

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Separation Science and Technology

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713708471>

Coupling Electrokinetics with Permeable Reactive Barriers of Zero-Valent Iron for Treating a Chromium Contaminated Soil

Long Cang^{ab}; Dong-Mei Zhou^a; Dan-Ya Wu^a; Akram N. Alshawabkeh^c

^a State Key Laboratory of Soil and Sustainable Agriculture, Institute of Soil Science, Chinese Academy of Sciences, Nanjing, China ^b Graduate School of the Chinese Academy of Sciences, Beijing, China ^c

Department of Civil and Environmental Engineering, Northeastern University, Boston, MA, USA

To cite this Article Cang, Long, Zhou, Dong-Mei, Wu, Dan-Ya and Alshawabkeh, Akram N. (2009) 'Coupling Electrokinetics with Permeable Reactive Barriers of Zero-Valent Iron for Treating a Chromium Contaminated Soil', *Separation Science and Technology*, 44: 10, 2188 — 2202

To link to this Article: DOI: 10.1080/01496390902976699

URL: <http://dx.doi.org/10.1080/01496390902976699>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Coupling Electrokinetics with Permeable Reactive Barriers of Zero-Valent Iron for Treating a Chromium Contaminated Soil

Long Cang,^{1,2} Dong-Mei Zhou,¹ Dan-Ya Wu,¹ and
Akram N. Alshawabkeh³

¹State Key Laboratory of Soil and Sustainable Agriculture,
Institute of Soil Science, Chinese Academy of Sciences, Nanjing, China

²Graduate School of the Chinese Academy of Sciences, Beijing, China

³Department of Civil and Environmental Engineering, Northeastern
University, Boston, MA, USA

Abstract: Electrokinetic (EK) remediation coupled with permeable reactive barriers (PRB) of zero-valent iron (ZVI) was applied for treating a Cr contaminated soil. Results show that loading ZVI-PRBs in different locations of soil column strongly affected the EK performance. Transport of Cr in the soil column was resulted from the balance of its electromigration and electroosmosis (EO). With increasing treatment time, the total Cr concentration of the soil column pore-water decreased in all the treatments. The lowest Cr concentration of the pore-water decreased to only 0.03 mg L^{-1} after a run for 384 h, and a maximum 71.5% of initial soil Cr(VI) was removed when two ZVI-PRBs were loaded at the two ends of the soil column. Additionally, the soil EC values were lower than the original one after the EK-PRB treatments, suggesting that these treatments did not introduce more ions into the soil.

Keywords: Chromium, electrokinetic, permeable reactive barrier, soil, zero-valent iron

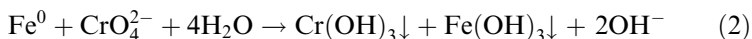
Received 30 August 2008; accepted 25 December 2008.

Address correspondence to Dong-Mei Zhou, State Key Laboratory of Soil and Sustainable Agriculture, Institute of Soil Science, Chinese Academy of Sciences, Nanjing 210008, China. Tel.: +86-25-86881180; Fax: +86-25-86881000. E-mail: dmzhou@issas.ac.cn

INTRODUCTION

Soil or groundwater chromium contamination has been concerned for years because of their high environmental risk. The most commonly encountered forms of chromium in soil and groundwater are trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)). Chromium(VI) is highly mobile and toxic compared to Cr(III). In many cases, Cr(VI) may react with soil components such as organic matter and ferrous iron to produce Cr(III) compounds which may precipitate and/or highly adsorb on the soil particles surface. Chromium(III) is less practically moved from soil when the pH is above 4, and it exists as hydroxide precipitates between pH 6.8–11.3 (1).

Several techniques have been proposed and evaluated for remediation of Cr-contaminated soil and groundwater (2–4). Zero-valent iron (ZVI)-permeable reactive barriers (PRB) are considered to be promising for cleanup of Cr(VI) in groundwater because of its practicality, reasonable cost, and effectiveness. Chromium(VI) in groundwater reacts with ZVI in the PRB, according to the following equations (5–7):



Fe^0 is ultimately oxidized to Fe(III), which precipitates as ferric hydroxides, while Cr(VI) is reduced to Cr(III). They form co-precipitation in the PRB and avoid the subsequent treatments. During the reactions, the released OH^- ions are beneficial for increasing the soil pH and correspondingly decrease the absorption capacity of Cr(VI) in the soil. The use of ZVI-PRB can be implemented for the treatment of contaminated groundwater in aquifers. However, treatment of contaminated soils, such as fine-grained or heterogeneous soils by ZVI-PRB is impractical due to the small advective flow in low permeable soils.

