

## Electrokinetic removal of chromium and copper from contaminated soils by lactic acid enhancement in the catholyte

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**Abstract:** The electrokinetic removal of chromium and copper from contaminated soils by adding lactic acid in cathode chamber as an enhancing reagent was evaluated. Two sets of duplicate experiments with chromium contaminated kaolinite and with a silty soil sampled from a superfund site in California of USA and polluted by Cr and Cu, were carried out in a constant current mode. Changes of soil water content and soil pH before and after the electrokinetic experiments, and variations of voltage drop and electroosmosis flow during the treatments were examined. The results indicated that Cr, spiked as Cr(VI) in the kaolinite, was accumulated mainly in the anode chamber, and some of Cr and metal hydroxides precipitated in the soil sections in contact with the cathode, which significantly increased electrical energy consumption. Treatment of the soil collected from the site showed accumulation of large amounts of Cr and Cu in the anode chamber while none was detected in the cathode one. The results suggested that the two metals either complexed with the injected lactic acid at the cathode or existed as negatively charged complex, and electromigrated toward the anode under a voltage gradient.

**Keywords:** electrokinetic remediation; metal; soil; lactic acid

### Introduction

Electrokinetic remediation is an emerging technology and has been successfully applied in remediating metal and organic polluted soils (Acar, 1993; Lageman, 1993; Probst, 1993; Chung, 1999). In the case of remediation of metal contaminated soil, some enhancing methods, such as using ion selective membranes to exclude OH<sup>-</sup> migration from cathode chamber to soil (Li, 1998), adding enhancing reagents to improve metal solubility from soil (Redd, 1995; Sah, 1998; Yang, 1998), conditioning cathode pH (Bonilla, 2000; Lee, 2000; Zhou, 2003) and applying sulfur bacteria in soil column (Miani, 2000) have been investigated and the results are usually very promising. However, the use of enhancing reagents for improving metal solubility in the field must be carefully assessed, because many of the agents might not be safe if they are applied in large quantities and possibly cause secondary environmental pollution.

Recently, more biodegradable chemical reagents are considered in remediating metal contaminated soils (Mulligan, 1997). Lactic acid is an easily degradable chemical and can be used as an enhancing reagent in chemical remediation of metal contaminated soil.

This paper examines electrokinetic removal of chromium and copper from a kaolinite and a metal contaminated soil in terms of the changes of soil water content, soil pH, electroosmosis flow and metal concentration in electrolytes. It aims to obtain basic information about metal migration

behavior in soil during electrokinetic process in the presence of lactic acid.

### 1 Materials and methods

Chromium contaminated kaolinite was artificially prepared by mixing 4 L 45 g/L Cr (prepared with Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) solution with 12 kg kaolinite thoroughly at a water content of 30%. Chromium concentration in the kaolinite was 1500 mg/kg. A chromium and copper contaminated silty soil was sampled from a superfund site, which is a waste filling field located in California. The chromium and copper concentrations in this soil were 2700 mg/kg and 2800 mg/kg, respectively.

A schematic of the electrokinetic remediation setup is presented in Fig. 1. The size of soil column is L35 cm × H17 cm × W5 cm. Two graphite plates were used as working electrodes, and were connected with a HP electric power supply. Both of the anode and cathode cell volumes were 4 L. By using a peristaltic pump, the catholyte was exchanged with a stock bottle, in which the pH was controlled by a controller. In addition, there was a stirrer in the stock bottle for continuous mixing. Two porous polyacrylic films were inserted between soil column and the anode chamber and between soil column and cathode chamber to prevent dispersion of the soil from the cell into electrode reservoirs. Four passive electrodes made of tungsten wires were installed in the soil column (and labeled 1 to 4 from anode to cathode) to measure voltage drop in the soil

column.

