soils into the pore-water and be transported by EK process to contact with other reactants. The PCE concentration in the soil actually consists of PCE in the pore-water and the soil particles. That most PCE desorbed from soil phase to the aqueous phase causes the high removal efficiency of PCE in the soil. However, the PCE concentration in the aqueous
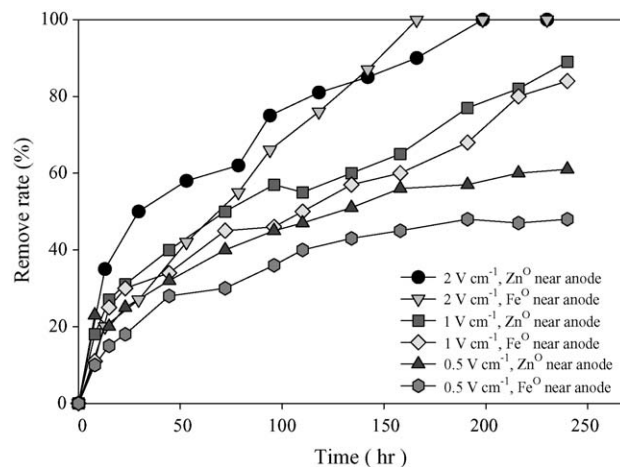
phase may increase by the PCE desorption. As a consequence, the results of different PCE removal efficiency seem to be conflict.

Fig. 9 presents that the 2.0 V/cm operation performs best removal efficiency for PCE soil remediation. This can be attributed to the coupled influence of the H^+ ions and electro-osmotic (EO) flow rate. On one hand, the higher voltage gradient, the more H^+ production at the anode for enhancing PCE degradation on the ZVM. On the other hand, the EO flow rate is significantly affected by the soil pH value (low soil pH decreases the EO flow rate). The CEEK system applied by 1.0 V/cm can induce the higher EO flow rate than that by 2.0 V/cm because of the neutral soil pH based on our previous study. Therefore, the PCE removal efficiency under 1.0 V/cm application also reaches almost 90%. To consider the impact of ions produced by ZVM, the EO flow rate is surly affected by the ion concentration in pore-water. Nevertheless, the amount of release ions by ZVM in comparison with the original electrolyte concentration (0.01 M Na_2CO_3) is relatively small. The stable current (shown in Fig. 4) throughout all experiments can support the above hypothesis. Thus, the EO flow rate and electricity consumption is not significantly influenced by the ions produced by ZVM reactions.

3.3. pH and ORP of the pore-water

In order to verify the occurrence of dehalogenation during treatment, the pH and ORP of the pore-water were monitored. The sampling positions are distributed at the specimen close to anode, that in the middle of specimen, and that close to cathode, respectively. Fig. 10 shows the pH of pore-water versus operation time under different ZVM and 1.0 V/cm voltage gradient. According to Fig. 10(a), the pH of pore-water near anode decreases with time under the EK process, which results from the H^+ produced at the anode. After a period of time, the pH gradually increases due to OH^- produced at the cathode, which migrate from cathode to anode. Additionally, the pH of pore-water near cathode increases with time due to OH^- produced at the cathode. In contrast to Fig. 10(a), the pH of pore-water under EK + ZVM treatment increases initially and gradually
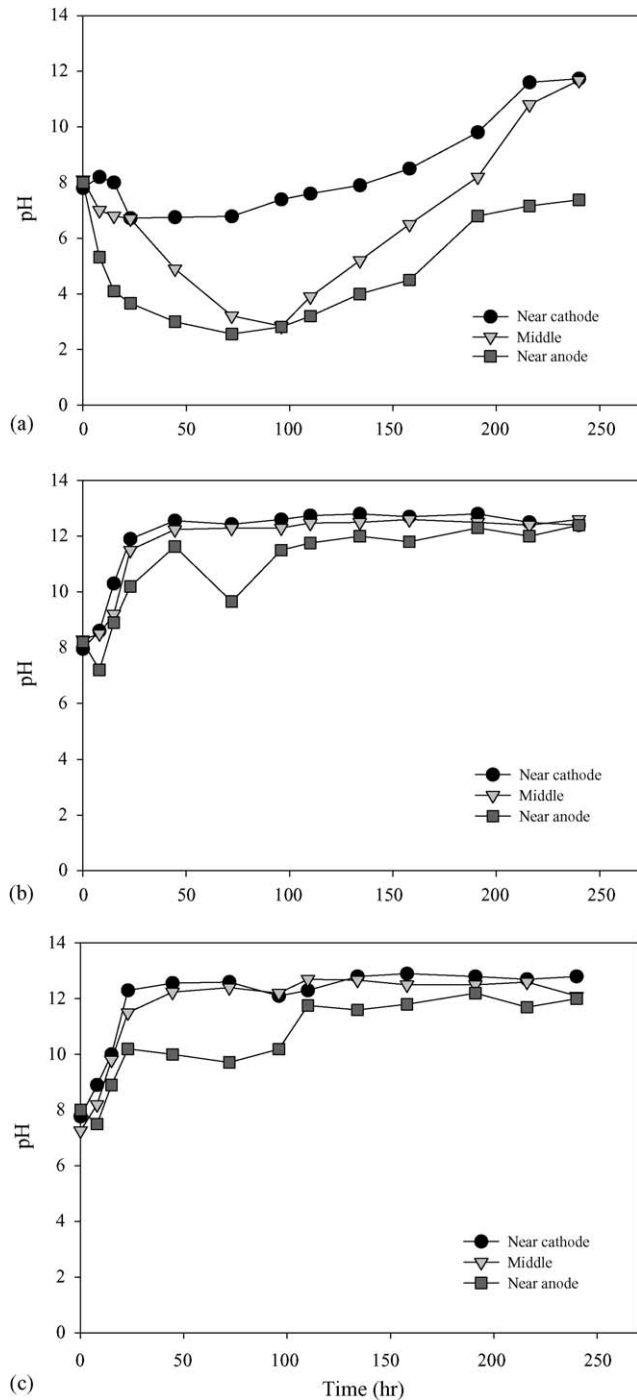
Fig. 10. The pH of pore-water vs. operation time under different ZVM and 1 V/cm voltage gradients: (a) only EK, (b) EK + iron, (c) EK + zinc.