Thus, electrokinetics (EK) has been considered to be a feasible one for remediating Cr contaminated soil with low permeability (8). The EK remediation system is composed of one pair of electrodes and run by direct-current power. The EK system employs electromigration (migration of ions to electrode opposite in polarity) and electroosmosis (EO) for transport within an electrolytic soil-water system (9,10), and also can be implemented for the extraction of contaminants and integrated with other chemical or biological techniques (11–13). A field study (14) reported the extraction of Cr(VI) from soil by EK, and showed the efficient accumulation of chromium in treatment wells. But the Cr solution in the well will still need to be further treated. So, coupling EK with

ZVI-PRB will be a good choice to remove soil Cr and treat the Cr solution simultaneously.

A study (15) documented the effectiveness of incorporating ZVI-PRB with EK to treat Cr(VI) contaminated clay. The ZVI-PRB was installed in the middle of the soil specimen between the anode and the cathode. The result showed that the reduction efficiency of Cr(VI) increased to 85.8% when 1 V cm^{-1} was applied in the presence of ZVI. However, 129 mg and 98 mg of Cr(VI) was collected in the anolyte and catholyte respectively after the treatment, indicating that the location of the ZVI-PRB has not been optimized to produce complete treatment. Yuan and Chiang (16) reported that the EK process coupled with PRB to the removal soil arsenic, but also did not examine the effect of PRB locations in the soil column on the amount of EO flow and the migration of arsenic. Additionally, limited study has paid attention to soil characteristics (for example pH, electrical conductivity (EC), and so on) after the EK-PRB treatment (13).

The main objectives of this work were to evaluate the performance of EK coupled with ZVI-PRB loaded in different locations of the soil column for treating a Cr contaminated soil and examine its effect on soil properties. The pH, EC, Cr(VI), and total Cr concentration of the pore-water in the soil column and of the soils sampled from different sections were measured to study the removal of soil Cr during EK-PRB treatment. The results would provide useful information for practical remediation of Cr contaminated sites by EK-PRB and optimize its design.

MATERIALS AND METHODS

Soil

A yellow brown soil (*Udic Argosols*) was sampled from the top 0 to 40 cm of a site at Nanjing, Jiangsu Province, China. The soil was air-dried, grounded, and sieved through a 20-mesh sieve. The soil pH, EC (1:2.5 soil to water) and soil organic matter (SOM) were 5.5, $2.5 \mu\text{S cm}^{-1}$, and 16.0 g kg^{-1} , respectively. Its cation exchange capacity (CEC) was $16.5 \text{ cmol}(+) \text{ kg}^{-1}$. The initial concentrations of soil Cu, Cr, Pb, Zn, and Cd were 34.4, 95.3, 36.7, 87.6, and 0.2 mg kg^{-1} , respectively. The clay ($<2 \mu\text{m}$), silt ($2\text{--}20 \mu\text{m}$), and sand ($>20 \mu\text{m}$) contents in the soil were 14.3%, 47.4%, and 38.3%, respectively. The pH of zero point charge (pH_{zpc}) of the soil was 1.84, and its hydraulic conductivity was $5.8 \times 10^{-5} \text{ cm s}^{-1}$.

A Cr contaminated soil was prepared by spiking a specific volume of $1000 \text{ mg Cr(VI) L}^{-1}$ solution with the soil to produce a final soil Cr

concentration of 1000 mg kg^{-1} . The soil was then thoroughly mixed, maintained in a jar, and was covered with 2 cm water at room temperature. After incubation for one month, the soil was air-dried, crushed, sieved through a 20-mesh sieve again, and was preserved at room temperature for one year to simulate the natural Cr contaminated soil. Before experiments, the soil characteristics were measured, and the soil pH, EC, total soil Cr, and Cr(VI) concentrations were 6.04 , $360 \mu\text{S cm}^{-1}$, 1 , 1086 , and 115 mg kg^{-1} , respectively.

Methods

Figure 1 shows a schematic of the experimental system for EK treatment coupled with ZVI-PRB. The system consists of a soil column, two electrolyte reservoirs, five soil pore-water sampling tubes (17), a direct-current (DC) electric power supply, and a four-channel peristaltic pump. The soil column was made from a 12 cm long PVC cylinder with an inner diameter of 6.6 cm. The peristaltic pump was used for circulating the electrolyte at a flow rate of 18 ml min^{-1} . Titanium alloy sheets ($3 \text{ cm} \times 3 \text{ cm}$) were used as the working electrodes. Two porous fritted glass sheets were used to prevent soil dispersion or leakage from soil column to electrolyte reservoirs. The soil sections were labeled as Regions I, II, III, VI, and V from anode to cathode. The ZVI-PRBs were placed in soil column at different locations (Regions I, III, and V), varied with

