

Effect of Alternative Electrolytes on Enhanced Electrokinetic Remediation of Hexavalent Chromium in Clayey Soil

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ABSTRACT: Hexavalent chromium is mobile and hazardous in the environment. Electrokinetic remediation of chromium (IV)-contaminated soils is intended either to remove or to reduce Cr (VI) to Cr (III). This study examines the effectiveness of utilizing EDTA and acetic acid solutions as alternative electrolytes in the electrokinetic (EK) process, with coupled nano-scale zero-valent iron (nZVI) as a barrier for the remediation of Cr (VI)-contaminated clay. An nZVI barrier was installed adjacent to the anode, and different electrolyte solutions (0.1 M EDTA and 1 M acetic acid) were used to investigate the effect of both on the electrokinetic remediation efficiency. Soil was contaminated to 300 ppm of Cr (IV), and a constant DC voltage gradient of 1 V/cm was applied to the soil sample for 72 h. It was found that an nZVI permeable reactive barrier (PRB) could improve the Cr (VI) remediation efficiency and reduce electrical energy consumption. Results also showed that acetic acid as electrolyte promoted the reduction of Cr (VI) to Cr (III), while EDTA application as electrolyte led to more chromium removal and reduction than an EK-nZVI barrier.

Key words: Chromium, Electrokinetic, Remediation, NZVI, EDTA, Acetic acid

INTRODUCTION

Industrial development has imposed lots of xenobiotics to the environment within recent decades (Lopez-Pineiro *et al.*, 2012; Miletic *et al.*, 2012; Krika *et al.*, 2012; Motesharezadeh and Savaghebi, 2012; Ghaderi *et al.*, 2012; Mesci and Elevli, 2012; Smaranda *et al.*, 2011; Rameshraj and Suresh, 2011; Young and Park, 2011; Oluseyi *et al.*, 2011; Dekhil *et al.*, 2011; Ajibola and Ladipo, 2011; Rafati *et al.*, 2011; Gousterova *et al.*, 2011). Cr-compounds containing chemical compounds are widely used in different industrial sectors (e.g. in electroplating, tanneries, and chemical industries) (Singh and Singh, 2012). Cr (VI)-contaminated soil mainly results from improper disposal of industrial wastes (Sawada *et al.* 2004). Hexavalent chromium is mostly present in hydrochromate anions such as HCrO_4^- , $\text{Cr}_2\text{O}_7^{2-}$ and CrO_4^{2-} , whereas Cr (III) is found as anionic, cationic and molecular forms such as $\text{Cr}(\text{OH})^{+2}$, $\text{Cr}(\text{OH})_2^+$, $\text{Cr}(\text{OH})_3$, $\text{Cr}(\text{OH})_4^-$ and $\text{Cr}(\text{OH})_5^{2-}$ (Virkyte *et al.*, 2002). Chromium (III) has low toxicity due to poor membrane permeability, while Cr (VI) is highly toxic due to strong

oxidation characteristics and ready membrane permeability. Cr (VI) is also known to be carcinogenic and mutagenic to living organisms (Weng *et al.*, 2007). On the other hand Cr (III) has lower toxicity. Remediation of fine-grain contaminated soil often tends to be inefficient based on conventional methods like soil washing and flushing (Tampouris *et al.*, 2001). Since the 1980s, extensive industrial experience with soil washing showed that its applicability is limited to soils containing less than 25% fine particles (Rulkens *et al.*, 1998). Electrokinetic remediation is an *in situ* method which can be used to treat fine soils and soils with variable charge minerals like kaolinite contaminated with heavy metals and/or polar organic materials (Li & Li, 2000). Electrokinetic processes involve an electric field in a soil matrix produced by applying a direct current between electrodes. As a result of the electrical gradient, contaminant ions or molecules are mobilized and migrate through the soil toward electrodes by three main mechanisms: electromigration, electro-osmosis and electrophoresis

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(Wang *et al.*, 2006). In Chromium EK remediation, Cr (VI) ions migrate toward the anode, while Cr (III) ions primarily travel towards the cathode. Because of geochemical differences of the Cr ion species, they behave differently in the soil matrix; while Cr (VI) adsorption onto soil particles with higher pH is negligible, Cr (III) ions mostly adsorb and/or precipitate onto high-pH particles (Reddy & Chinthamreddy, 2003). The advantages of the EK process in fine soils remediation have led to many studies being performed in order to enhance the efficiency of the process for remediation of various contaminants (e.g. Cr, Pb, Cd, Cu, Mn and Ni) (Li & Li, 2000; Acar & Alshwabkeh, 1993; Reddy & Chinthamreddy, 2001; Reddy & Chinthamreddy, 1999; Sah & Chen, 1998). One such enhancement involves integration of EK with other methods of subsurface environment remediation like permeable reactive barriers (PRBs). This concept was first studied at the University of Waterloo, with the first pilot-scale PRB installed in Ontario in 1991 (Bronstein, 2005).

Although the method is mostly applied for groundwater remediation and contaminant plume treatment, a few studies have been reported on simultaneous application of PRBs and EK to enhance soil remediation efficiencies. Chung and Lee (2007) reported satisfactory results of EK-PRB to remediate cadmium-contaminated clayey soil based on laboratory experiments. They achieved 90% removal efficiency for Cadmium and TCE using atomizing slag as PRB. Saeedi *et al.* (2009) studied the application of an activated carbon barrier in an EK process to remove Ni from contaminated kaolinite. They were able to achieve Ni migration efficiency of 50% in high-pH kaolinite soil. Weng *et al.* (2006) evaluated Cr (VI) removal from clay by EK incorporated with a ZVI barrier based on a series of laboratory-scale experiments. They applied constant electric gradient of 2 V/cm for 144 h and reported 60-70% Cr (VI) removal and 100% reduction efficiencies. Energy expenditure in such operations can be quite high. Weng *et al.* (2007) also investigated the effectiveness of ZVI into electrokinetic (EK) to remediate hyper-Cr(VI)-contaminated clay (2,497 mg/kg). They reported that the efficiency of reduction increased from 68.2 to 85.8% for a 1 V/cm gradient. The costs for energy and ZVI in this process were US\$ 41.0 and 57.5 per m³ for the system.