Fig. 11. The ORP of pore-water vs. operation time under different ZVM and 1 V/cm voltage gradients: (a) only EK, (b) EK + iron, (c) EK + zinc.

reaches around 12.0 shown in Fig. 10(b) and (c). The phenomena illustrate that PCE consumed the H$^+$ to precede dehalogenation reaction according to Eq. (3). Theoretically speaking, this dehalogenation reaction will be inhibited under high pH conditions because of few protons. Therefore, PCE removal efficiency gradually ceases after 50 h treatment shown in Fig. 6. Moreover, the high pH causes hydroxide and salt precipitates on the ZVM surface to decay the reaction activity of ZVM [20]. In addition to the pH condition, the pE circumstance should be under reduc-
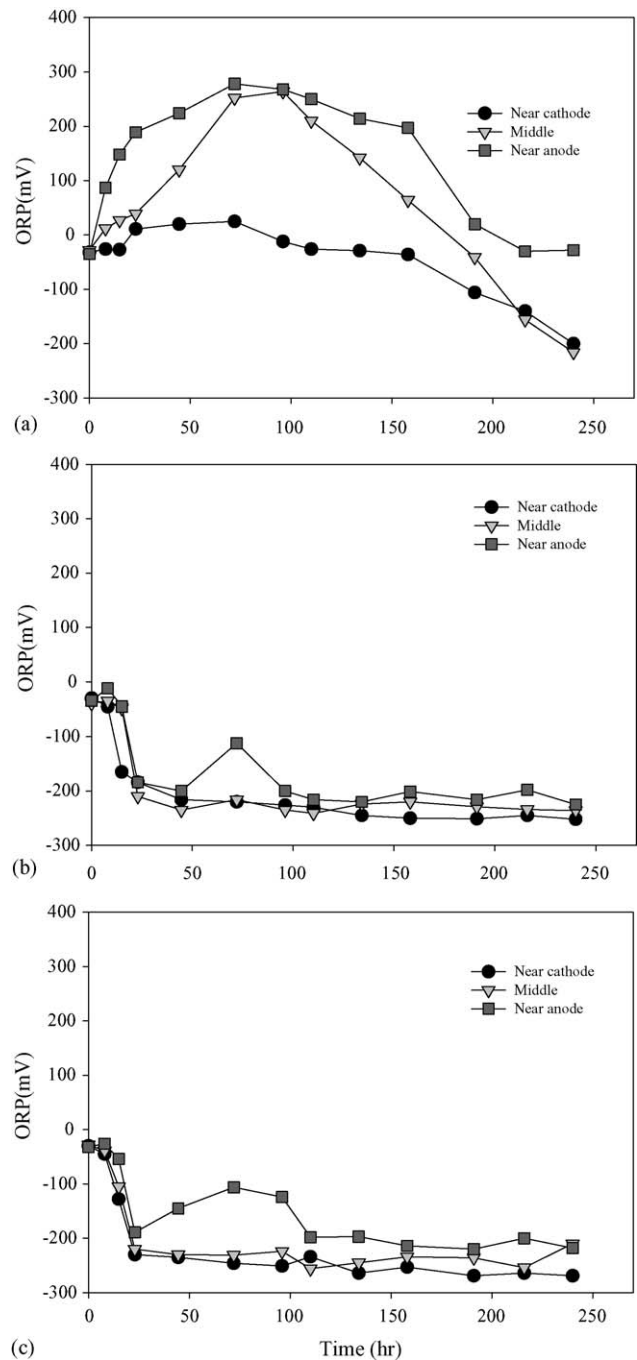
tion status to induce the dehalogenation [21]. Fig. 11 shows the ORP of pore-water versus operation time under different ZVM. From Fig. 11(b) and (c), the ORP decreases dramatically in the beginning of tests, then, approaches around −250 to −200 mV. These ORP data demonstrate that the dehalogenation process works in the EK + ZVM system.