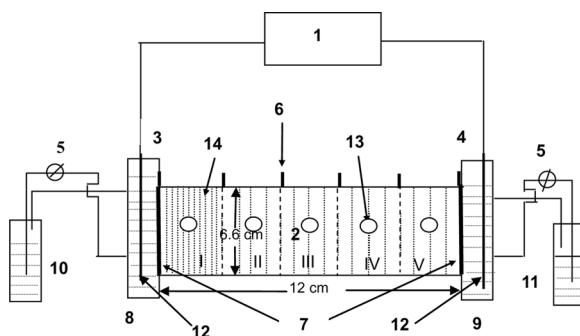


Figure 1. A schematic of EK-PRB system. 1. DC power supply; 2. Soil; 3. Anode; 4. Cathode; 5. Peristaltic pump; 6. Voltage measurement ports; 7. Porous fritted glasses; 8. Anolyte pool; 9. Catholyte pool; 10. Anode treatment pool; 11. Cathode treatment pool; 12. Titanium alloy sheets; 13. Soil pore water collection hole; 14. ZVI-PRB. Note: There are five regions in the soil column and labeled as Regions I, II, III, IV and V from anode to cathode, respectively.

Table 1. Experimental design of EK-PRB treatments

	PRB located at	Anolyte and catholyte	Electric field gradient (V/cm)	Soil (g)
Exp-01	(quartz in) Region I*	0.01 M NaCl	1.0	440
Exp-02	Region I	0.01 M NaCl	1.0	475
Exp-03	Region III	0.01 M NaCl	1.0	465
Exp-04	Region V	0.01 M NaCl	1.0	470
Exp-05	Regions I and V	0.01 M NaCl	1.0	345

*Soil column labeled as Region I ~ V from anode to cathode.

different treatments. Table 1 summarizes the locations of the ZVI-PRBs within the soil column.

A control experiment (Exp-01) was conducted under EK without ZVI-PRB application. The ZVI-PRB was prepared by mixing 10 g of Fe⁰ powder (Φ 0.3 mm) with 120 g of sand (quartz). The thickness of ZVI-PRB was 2.0 cm and larger than that reported by Weng (15) to make sure that the Cr(VI) solution passing through the barrier would be completely reduced to Cr(III). The ZVI-PRBs and soil of 345–475 g varied with different treatments were compacted in the column (Table 1). A filter paper was placed between the ZVI-PRB and soil to prevent the transport of iron particles (ferrous and ferric ions can migrate through the filter). After the set-up was assembled, 0.01 mol L⁻¹ NaCl was circulated for 24 h to saturate the soil before the application of electric field gradient (18). A constant DC voltage of 10 volts was then applied through the cell.

Each experiment was run for 384 h. Pore water samples were collected intermittently for measurement of the pH and total Cr concentration for understanding the processes of the EK-PRB. After the treatments, the set-ups were dismantled. The soil in each column was cut into five equal sections, and the soil pH, EC, total soil Cr and Cr(VI) concentrations were measured for each section.

Analysis of Soil Subsamples

All chemicals used in the experiments are of analytical grade. Deionized water was used throughout the experiments. Soil pH, EC, SOM content, and heavy metal concentrations were analyzed using general analytical methods. The pH and EC of pore water were determined by a pH meter (Shanghai REX Instrument Factory, model PHS-3B, China) and an EC meter (Shanghai REX Instrument Factory, model DDS-11A, China),

respectively. Soil pH and EC were measured by preparing a slurry of 1:2.5 soil to water. SOM was analyzed by dichromate oxidation method. The pH_{zpc} of soil samples was determined by a zeta potential instrument (JS94H Zeta Meter Inc., Shanghai Zhongchen Co Ltd., China). The hydraulic conductivity for the soil sample was $5.8 \times 10^{-5} \text{ cm s}^{-1}$ measured by a falling head permeability meter (Model Nan-55, Nanjing Soil Instrument Factory, China). The EO flow was calculated by measuring the change of anolyte volume.

The soil samples were air-dried, grounded to pass through a 100-mesh screen (Φ 0.149 mm), and were digested with $\text{HF-HNO}_3\text{-HClO}_4$ for the determination of soil total Cr by a Hitachi 180-80 Atomic Absorbance Spectrometer (AAS). Two standard soil samples (China National Soil Certified Reference Material: GBW07404 and GBW07407) were used for controlling the analytical results. Chromium(VI) was analyzed according to USEPA method 3060A (19,20). Within this method, 2.5 g of soil was extracted by 50 mL of $20 \text{ g L}^{-1} \text{ NaOH} + 30 \text{ g L}^{-1} \text{ Na}_2\text{CO}_3$ and 0.5 mL of 1.0 mol L^{-1} phosphate buffer (pH 7.0) at 90–95°C for 1 h, adjusted with $5.0 \text{ mol L}^{-1} \text{ HNO}_3$ to $\text{pH } 7.5 \pm 0.5$, and then filtered through a $0.45 \mu\text{m}$ membrane. The Cr(VI) concentration in the supernatant was determined by AAS.