Application of nano-scale zero valent iron (nZVI) as PRB has also been reported to enhance EK remediation of chromium contaminated clay (Shariatmadari *et al.*, 2009). Applying a voltage gradient of 2 V/cm for 24 h helped to provide 88% Cr(VI) reduction and 19% removal sufficiency, with a total (energy and nZVI) cost of 250.5 US\$ per m³ of

remediated soil. The previous studies indicate that although great reduction and removal efficiencies of Cr(VI) from clay soil can be achieved, these require high electric gradients, energy expenditures and costly barrier materials. Application of chelate agents or pH conditioning of electrolytes has also been reported to enhance the EK process for metals and remediation of other pollutants during laboratory scale investigations (Popov *et al.*, 2001; Giannis & Gidarakos, 2005; Gidarakos & Giannis, 2006). Popov *et al.* (2001) used 1-hydroxyethane-1,1-diphosphonic acid in electro-osmotic flow of EK to remove 80-90% phenol from soil. Giannis & Gidarakos (2005) found that application of citric acid, nitric acid and EDTA as electrolytes could give about 85% cadmium removal from real contaminated soil. It has also been reported (Reddy & Chinthamreddy, 2003) that use of some purging solutions in catholyte during EK can enhance remediation of metals for clayey soils with low buffering capacity.

As mentioned above, PRB technology and purging solutions as electrokinetic enhancements have been examined separately in previous studies showing significant improvements in removal/reduction efficiencies. However, such efficiencies have required strong electric fields and long remediation periods (up to 144 h), implying high treatment costs. Application of nano-scale zero valent iron PRB with alternative electrolytes to remediate Cr (VI) in soil has not yet been studied.

In the present study, EK-nZVI-PRB technology combined with purging solutions is examined for the first time as a possible means of remediating Cr (VI) contaminated clay. To enhance EK-nZVI-PRB technology, two purging solutions, 1 M acetic acid and 0.1 M EDTA, are also evaluated as alternative catholytes.

MATERIALS & METHODS

All chemicals and reagents that were used in experiments were analytical grades made by MERCK Company. Marand kaolinite clay (from Marand clay company, Tabriz, Azerbaijan, Iran) was used as the prototype soil matrix for the tests. Major characteristics of this kaolinite are presented in Table 1 based on information provided by the Marand Clay Company. Each soil matrix was prepared by adding the appropriate amounts of dissolved K₂Cr₂O₇ solution to 2 kg of soil and agitating the mixture for two days to give an initial concentration of 300 ppm Cr (VI). Preliminary analyses on the prepared soil showed that the liquid limit of the soil was about 39%. The moisture content of the soil samples was kept at 40±1% to maintain its saturation state. Preliminary analyses also

revealed that the background chromium content of the soil was about 10 mg kg⁻¹.

Table 1. Characteristics of the used kaolinite in the tests

Chemical composition (%)	L.O.I ¹	9.18
	SiO ₂	36.2
	Al ₂ O ₃	24.68
	Fe ₂ O ₃	0.5-0.65
	CaO	1.24
	MgO	0.29
	TiO ₂	0.04
	Na ₂ O	0.4
	K ₂ O	0.57
	Se ₂ O ₃	0.59
	P ₂ O ₅	0.09
SO ₃	0.07	
Sr	0.05	
Mineralogy (%)	Kaolinite	60
	Quartz	31
	Calcite	2.7
	others	6.3
Atterberg Limit	Liquid limit	39
	Plastic limit	32.2
	Plastic index	9.4
Particle size distribution (%)	<32µm	100%
	<20µm	98%
	<2µm	40%

1. Loss On Ignition

To prevent entrapment of air bubbles within the soil matrix which could affect the EK process, contaminated soil was gradually loaded and compacted to ensure venting of air from the system at each loading step. All tools, glassware and containers were thoroughly rinsed and decontaminated prior to each test to prevent cross-contamination.

The reactive barrier was composed of Ottawa sand (ASTM C778) and nano-scale zero valent iron from Lehigh NanoTech LLC (Bethlehem, PA) with typically more than 92% particles finer than 100 nm, an average diameter of 60 nm and average specific surface area of 14.5 m² g⁻¹ (Sun *et al.*, 2006). A scanning electron microscope (SEM-XL30 Philips) provided photomicrographs of nano particles and precipitates in the nZVI barrier after each test, one of which is shown in Fig. 1.

A reactive barrier of Ottawa sand and nZVI with a thickness of 5 mm and an nZVI-to-sand ratio of 1/15 was installed 30 mm from the anode.

Laboratory-scale electrokinetic experiments were conducted in a rectangular 300×120×100 mm Plexiglas container of inner length 150 mm (Fig. 2). Reservoirs were connected to the chambers to maintain the water level and avoid hydraulic gradients which could affect the electro-osmotic flow. Electro-osmosis (EO) causes water to migrate from the anode to the cathode compartment. In this study, the volumetric electro-osmosis flow was measured at different times to determine EO variations. The EO permeability can be calculated (Haran *et al.*, 1997) as:

$$K_e = Q_e / i.A \quad (1)$$

where Q_e is the volume of electro-osmotic flow, i is the electrical gradient and A is the cross-sectional area of the soil sample.