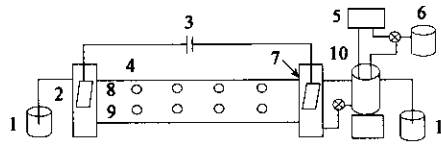


Fig. 1 Electrokinetic remediation setup

During the electrokinetic experiments, the electroosmotic flow was collected and measured periodically, and the voltage drop in the soil column between the different passive electrodes was measured periodically. Two duplicate experiments were performed with Cr polluted kaolinite (Experiment I) and Cr/Cu polluted soil (Experiment II) for 20 d and 15 d respectively. After the electrokinetic treatments, the soil column was cut into ten equal sections, and the soil water content and pH profiles were determined. The soil pH was determined by a pH meter using soil to water ratio of 1 : 2.5. Electrolytes were filtrated through a filter paper, and the metals concentrations in the electrolytes were determined by a Varian Atomic Absorption Spectrometer.

## 2 Results and discussion

Chromium exists in the environment mainly in two valences: as Cr(III) and Cr(VI). Cr(VI) is more toxic than Cr(III) and appears mainly as oxyanions with negative charges (Zhou, 2001). When a voltage is applied across soil column, Cr(VI), unlike cations of Cu(II) and Pb(II), will electromigrate toward the anode chamber.

During Experiment I, the anolyte color changed from colorless in the initial state to yellow. No color change occurred in the cathode chamber, but some white precipitation was observed. For Experiment II, the catholyte color did not change, but the anolyte color changed from colorless to green, suggesting that Cu negatively charged complexes moved from the soil column into the anode chamber.

A constant current was applied across the soil column for these two experiments. It was observed that the electric resistance of soil column increased with the treatment time resulting in a continuous increase of the voltage. However, the range of the electric power supply was limited to a max of 135 V. When the voltage exceeded the maximum capacity, the current decreased to account for the increase in electrical resistance. For Experiment I, most of the voltage drop was distributed evenly in the first 10 d and then most of the drop occurred in the soil sections covered by voltage probes No. 3 and 4. This is possibly due to the complex chemistry of Cr. Although the initial form of Cr was soluble, the pH profile during the electrokinetic process caused Cr accumulation and maybe immobilization at these locations. Lactic acid was used as an enhancing reagent for adjusting the catholyte pH, which neutralized the released OH<sup>-</sup> from electrochemical reactions

at the cathode, and complexed with metal ions to enhance their solubility in the soil column. Approximately 40 ml per day of lactic acid solution (0.6 mol/L) was supplied into the cathode chamber by a pump, which was controlled by a pH controller. The experimental results exhibited that the pH in the catholyte was well kept at 6.0 with a variation range of  $\pm 0.2$ .

### 2.1 Soil water content and soil pH

The final water content varied across the soil, as shown in Fig. 2. A minimum value measured at midsection of the soil (sections 6 and 7), which indicates physical or chemical changes in this region. The sides of the sample are in direct contact with the electrolyte resulting in dispersed, higher water content regions. At the same time, Alshawabkeh *et al.* (Alshawabkeh, 2004) showed that injection of organic acids at the cathode may result in a positive pore water pressure, swelling and accordingly an increase in the soil water content (compared to the initial value of 30%).

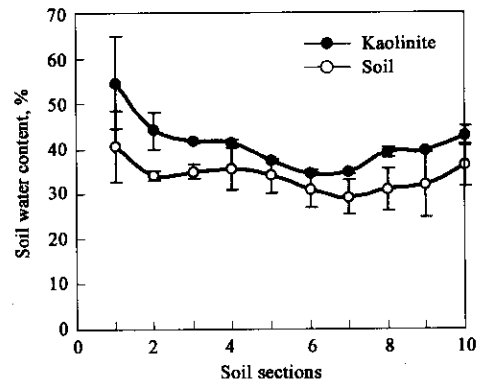


Fig. 2 Change of water content in the kaolinite and the soil after electrokinetic treatments