RESULTS AND DISCUSSION

Electrical Current and EO Flow

The change of electric currents with treatment time for the five experiments is shown in Fig. 2(a). For Exp-03 and -04, the currents increased at the beginning and then decreased to a very low value. When the ZVI-PRB was loaded in Region I for Exp-02 and -05, however, the currents decreased quickly after the application of the electric field, and then increased to a stable value. The current for Exp-01 without ZVI-PRB was higher than those of the other experiments with ZVI-PRB after 100 h. This result indicates that ZVI-PRB reacted with Cr(VI) to form co-precipitation in the ZVI-PRB (15). In all the treatments, the currents were below 10 mA.

Figure 2(b) shows the change of cumulative EO flow across the soil column with time. All the experiments, except Exp-03, produced almost steady EO flow towards the cathode because of negative surface charge of the soil. The amount of EO flow in Exp-05 (two ZVI-PRBs were located at Regions I and V) was the largest in all the treatments, and the orders were Exp-05 > Exp-02 (ZVI-PRB in Region I) > Exp-01 (without ZVI-PRB) > Exp-04 (ZVI-PRB in Region V) > Exp-03 (ZVI-PRB in

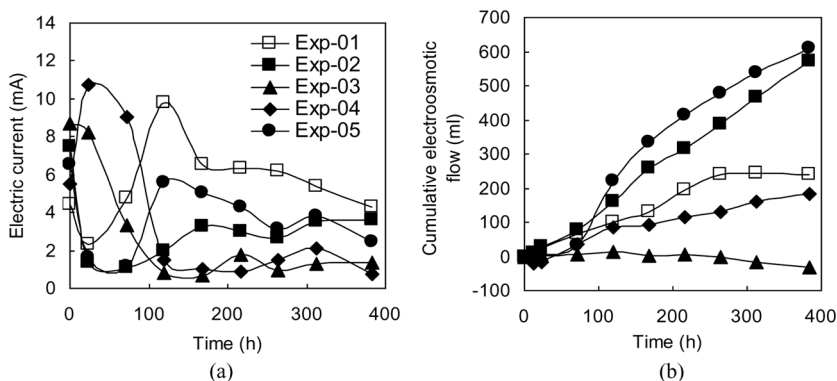


Figure 2. Change of electric current (a) and cumulative EO flow (b) with treatment time for different treatments. Minus value refers to the EO flow towards the anode.

Region III). It was attributed to the smaller average soil ECs in Exp-05 and -02 than those in Exp-01 and -04 (from Table 4). According to the calculated equation of EO flow (10), the larger soil EC would decrease the zeta potential, and then the EO flow would be inhibited. The EO flow for Exp-03 moved towards the anode after 216 h. This behavior was similar to the results reported by Weng (15). When PRB was located at Region III (the middle of soil column) in Exp-03, a lot of hydroxide ions were originated from the reaction of Cr(VI) and ZVI. The hydroxide ions reversed EO flow towards the anode along with the treatment time.

Soil Solution pH and Total Cr Concentration

The pH values of soil pore-water changed with the treatment time, which were closely related to Cr removal from the soil column. Figures 3a–c indicated the pH of pore water in different treatments and their change with time. It shows that the pore-water pH was affected by the locations of ZVI-PRB in the soil column. In Exp-01 without ZVI-PRB, the pore-water pH dropped from initial 4.9 to 2.0 in Region I, and increased from 6.2 to 12.5 in Region V after 384 h. This was a general trend for an EK treatment. But, when a ZVI-PRB was set in Region I in Exp-02, ZVI reacted with Cr(VI) to produce Cr(III) and OH^- ions according to Equations 1 and 2. So, OH^- ions neutralized H^+ ions coming from the anodic reaction, and prevented the introduction of H^+ ions into the soil column. At the same time, the pH of pore water in Region I was very high near 10 at 0 h. It is ascribed that Cr(VI) diffused towards the anode and reacted