All tests were conducted using perforated stainless steel electrodes (A316) of dimensions 100 x 120 x 6 mm. To avoid corrosion effects on the results, new electrodes were used for each test. A direct current power supply with capacity 30 v and 2 A was used for the experiments. In total, six tests were performed, with details of the experimental condition presented in Table 2. Because of the acidic conditions nearby the anode electrode ideal for Cr (VI) reduction and preliminary laboratory assessments which confirmed earlier

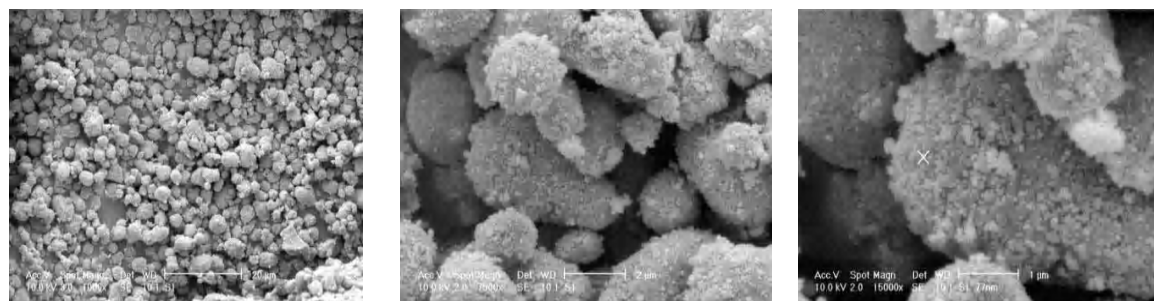


Fig. 1. SEM image of iron nano particles used in the study (1000x, 7500x and 15000x)

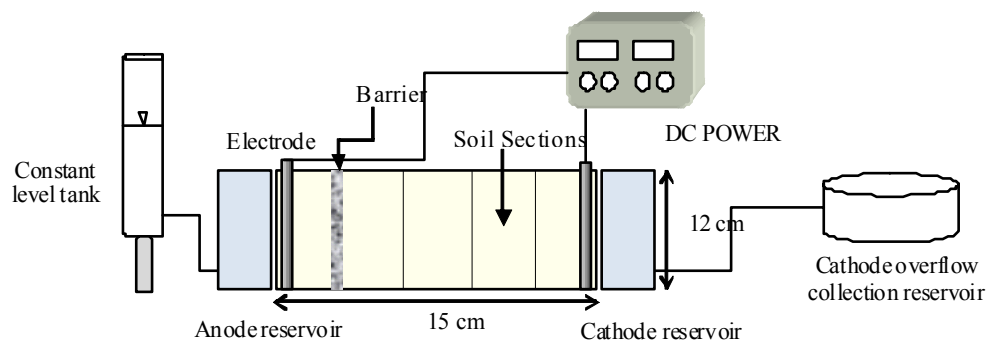


Fig. 2. Schematics of EK experimental setup

research Shariatmadari *et al.*, 2009), the barrier was placed 30 mm from the anode for the tests conducted using PRB. Better efficiencies with the barrier next to the anode have also been reported previously (Shariatmadari *et al.*, 2009) in an EK-PRB system used to remediate chromium.

In test number 2, 1 M acetic acid was used instead of water as Catholyte, whereas 0.1 M EDTA was the catholyte solution for tests 3 and 6. The duration of each test was 72 h with an electrical gradient of 1 V/cm. At the end of each test, the soil sample was removed from the cell and divided into five equal sections longitudinally to provide a length profile of chromium (VI) and III contents along the soil matrix. Homogenized sub-samples from each section were taken to determine pH, moisture and Cr (VI) and Cr (III) concentrations.

For total chromium determination, soil was digested according to the EPA-3050 B method and analyzed by atomic absorption spectrometry (Buck Scientific 210VGP). Alkaline extraction of soil based on the EPA-3060A method was used to extract Cr (VI) for analysis. The concentration of Cr (VI) then was determined by spectrophotometry (HACH DR 4000). Subtracting the Cr (VI) values from the total chromium gave the Cr (III) concentration for each sub-sample.

RESULTS & DISCUSSION

With the voltage constant at 1 V/cm during all tests, the electric current variations for tests conducted with and without PRB are depicted in Figs. 3a and 3b. It is seen that the current reduction in the earlier hours of the tests (first 30 hours) is greater than later during the tests. With time, the electrical current seems to approach more stable levels. Reduction of electrical current through soil during the tests relates to increasing resistance of the soil matrix electrical due to precipitation of ions as insoluble products, particularly next to the electrodes. A similar trend was observed by Weng *et al.* (2007). The electrical current through the soil indicates ionic migration towards oppositely charged electrodes being reduced during the tests due to precipitation of reaction products raising the soil resistivity (Reddy & Chinthamreddy, 2003). Zhou *et al.* (2005) indicated that solutions such as EDTA could increase the current through the soil. The soil electrical resistivity could be decreased by preventing reaction product precipitation by formation of soluble EDTA-metal complexes in the system. Reddy & Chinthamreddy (2003) also indicated that dissociation of some compounds such as acetic acid may increase the soil electrical conductivity during the tests. Our results for tests 2, 3, 5 and 6 confirm that both EDTA and acetic acid had positive enhanced electrical current

Table 2. Details on the conditions of experimental program

Test Number	Chromium primary conc. (mg kg ⁻¹ soil)	Test duration (hr)	Catholyte	Anolyte	Barrier	Electric gradient (v cm ⁻¹)
1	300	72	Distilled water	Distilled water	N/A	1
2	300	72	1 M acetic acid	Distilled water	N/A	1
3	300	72	0.1 M EDTA	Distilled water	N/A	1
4	300	72	Distilled water	Distilled water	YES	1
5	300	72	1 M acetic acid	Distilled water	YES	1
6	300	72	0.1 M EDTA	Distilled water	YES	1

through the soil, with potential positive impacts on migration of contaminants through the soil matrix. On the other hand, as it is obvious that the electrical current through soil for the tests with PRB was lower than without a barrier (Fig. 3b). Among ionic species, those whose hydroxides would precipitate within the soil matrix and hinder electric current are Fe (III), Cr (III), Ca (II) and Mg (II). In addition to the soil matrix, $\text{Fe}(\text{OH})_3$, $\text{Cr}(\text{OH})_3$ and $\text{Cr}_x\text{Fe}_{1-x}(\text{OH})_3$ are precipitates among the reaction products occurring in the nZVI barrier that would raise the resistance against electric current (Weng *et al.*, 2007). That is the main reason for the different electric current profile through soil in tests with and without nZVI-PRB.