Fig. 3 shows the change of soil pH in the soil samples after the treatments. In the case of remediating the Cr contaminated kaolinite, the soil pH in the soil sections near the anode was less than that close to the cathode, due to electrochemical acidification at the anode. Meanwhile, the pH value was far less than the initial value at pH 7.25, which is expected due to the low pH buffering capacity of

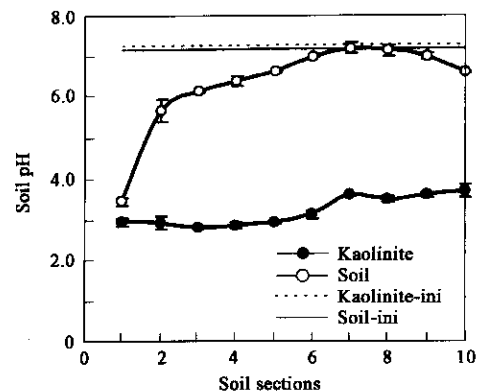


Fig. 3 Change of soil pH in the kaolinite and the soil after electrokinetic treatments

kaolinite. For Experiment II, the soil pH showed a similar increasing trend from the anode to the cathode. However, after midsections the soil pH decreased towards the cathode due to injection of lactic acid at the cathode. The soil pH across the sample was less than the initial soil pH, indicating the success of catholyte pH control system.

## 2.2 Voltage drop and electroosmosis flow volume

Fig. 4 shows the variation of the voltage potential across the soil sample with treatment time at a constant current. A similar tendency of an increase in the voltage potential across the sample was observed in all experiments, indicating an increase in sample resistance, i. e. a decrease in the soil ionic content or electrolytes strength. Contaminants extraction, pH profile and minerals precipitation contributed to the increase in electrical resistance.

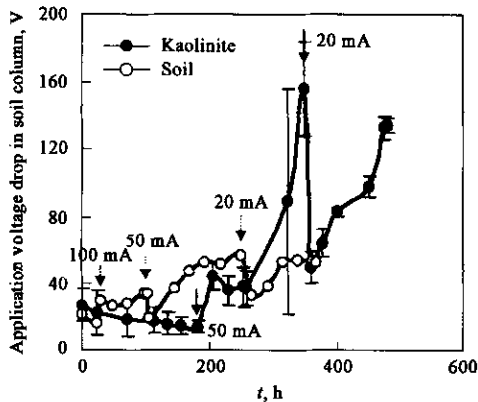


Fig. 4 Dependence of voltage drop in soil column on treatment time at a constant current mode

The voltage drop across the acrylic membrane that separates the soil and electrolytes was significant, thus increasing energy expenditure and decreasing the electroosmotic efficiency. This effect should be further assessed and innovative methods should be evaluated to minimize this effect. The easiest possible solution is frequent replacement the electrolytes. Accumulated electroosmotic flow volume increased with time in both sets of experiments, as shown in Fig. 5.

The first 10 d of treatment showed that the total flow was smaller in kaolinite than the silty soil. After that, significant flow continued to occur in the kaolinite specimen and the total flow was then more than that from the silty sample. The kaolinite sample was prepared by compacting the soil in cell, while the silty soil was maintained as a slurry without any compaction. The initial compacted condition of kaolinite may have resulted in a delay of the electroosmotic flow, which was significant after few days of current application. On the other hand, the silty soil had a higher initial electric conductivity and ionic content, resulting in a smaller diffuse double layer and less electroosmotic flow than kaolinite. A combination of the two factors resulted in higher electroosmosis in the silt at early stages, but higher total flow

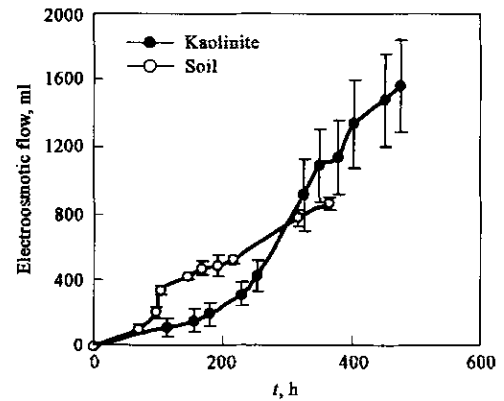


Fig. 5 Dependence of electroosmosis flow in soil column on time at a constant current mode

in the kaolinite at the end of testing.