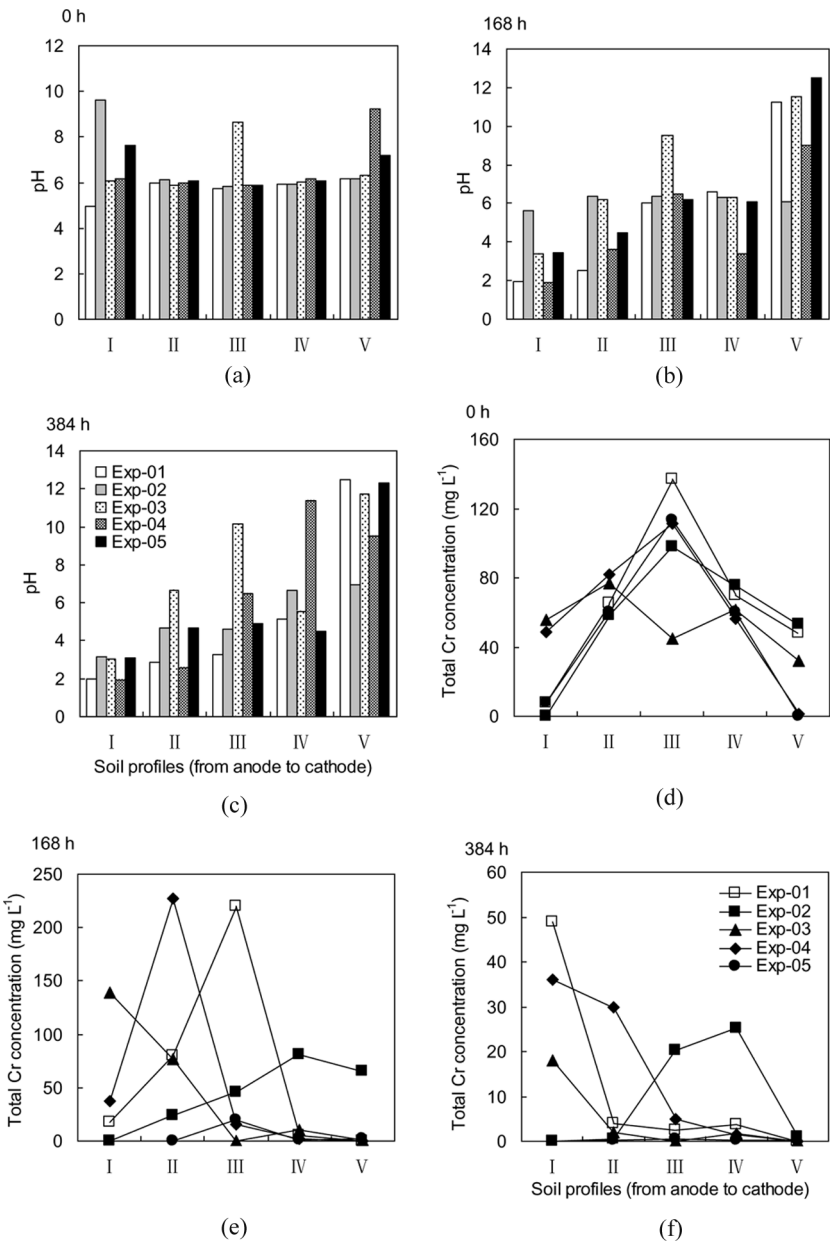


Figure 3. Change of pH (a, b, c) and total Cr concentration (d, e, f) of soil pore-water in different soil sections with treatment time.

with ZVI to produce hydroxide ions according to Equations (1) and (2). After the experiment was finished, the pore-water pH decreased to a low value, which was resulted from the balance of H^+ ions release from the anode and the OH^- ions released from the reaction of Cr(VI) and ZVI. By this mechanism, the pore-water pH at different positions can hold in a narrow range (from 3.2 to 6.9).

In Exp-03, a ZVI-PRB was located at Region III. The pH value of soil pore-water at Region III was higher than those at other regions at the beginning. As for Exp-04 with a ZVI-PRB in Region V, the pH of soil pore water at Region V was higher than those at other soil regions. When two ZVI-PRBs were located at Regions I and V, the pH of pore water at Regions II to IV ranged from 4.6 to 4.9 and was smaller than those in other experiments.

Figures 3d–f shows the change of total Cr concentration in pore-water with time. At the beginning, the total Cr concentrations of pore-water in all the experiments except Exp-03 show a similar peak shape, which were ascribed to the equilibrium of soil column with 0.01 M NaCl solution before the experiments. When a ZVI-PRB was located at Region III, Cr(VI) in the pore water reacted with ZVI and its concentration decreased to a low value. After the electric field was applied, the peak shapes of Cr distribution in the pore water changed. In Exp-02, pore water Cr migrated towards the anode and the solution Cr concentrations decreased with time. But the pore water Cr at Regions III and IV always kept at a high value than other regions, which may be ascribed that the EO flow in this treatment was relatively higher and the Cr of soil pore water was driven towards the cathode in opposite to the electromigration. However, when the ZVI-PRB was located at Region III (Exp-03), the electromigration came to be important, and the change was similar to that in Exp-01. In Exp-04, soil pore water Cr migrated towards the anode and the Cr concentration in the pore water increased from the Regions V to I. When two ZVI-PRBs were located at the Regions I and V in Exp-05, the pore water Cr migrated towards the anode region. Moreover, Cr concentration rapidly decreased to a very low value after 168 h, showing a promising performance. After 384 h, the smallest total Cr concentration of pore-water was only 0.03 mg L^{-1} . The Cr concentration was below the Standard III of the Chinese National Standard of Groundwater Quality GB/T14848-93.