Due to the DC voltage applied between the electrodes, OH^- and H^+ ions were generated in the catholyte and anolyte compartments, respectively, resulting in pH variation in the reservoirs. In tests 1 and 4, in which water was used as electrolyte, generation of H^+ ions resulted in decreasing the pH in the anode reservoir to reach a value of about 2.5-3, while the catholyte pH increased to 12.5 at the end of the experiments due to production of OH^- ions. This phenomenon was reported by Acar & Alshawabkeh (1993) under similar conditions without enhancement. Acetic acid as a catholyte in tests 2 and 5 dissociated, so that the H^+ ions decreased the pH of the catholyte to the 3 to 5 range. EDTA also decreased the catholyte pH in the earlier stages of experiments 3 and 6. The H^+ ions produced by dissociation of EDTA partially depolarized hydroxyl ions in the catholyte, with the pH increasing over time to 12.5. Figs 4(a) and 4(b) show the variation of pH during these tests. The results reveal that installation of nZVI barrier did not affect the pH variation very much. It seems that the pH values of reservoirs are mostly dependent upon the electrolyte, initial pH and the electrolysis itself.

Figs 4(c) and 4(d) shows the soil pH profile at the end of the tests. The results indicate a general trend in soil pH distribution. The base front moves toward the anode, whereas the acid front propagates in the opposite direction, resulting in low pH adjacent to the anode and high soil pH near the cathode relative to the initial conditions (dashed line). Propagation of the base front from the cathode was limited in tests 2 and 5 where acetic acid was used as the catholyte. Hence, the soil pH did not tend to rise and maintained a pH close to its initial value. The negatively charged EDTA ions move toward the anode and complex with H^+ and other positively charged metal ions. This phenomenon not only aids metal solution in the soil, but it also increases the soil pH (Reddy & Chinthamreddy, 2003). The pH profile for EDTA-enhanced tests was similar to those seen in without enhancement, as shown in Figs 4(c) and 4(d).

As shown in Fig. 5, the EO permeability increased at the beginning of the test and then decreased gradually after reaching a maximum value. Figure 5 also plots the accumulative variation of electro-osmotic flow in each test. EDTA as catholyte noticeably increased the accumulative volume of EO flow, reflecting an increase in Cr removal. The increase in EO flow induced by chelating agents like EDTA is due to interaction of these complexants with the soil surface. Popov *et al.* (1999) demonstrated that these agents can affect the EO flow by increasing the negative charge on the soil particles and replacing multivalent ions by univalent ones which are less effective in diffuse layer compression. Electro-osmotic flow measurements for tests in which acetic acid was used did not show any significant difference in volume of EO flow compared with conditions without enhancement, although the data revealed some