Many research reported the reduction pathways and byproducts of PCE dechlorination [22,23]. The initial byproducts include trichloethylene (TCE), 1,1-dichloethylene (1,1-DCE) and other chlorinated organics. Afterwards, these chlorinated organics will be degraded into ethylene and final product is
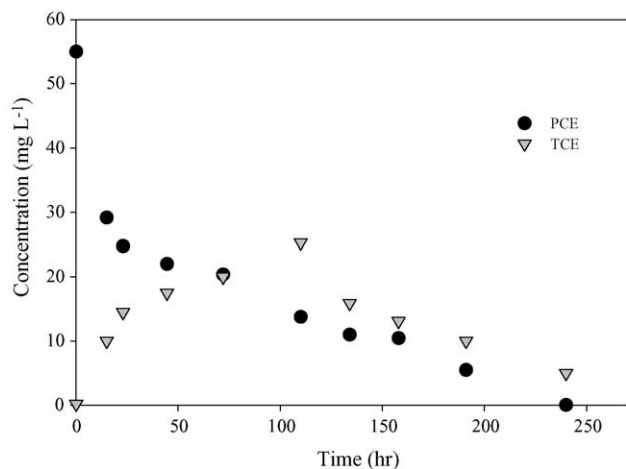
Fig. 12. The PCE and TCE concentration in soils vs. operation time under 1.0 V/cm, 0.01 M Na$_2$CO$_3$, and graphite application.

ethane. The organics with less chlorine atoms will be more difficult to be reduced [23]. For verifying the EK + ZVM process whether degrade PCE, the PCE and TCE concentration in the soil specimen were measured. Fig. 12 shows the PCE and TCE concentration in soils versus operation time. Results reflect that PCE decreases and TCE increases with time, i.e., the amount of PCE and TCE is balanced with each other during 75 h treatment. This illustrates that PCE can be dechlorinated by the EK + ZVM system to transform as TCE. The TCE is the major by-product for PCE dechlorination by ZVM [24]. Hence, the appearance of TCE demonstrates the occurrence of chlorination reaction in the integration system. Afterwards, TCE decreases gradually, which implies TCE may be degraded as other compounds or just evaporates to the atmosphere.

3.4. pH, water content, and organic matter of treated soils

After 10-day treatment, the soil specimen was sampled to measure its pH, water content, and organic matter (data not shown in the paper) for investigating the remediation impacts on soils. The initial pH, water content, and organic matter is around 7.6%, 22%, and 2.4%, respectively. Results present the soil pH remains at the neutral range (from 7.2 to 8.5) regardless of the ZVM species. The neutral soil pH can be attributed to the buffering electrolyte and soil itself. The water content of treated soils maintains from 19% to 20% regardless of voltage gradient and ZVM species, which is close to the original water content of soils. For the consideration of organic matter, the treated soil under different experimental conditions seems to contain the same amount of organic matter as original soils. To sum up the above observation, the integration technique basically sustains the original soil characteristics.

4. Conclusions

According to experimental results, some conclusions can be drawn as follows:

1. The EK + ZVM technique can maintain the neutral pH status and stable electricity consumption under certain operational conditions.
2. The integration technique is feasible to clean up the PCE contaminated soils in a lab scale; the best PCE removal efficiency can reach 99% after the 10-day treatment.
3. The zero-valent zinc possesses better PCE degradation than zero-valent iron.
4. For consideration of maintaining neutral pH soils and removal efficiency, the appropriate operational parameters include: sodium carbonate of 0.01 M, 1.0 V/cm voltage gradient, ZVM installation close to the anode.
5. The soils treated by EK + ZVM roughly maintain their original properties.

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