Cr Distribution in Electrolyte and Soil After Treatment

Table 2 shows the total Cr and Cr(VI) concentration in different soil sections after the treatments. The results show that EK-PRB technique

Table 2. The total Cr and Cr(VI) concentrations of soil after different treatments (mg kg^{-1})

Treatment	Total Cr					Cr(VI)				
	I	II	III	IV	V	I	II	III	IV	V
Initial	1086	1086	1086	1086	1086	115	115	115	115	115
Exp-01	/	642	578	597	1001	/	73.4	67.8	69.6	48.3
Exp-02	/	677	842	555	601	/	29.1	52.8	95.6	72.2
Exp-03	717	649	/	614	585	80.9	80.0	/	48.8	58.8
Exp-04	675	599	601	639	/	98.5	83	81.9	55.7	/
Exp-05	/	751	606	554	/	/	19.6	24.6	53.9	/

Note: “/” shows the location of ZVI-PRB.

significantly reduced the total soil Cr concentration from 1086 mg kg^{-1} to $554\text{--}1001 \text{ mg kg}^{-1}$, and then the removed soil Cr concentration varied from 85 to 532 mg kg^{-1} . The Cr(VI) concentration in different soil sections varied from 19.6 to 98.5 mg kg^{-1} , and was significantly lower than the initial value (115 mg kg^{-1}). The amount of Cr removed from the soil column ($85\text{--}532 \text{ mg kg}^{-1}$) was higher than the initial amount of soil Cr(VI) (115 mg kg^{-1}), suggesting that the removed Cr contains some Cr(III). It might be attributed to:

1. the Cr(III) migration towards cathode in the low pH condition that developed in the vicinity of anode,
2. the mutual transformation of Cr(VI) and Cr(III) under certain conditions during the EK-PRB process (15).

According to the Cr(VI) distribution in the different soil sections, Cr(VI) concentrations in the soil near the anode in Exp-03 and -04 were higher than those in the other soil sections. But, the Cr(VI) concentrations in the soil sections close to the cathode in Exp-02 and -05 were higher than those in the other soil sections. The results indicated that the migration mechanisms of soil Cr(VI) were not the same among the different treatments. In this study, the directions of Cr(VI) electromigration and EO flow were on the contrary in most cases, which was disadvantageous to the removal of soil Cr(VI). When the EO flow was small (for example in Exp-01, -03 and -04), the electromigration of Cr(VI) played a leading role in Cr(VI) migration towards the anode, so the soil Cr(VI) concentration near the anode was higher than that near the cathode. However, when the EO flow was high (for example in Exp-02 and -05), it prevented the migration of Cr(VI) towards the anode, so the

soil Cr(VI) concentration near the cathode were higher than that near the anode. Therefore, EO flow was very important in controlling Cr(VI) transport and should be considered during the remediation process (3,21).

Table 3 shows the total Cr content in the anolyte, catholyte, PRB and soil after each treatment. Most of the Cr existed in the anolyte as a result of electromigration of Cr(VI) driven by the electric field when no ZVI-PRB was loaded in the soil column. However, Cr appeared in the catholyte in Exp-02 with a high EO flow. For Exp-03 and -04, Cr was accumulated in the anolyte, and little Cr was observed in the catholyte. When ZVI-PRBs were loaded in the two ends of the soil column at the same time in Exp-05, the Cr concentrations in both the electrolytes were very low (about 0.11 mg). The total Cr mass in PRB was different among Exp-01, 02, 03, 04, and 05. When PRB was located at Regions I and V (Exp-05), ZVI reacted with Cr(VI) to prevent Cr(VI) from moving to the anode and cathode reservoirs, so the accumulated total Cr mass in the PRB was the highest among all the treatments. From the removal efficiency in Table 3, the removal percents of the total soil Cr varied from 35% to 42%, and were similar in different treatments, but the range of removal efficiency of Cr(VI) varied from 30.2% to 71.5%. According to the mass balance, the best performance was obtained when the ZVI-PRBs were loaded in both the ends of the soil column (Exp-05). From Table 3, the recovery percentages of all the experiments were from 61.8% to 72.2%. The recovery percentages were lower than those reported by Reddy and Chinthamreddy (22,23) and Yuan and Chiang (16), but were similar with the recovery percentages with the results of Reddy and Parupudi (24). The loss of Cr might be due to the loss of soil during the experiments and Cr adsorption or precipitation onto the porous fritted glasses and tubes.

pH and EC of Soil Subsamples After Treatments

Table 4 shows the soil pH and EC distribution in different soil sections after the treatments. The soil pH varied from 3.1 to 10.7 in Exp-01 without ZVI-PRB, from 4.6 to 8.3 in Exp-02 with ZVI-PRB in Region I, from 3.5 to 9.1 in Exp-03 with ZVI-PRB in Region III, from 2.3 to 10.5 in Exp-04 with ZVI-PRB in Region V, and from 4.8 to 6.0 in Exp-05 with ZVI-PRB in Regions I and V. The change of soil pH in Exp-05 was the smallest among all the treatments. It suggests that to locate ZVI-PRBs at Regions I and V may be a good choice for controlling soil pH.