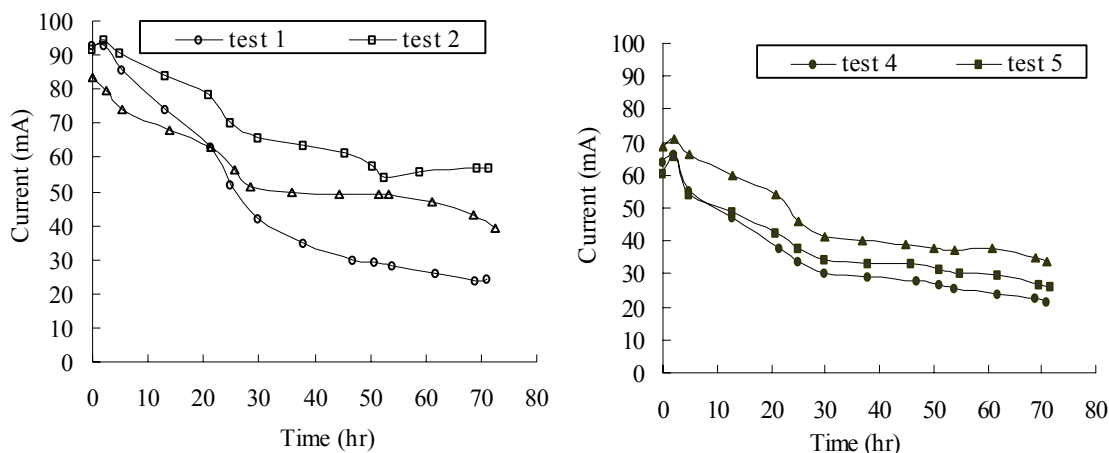


Fig. 3. Current variation of (a) EK Tests without PRB and (b) EK/PRB Tests

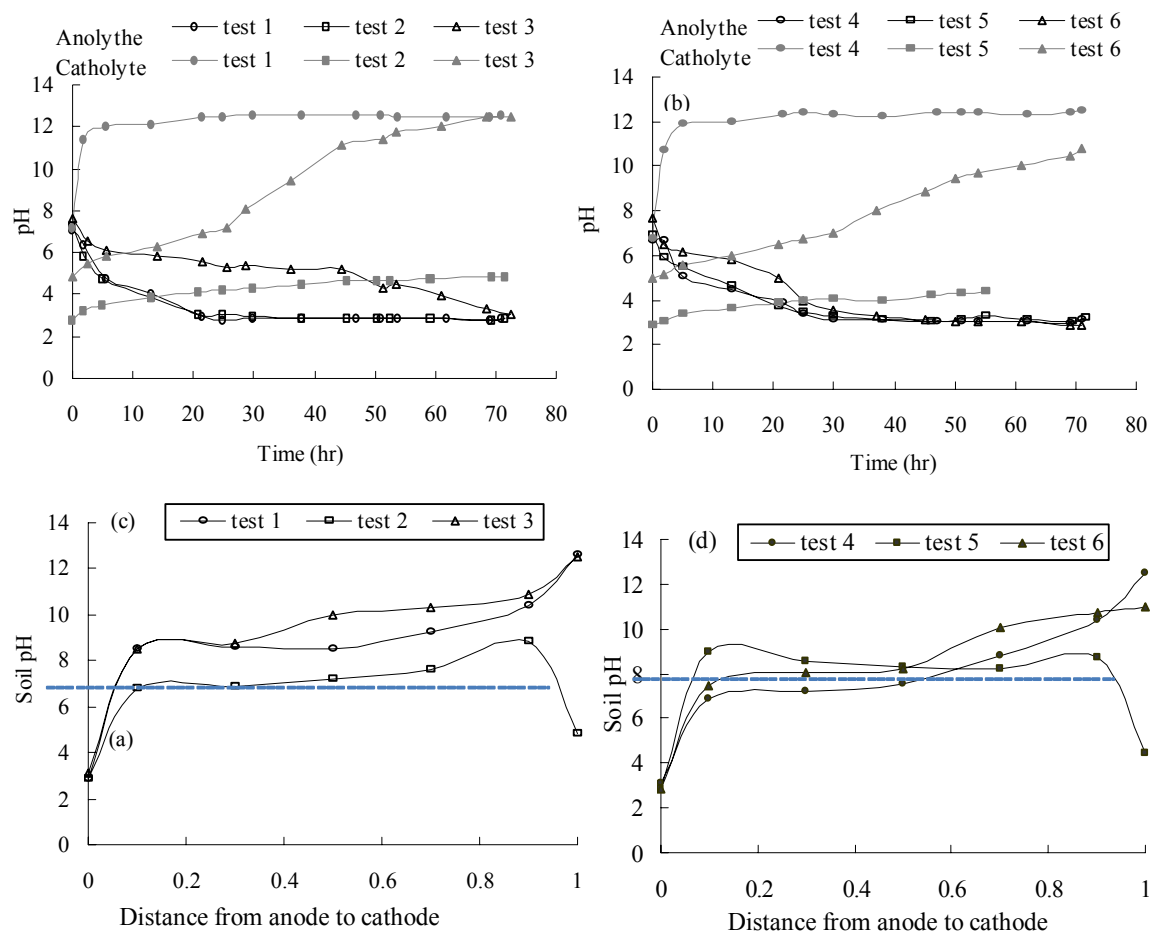


Fig. 4. pH variation of reservoirs in (a) EK Tests without PRB and (b) EK/PRB Tests and pH profile in soil after Experiment in (c) EK Tests without PRB and (d) EK/PRB Tests

variation in K_c values. In general, by comparing the results of tests with and without an nZVI barrier, it can be inferred that addition of a barrier decreased the maximum value of K_c and also the accumulative volume of EO flow. In other words, installing the permeable reactive wall resulted in producing Fe (III) and Cr (III) adjacent the wall. By increasing the metal precipitation, the current intensity and, consequently, the EO flow volume decrease. This resulted in less chromium mobilization through the soil.

Fig. 6 shows the distribution of both Cr (III) and Cr (VI) in soil for all tests. Results of test no.1 (no enhancement) show that most Cr near the anode is in the form of Cr(VI), whereas most of the soil chromium content near the cathode is in the form of Cr(III). Distribution profiles of Cr (III) and Cr (VI) along the soil matrix in this case were in agreement with the results reported by Weng et al. (2007). The main reason for Cr (VI) reduction to Cr (III) under electrokinetic conditions in the soil, as mentioned by Reddy & Parupudi (1997),

may be the presence of sulfides, organic matter and Fe (II) complexes in the soil media.

Acetic acid is biodegradable and its low concentration (e.g. 1 M) is often adequate to reduce soil pH (Ugaz *et al.*, 1994). In addition, it is a weak acid, unable to highly dissociate; hence addition of acetic acid to soil will not result in a major increase in soil electrical conductivity (Reddy & Chinthamreddy, 2003). Thus, 1 M acetic acid was used as the catholyte in test 2. At the end of this test, the Cr (VI) content in soil near the anode electrode was higher than in other parts of the soil, with a similar pattern to the results of test1 (basic test). On the other hand, in the other parts of the soil matrix, the distribution of these two forms of chromium was relatively uniform, i.e. there was no significant longitudinal profile for either Cr (III) or for the Cr (VI) fractions of total chromium.

The addition of acetic acid, limiting base front propagation (Fig. 4c) from the cathode, seems to be responsible for the uniform distribution of the two