It should be noted that the anode chamber color changed to green in the experimental set II (silty soil), which can be attributed to the migration of negatively charged organic complexes of copper.

## 2.3 Chromium and Cu concentration in electrolytes

Fig. 6 shows the change of Cr and Cu concentrations in the anolytes with time. In Experiment I, the final Cr concentrations in anode reservoir and cathode reservoir after the electrokinetic treatments were about 100 ppm and only several ppm, respectively. Based on Cr concentration in the electrolytes, only 500 mg, or 7% of total Cr, was removed from the kaolinite and most of Cr seems to be in the soil column after the electroremediation.

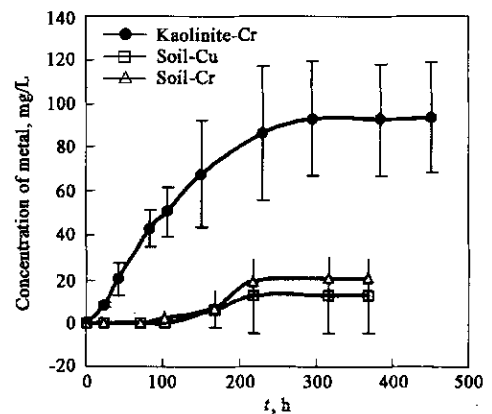


Fig. 6 Change of metal concentration in the anolytes on treatment time for the experiments I and II, respectively

Reddy and Chinthamreddy (Reddy, 2003) studied the effects of initial forms of chromium on electrokinetics remediation in clays. The results showed that chromium migration was the highest when it was present in kaolin in the Cr(III) form. When Cr(III) was present, migration occurred towards the cathode as Cr(III) cation and/or cationic hydroxide complexes. However, when chromium was present in Cr(VI) form, the migration occurred towards the anode, due to the existence of Cr(VI) soluble oxyanions, but the removal percentage of Cr was not high.

In Experiment II, Cr and Cu concentrations in the anolyte increased with the treatment time. High metal release rate was detected in the period of 7th—9th day. Average maximum Cu and Cr concentration from the replicate experiments reached to 12.25 and 20.18 mg/L, respectively, in the anolyte reservoir. The metal was not detected in the cathode chamber. Due to the higher concentration of metal in the initial soil column and the lower amounts determined in the electrolytes after electrokinetic treatments compared with the Experiment I, the removal percent of Cr and Cu was less than 5% for the experiment II.

As shown in Fig. 5, Cr and Cu concentrations in the anode chamber did not change after the 10th day of treatment, although the electroosmotic flow was maintained after that period.

According to the results, it can be concluded that only small portions of the contaminants as Cr(VI) and Cu complex in the polluted soils were successfully removed. In fact, Cr(VI), as a negative charge ion, electromigrated toward anode under application of voltage drop. However, low pH may result in significantly increase of Cr(VI) adsorption in kaolinite (Zhou, 2000). The low pH in the soil column close to anode may reverse the surface charge of soil particles to be positive instead of negative resulting in strong adsorption of Cr(VI) negative complexes. Controlling the pH in anode chamber maybe very important for the successful removal of Cr(VI) from the soil column. Similar to Cr(VI), Cu(II) complexes were also strongly adsorbed in the soil column near the anode. Diaz-Barrientos *et al.* (Diaz-Barrientos, 2003) also observed that Cu complexes were difficult to dissolve from an organic amendment soil because of its high affinity between Cu complex and soil.

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