Soil EC is related to ion concentrations in soil solution (25). Different treatments resulted in the variations of the final soil EC, as shown in

Table 3. Fractional distribution of chromium in the EK-PRB systems

Treatment	Initial Cr mass in soil (mg)		Total Cr mass after treatments (mg)			Total Cr mass of soil pore water from soil column (mg)		Removal efficiency (%)	
	Total Cr	Cr(VI)	Remaining in soil	Anode reservoir	Cathode reservoir	Total Cr mass in PRB (mg)	water from soil column (mg)	Total Cr	Cr(VI) balance (%)
Exp-01	478	50.6	310	21.4	0.16	4.78	5.00	35.1	43.7
Exp-02	516	54.6	318	0.02	5.95	5.95	4.28	38.4	45.6
Exp-03	505	53.5	298	19.7	0.14	26.9	4.70	41.0	41.8
Exp-04	510	54.1	296	12.7	bd	1.40	5.09	42.0	30.2
Exp-05	375	39.7	220	0.03	0.08	48.3	2.19	41.3	71.5
									72.2

Note: "bd" means the content below the detection limit. Mass balance (%) = (Total soil Cr mass after treatments + Total Cr mass in PRB + Total Cr mass of soil pore-water from soil column) \times 100/Initial Cr mass in soil.

Table 4. The pH and EC of soil subsamples after different treatments

Treatment	pH					Average value	EC ($\mu\text{S cm}^{-1}$)					Average value
	I	II	III	IV	V		I	II	III	IV	V	
Initial	6.2	6.2	6.2	6.2	6.2	6.2	360	360	360	360	360	360
Exp-01	/	3.1	3.5	4.3	10.7	5.4	/	290	125	62	203	170
Exp-02	/	4.6	5.8	6.7	8.3	6.4	/	155	47	68	108	94.5
Exp-03	3.5	8.3	/	5.7	9.1	6.7	275	192	/	87	157	178
Exp-04	2.3	3.4	6.7	10.5	/	5.7	790	270	96	182	/	335
Exp-05	/	4.8	5.4	6.0	/	5.4	/	84	79	183	/	115

Note: “/” shows the location of ZVI-PRB.

Table 4. The EC values in most of the soil subsamples were smaller than the initial one ($360 \mu\text{S cm}^{-1}$). So, loading of the ZVI-PRB in soil column did not introduce more ions into the soil. But in Exp-04, the soil EC in Region I was high because of its low pH and high Cr concentration of pore water.

CONCLUSIONS

According to the experimental results, it can be concluded that the technique integrating EK with ZVI-PRB is feasible to cleanup of Cr contaminated soil. The maximal Cr(VI) removal efficiency reached 72% and the minimum Cr concentration in pore water was only 0.03 mg L^{-1} after 384-h treatment. The Cr mass in the anode and cathode reservoirs with PRB treatment was smaller than that without PRB, which was beneficial to the further treatment of the electrolyte. The location of the ZVI-PRB in soil column affected the volume and direction of EO flow. After the experiments, the change of soil pH with EK-PRB treatment was small. Additionally, the soil EC values were less than the original one after the EK-PRB treatments, suggesting the treatment does not introduce more ions into the soil. To reach a neutral soil and pore-water and a high removal efficiency, to load two ZVI-PRBs at both the ends of soil column is a good choice.

ACKNOWLEDGEMENTS

This study was supported by the National Natural Science Foundation of China (20807044) and the State Key Laboratory of Soil and Sustainable Agriculture, Institute of Soil Science, Chinese Academy of Sciences.