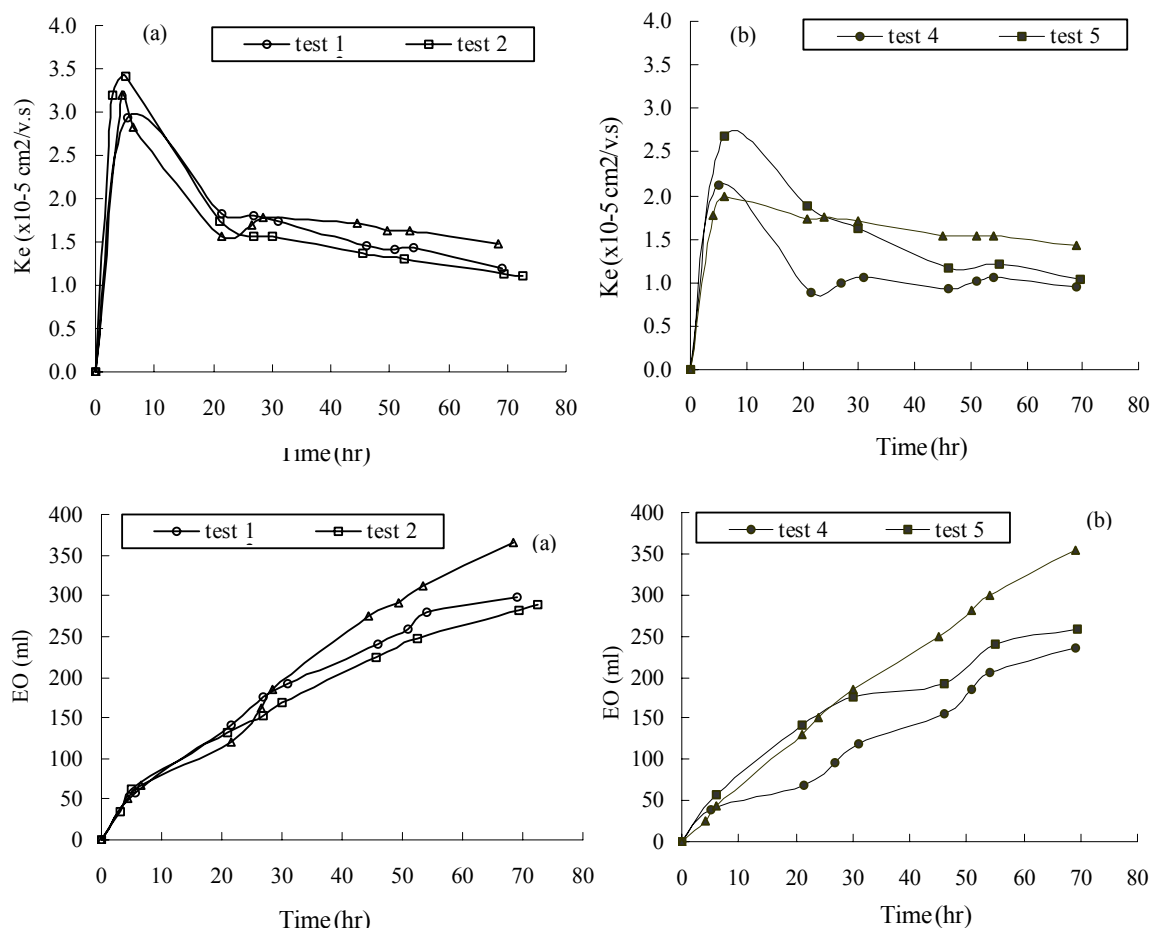


Fig. 5. EO permeability variation and accumulative EO flow vs. time in (a) EK Tests without PRB and (b) EK/PRB Tests

forms of chromium. Results also showed that application of 1 M acetic acid as catholyte raised the reduction of Cr (VI) to Cr (III) by about 10% relative to basic test conditions. However note that this would lead to less Cr removal from the soil. Enhancement of the process by introducing the nZVI barrier into the soil and acetic acid 1 M as catholyte (test no.5) led to an overall reduction of 72%, but placement of the barrier seems to have reduced overall chromium removal from the soil due to reduced electro-osmotic flow. Comparison of all three tests with placement of nZVI barrier with those without barrier Cr (III) ions shows that precipitation takes place around the barrier, reducing the overall removal efficiency. This was reported also by Shariatmadari et al. (2009).

Ethylene diamine tetra acetic Acid (EDTA), a strong chelating agent, is a hexadentate ligand that can interact with metal cations at six different positions. EDTA forms stable and soluble complexes with heavy metals (Reddy & Chinthamreddy, 2003). One of its advantages compared with acids is that EDTA has less effect on

soil properties. It can remove metals without creating a strong acidic environment in the soil. In alkaline environments, EDTA could effectively complex with metals resulting in more mobilization of metals throughout the soil and increase removal efficiency as a result of the EK remediation process (Saeedi & Khataei, 2011; Lindsay, 1979). In some previous studies, EDTA has been used to enhance the removal efficiency of the EK process to remediate lead, zinc and other metals (Reed *et al.*, 1995; Yeung *et al.*, 1996). In the case of chromium remediation, Reddy & Chinthamreddy (2003) showed that EDTA enhanced removal efficiency in high buffering and clayey soils. EDTA, in this case, is helps to form complexes and hence to mobilize Cr (III) ions. Mobilization of Cr (VI) from the soil toward the anode takes place as an indirect effect of EDTA, which makes complexes with H^+ ions or adsorbs onto soil particle surfaces, facilitating release of Cr (VI) from soil and mobilization toward the anode via electro-osmotic flow (Reddy & Chinthamreddy, 2003). Results of test 3 (0.1 M EDTA as catholyte) demonstrate removal of more than 31% of chromium from the soil, the highest value

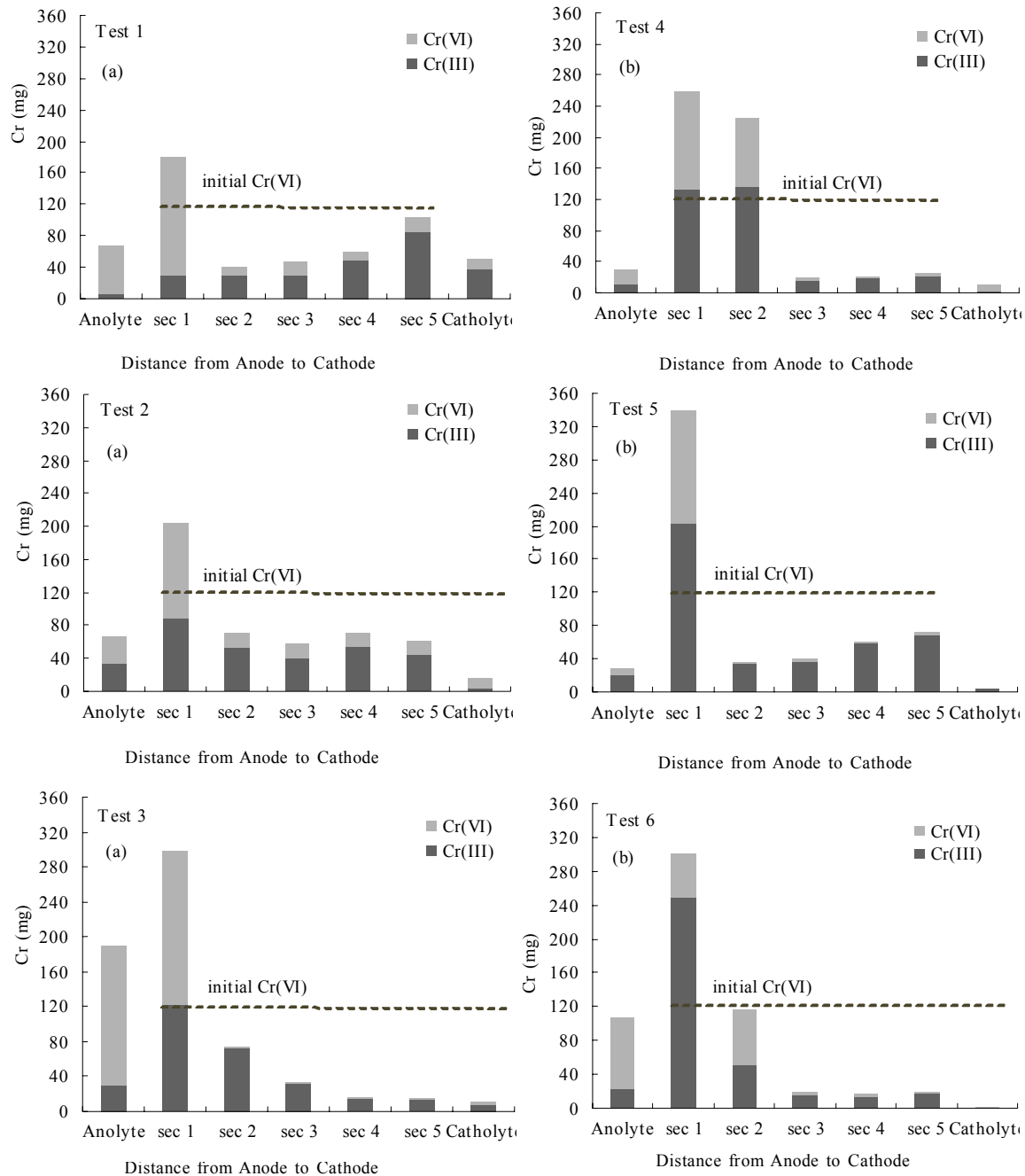


Fig. 6. Chromium distribution in soil and reservoirs after (a) EK treatment without PRB and (b) EK/PRB Tests

among all tests. This shows the positive effect of EDTA in enhancing chromium removal by the EK process. For test 6 (0.1 M EDTA as catholyte and nZVI barrier), chromium removal decreased by about 12.5% but reduction of Cr (VI) to Cr (III) increased from 46% to about 63%.

Organic compounds in the soil matrix could retard chromium migration and removal (Akretche, 2002).

Hence, the relatively high organic content of the soil studied (9.18 % L.O.I) may be responsible for the lower increase in chromium removal compared with related previous reports in the literature. For better evaluation and comparison of the effectiveness of each test, Table 3 summarizes the results of all six tests, including power consumption, energy consumption, barrier and total cost. Fig 7 shows SEM images after completion of the experiments of the barriers installed in tests 5 and 6.

The energy requirement ($W.h/m^3$), defined per unit volume of soil, can be estimated (Hamed *et al.*, 1991) from:

$$E_u = \frac{1}{V_s} \int VI dt$$

Where V_s is volume of the soil sample (m^3); I is the current intensity (A) and V is the applied voltage difference (V). Table 3 summarizes the total energy consumption of each test. As this table shows, the maximum electrical energy consumption corresponded to test 2 (where acetic acid was used as catholyte with no barrier installed), while the minimum was in test 4 (distilled water as electrolyte, with an nZVI barrier). By comparing the power consumption in tests with and without a barrier, it can be concluded that the permeable reactive barrier may be responsible for a considerable decrease in energy consumption, regardless of its effect on chromium reduction and removal. Apparently, the barriers resulted in an increase in the soil matrix

electrical resistance due to precipitation of ions, particularly next to the barrier, causing a decrease in the current through the soil sample. Choosing the best enhancement method not only depends on the percentage of reduction/removal that can be obtained, but also on economic considerations. Note that the economic analysis of tests in this study only includes energy expenditures and nZVI costs. For contaminated sites, other expenditures may be significant. Overall, comparison of the results of tests 4, 5 and 6 reveals (Table 3) that application of 1 M acetic acid in the cathode chamber of EK-nZVI barrier test (test 4) led to about 16% more Cr (VI) reduction, while 0.1 M EDTA as catholyte in the EK-nZVI barrier test (test 4) resulted in 7% more chromium reduction and 12% more removal. Table 4 provides technical and economic comparisons among published studies on Cr(VI) remediation from clayey soils by EK coupled with ZVI/nZVI. As indicated in Table 4, Cr (VI) removal and reduction efficiencies of previous studies were better than in this study. However, it is important to point out that in all three