REFERENCES

1. Reddy, K.R.; Chinthamreddy, S. (1999) Electrokinetic remediation of heavy metal-contaminated soils under reducing environments. *Waste Manage.*, 19: 269.
2. Nishtar, N.F.; Rathlnam, A.; Jonnalagadda, R.R.; Balachandran, U.N. (2005) Solid waste removes toxic liquid waste: adsorption of chromium(VI) by iron complexed protein waste. *Environ. Sci. Technol.*, 39: 2804.
3. Wilkin, R.T.; Su, C.; Ford, R.G.; Paul, C.J. (2005) Chromium-removal processes during groundwater remediation by a zero valent iron permeable reactive barrier. *Environ. Sci. Technol.*, 39: 4599.
4. Zhou, D.M.; Alshawabkeh, A.N.; Deng, C.F.; Cang, L. (2004) Electrokinetic removal of chromium and copper from contaminated soils by lactic acid enhancement in the catholyte. *J. Environ. Sci-China*, 16 (4): 529.
5. Furukawa, Y.; Kim, J.W.; Watkins, J.; Wilkin, R.T. (2002) Formation of ferrihydrite and associated iron corrosion products in permeable reactive barriers of zero-valent iron. *Environ. Sci. Technol.*, 36: 5469.
6. Powell, R.M.; Puls, R.W.; Hightower, S.K.; Sabatin, D.A. (1995) Coupled iron corrosion and chromate reduction: mechanisms for subsurface remediation. *Environ. Sci. Technol.*, 29: 1913.
7. Chin, F.C.; Zhang, T.C. (1998) In-situ remediation of nitrate contaminated groundwater by electrokinetics/iron wall processes. *Water Sci. Technol.*, 38 (7): 135.
8. Pamukcu, S.; Weeks, A.; Wittle, J.K. (2004) Enhanced reduction of Cr(VI) by direct electric current in a contaminated clay. *Environ. Sci. Technol.*, 38: 1236.
9. Acar, Y.B.; Alshawabkeh, A.N. (1993) Principles of electrokinetic remediation. *Environ. Sci. Technol.*, 27: 2638.
10. Probststein, R.F.; Hicks, R.E. (1993) Removal of contaminants from soils by electric fields. *Science*, 260: 498.
11. Zhou, D.M.; Deng, C.F.; Cang, L.; Alshawabkeh, A.N. (2005) Electrokinetic remediation of a Cu-Zn contaminated red soil by controlling the voltage and conditioning catholyte pH. *Chemosphere*, 61 (4): 519.
12. Yang, G.C.C.; Liu, C.Y. (2001) Remediation of TCE contaminated soil by in situ EK-Fenton process. *J. Hazard. Mater.*, 85: 317–331.
13. Chang, J.H.; Cheng, S.F. (2006) The remediation performance of a specific electrokinetics integrated with zero-valent metals for perchloroethylene contaminated soils. *J. Hazard. Mater.*, 131: 153.
14. Gent, D.B.; Bricka, R.M.; Alshawabkeh, A.N.; Larson, S.L.; Fabian, G.; Granade, S. (2004) Bench- and field-scale evaluation of chromium and cadmium extraction by electrokinetics. *J. Hazard. Mater.*, 110: 53.
15. Weng, C.H.; Lin, Y.T.; Lin, T.Y.; Kao, C.M. (2007) Enhancement of electrokinetic remediation of hyper-Cr(VI) contaminated clay by zero-valent iron. *J. Hazard. Mater.*, 149 (2): 292.
16. Yuan, C.; Chiang, T.S. (2007) The mechanisms of arsenic removal from soil by electrokinetic process couple with iron permeable reaction barrier. *Chemosphere*, 67: 1533.

17. Cang, L.; Zhou, D.M.; Chen, H.F.; Luo, X.S. A kind of soil solution sampler in suit (In Chinese), China invention patent published number: CN1881996A, July 11, 2006
18. Li, Z.M.; Yu, J.W.; Neretnieks, I. (1998) Electroremediation: Removal of heavy metals from soils by using cation selective membrane. *Environ. Sci. Technol.*, 32: 394.
19. Reddy, K.R.; Asce, M.; Chinthamreddy, S. (2003) Sequentially enhanced electrokinetic remediation of heavy metals in low buffering clayey soils. *J. Geotech. & Geoenviron. Engineer.*, 129 (3): 2637.
20. Zhou, D.M.; Chen, H.M.; Zheng, C.R.; Tu, C. (2001) Catalytic effect of soil colloids on the reaction between Cr-VI and p-methoxyphenol. *Environ. Pollut.*, 111 (1): 75–81.
21. Ko, S.O.; Schlautman, M.A.; Carraway, E.R. (2000) Cyclodextrin-enhanced electrokinetic removal of phenanthrene from a model clay soil. *Environ. Sci. Technol.*, 34: 1535.
22. Reddy, K.R.; Chinthamreddy, S. (1999) Electrokinetic remediation of heavy-contaminated soils under reducing environments. *Waste Manage.*, 19: 269.
23. Reddy, K.R.; Chinthamreddy, S. (2003) Effects of initial form of chromium on electrokinetic remediation in clays. *Adv. Environ. Res.*, 7: 353.
24. Reddy, K.R.; Parupudi, U.S. (1997) Removal of chromium, nickel and cadmium from clays by in-situ electrokinetic remediation. *J. Soil Contam.*, 6 (4): 3917.
25. Rhoades, J.D.; Manteghi, N.A.; Shouse, P.J.; Alves, W.J. (1989) Soil electrical conductivity and soil salinity: New formulations and calibrations. *Soil Sci. Soc. Am. J.*, 53: 433.