Table 3. Summarized results of all experiments

Test	Reduction (%)	Removal (%)	Power consumption (kwh m^{-3})	Energy expenditure (US\$ m^{-3}) ¹	Barrier cost (US\$ m^{-3} of soil) ²	Total cost(US\$ m^{-3})	Mass balance error (%)
1	48.75	21.77	32.32	2.47	0	2.47	-8.1
2	58.09	15.14	50.9	3.89	0	3.89	-8.4
3	45.97	31.41	42.83	3.27	0	3.27	6
4	56.86	6.98	22.34	1.71	26.7	28.41	-1.2
5	72.75	5.65	23.98	1.83	26.7	28.53	-3.2
6	63.75	18.9	35.04	2.68	26.7	29.38	-3.2

¹ considering the electricity fee in Iran which is estimated approximately US\$ 0.0707 per kwh

² Only the n-ZVI cost (20 US\$ /kg) was considered regardless of other expenditures such as barrier construction and maintenance

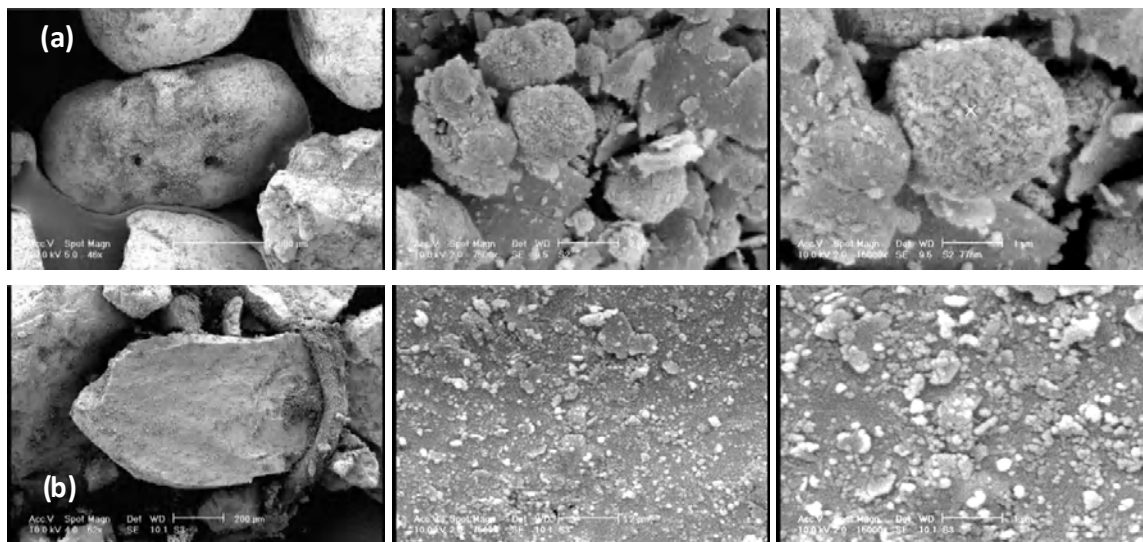


Fig. 7. SEM image of installed barriers in (a) test 5 (b) test 6 (1000x, 7500x and 15000x)

Table 4. Technical and economic comparison among different works using EK-PRBs to remediate Cr(VI)

Study	Initial Cr (VI) in soil (mg kg ⁻¹)	Barrier position	Electrolytes	Soil organic matter (L.O.I) (%)	Electric Gradient (V cm ⁻¹)	Processing Time (hr)	Fe/Sand Ratio (g g ⁻¹)	Total Cr removal (%)	Cr (VI) Reduction Efficiency (%)	Power Expenditure (kWh m ⁻³)	Barrier cost (US\$ m ⁻³)	Total cost (US\$ m ⁻³)
Present study	300	3 cm away from anode (nzvi)	Water	9	1	72	1/15	6.98	56.86	22.34	26.7	28.41
Present study	300	3 cm away from anode (nzvi)	Anolyte; water Catholyte; 0.1 M EDTA	9	1	72	1/15	19	63.75	35.04	26.7	28.53
Present study	300	3 cm away from anode (nzvi)	Anolyte; water Catholyte; 1 M acetic acid	9	1	72	1/15	5.65	72.75	23.98	26.7	29.38
Weng et al. 2007	2497	Middle (zvi)	water	1.79	2	6	5/5	42	92.5	706	15.1	57.5
Weng et al. 2006	1150	Middle (zvi)	water	1.79	2	144	2.5/2.5	71	100	Not provided	Not provided	Not provided
Shariatmadari et al. 2009	100	2 cm away from anode (nzvi)	water	0	2	24	1/2.5	42	89	24.5	248.8	250.47

previous studies higher electric gradient and much higher amounts of ZVI/nZVI were needed to achieve such efficiencies. Except for Weng et al. (2007), the other researchers also used longer processing times. All of these factors (i.e. high ZVI/nZVI amount, longer processing time and higher electrical gradients) clearly resulted in much higher power consumption, barrier costs and total costs of the remediation process.

While the positive effects of EDTA and acetic acid on the enhancement of EK-nZVI remediation of chromium from soil were disclosed in this study, further investigations on the application of these enhancements to the EK- nZVI process may lead to increased overall chromium removal, which in all previous studies of this nature were less than 70%.

CONCLUSION

Experimental procedures were developed to assess the effect of combining two methods of enhancing the EK process for soil remediation. Acetic acid and EDTA were tested as catholytes, as well as installation an nZVI barrier adjacent to the anode. 1M acetic acid as a catholyte increased the reduction efficiency of Cr (VI) relative to cases where there was no enhancement. Introducing 0.1M EDTA into the cathode chamber increased the removal and reduction of chromium from soil. The data in tests with and without a barrier demonstrated that incorporation of an nZVI barrier increased the reduction potential of Cr (VI). In addition, a barrier caused a decrease in the electro-osmotic flow, current intensity and energy consumption. As EK is a complex process, study of higher applied voltage, longer test duration and barrier position in the EK-nZVI process enhanced by EDTA and acetic acid is needed to achieve higher removal efficiencies at lower costs.

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