

## Electrokinetic Enhanced Transport of Zero Valent Iron Nanoparticles for Chromium(VI) Reduction in Soils

Helena I. Gomes<sup>a,b,\*</sup>, Celia Dias-Ferreira<sup>c</sup>, Alexandra B. Ribeiro<sup>b</sup>, Sibel Pamukcu<sup>a</sup>

<sup>a</sup>Department of Civil and Environmental Engineering, Fritz Engineering Laboratory, 13 E. Packer Avenue, Lehigh University, Bethlehem, PA 18015-4729, USA

<sup>b</sup>CENSE, Departamento de Ciências e Engenharia do Ambiente, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal

<sup>c</sup>CERNAS, Departamento de Ambiente, Escola Superior Agrária de Coimbra, Bencanta, 3040-316 Coimbra, Portugal  
[hig311@lehigh.edu](mailto:hig311@lehigh.edu)

Zero valent iron nanoparticles (nZVI) are a promising technology that could provide cost-effective solutions to soil and groundwater remediation. However, transport of nZVI is normally limited by their aggregation and settling, and with mobility being normally less than a few meters. The main research objective of this study is to find out if coupling electrokinetics and reactive iron nanoparticles can be an effective method for treating chromium contaminated clay soils. Direct current was used to enhance poly(acrylic acid), sodium salt (PAA) coated iron nanoparticles (PAA-nZVI) mobility in Cr(VI) spiked kaolin. A commercially available electrophoretic cell was modified for these experiments and equipped with internal auxiliary electrodes that allow to measure the redox potential directly in the clay. A constant potential of 5.0 V was applied across the test bed. Experimental results show that electrokinetics can enhance the delivery of nanoscale iron particles for the reduction of hexavalent chromium to the less toxic trivalent chromium. Direct current enhanced nZVI transport up to 74 % when compared with diffusion, maximum value found when comparing iron concentrations ratios. Activation of nZVI was also observed with a decrease in the redox potential of 531 mV, in average, after the injection point.

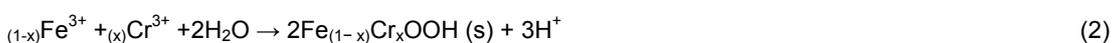
### 1. Introduction

Large quantities of chromium have been discharged into the environment, mainly to soils and groundwater, due to improper disposal and leakage in industrial activities (ore refining, production of steel and alloys, metal plating, tannery, wood preservation and pigmentation). Chromium is one of the most frequent metal soil contaminants and is one of the top 20 contaminants on the Superfund priority list of hazardous substances for the past 15 years (Chrysochoou et al., 2011).

Oxidation states of Cr range from -4 to +6, but only the +3 (III) and +6 (VI) states are stable under most natural environments. These two oxidation states are drastically different in charge, physicochemical properties as well as chemical and biochemical reactivity (Bagchiet al., 2002). Cr(VI) is extremely mobile in the environment and is toxic to humans, animals, plants, and microorganisms. Because of its significant mobility in the subsurface environment, the potential risk of groundwater contamination is high. Cr(III), on the other hand, is less toxic, immobile, and readily precipitates as Cr(OH)<sub>3</sub> (Singhet al.,

2011).Cr(III) is also considered to be a trace element essential for the proper functioning of living organisms(Kotaś and Stasicka, 2000).

Several researchers have already demonstrated, at bench-scale, that nZVI could be used to promote reduction of Cr(VI) to Cr(III) in groundwater (Ponderet al., 2000; Melitaset al., 2001; Drieset al., 2005) and also in soils (Xu and Zhao, 2007; Francoet al., 2009; Chrysochoouet al., 2011; Singhet al., 2011, 2012).Experimental results from X-ray photoelectron spectroscopy and X-ray absorption spectroscopy showed that nano Fe<sup>0</sup> reduces Cr(VI) and corrodes to form lepidocrocite[a product of Fe(II) oxidation - γFeOOH] which then acts as a substrate for precipitation of Cr(OH)<sub>3</sub> and/or Cr<sub>x</sub>Fe<sub>1-x</sub>(OH)<sub>3</sub> (Manninget al., 2007). Fe<sup>0</sup> is ultimately oxidized to Fe(III), which precipitates as ferric hydroxides, while Cr(VI) is reduced to Cr(III).The net reactions of Cr(VI) reduction with Fe(0) and coprecipitation of Cr(III) and Fe(III) are as follows(Qianet al., 2008), involving also indirect reduction by Fe(II) according to the reactions (3) and (4)(Chrysochoouet al., 2011):



where x can vary from 0 to 1.



In field applications, nZVI are traditionally injected under pressure and/or by gravity. However, transport of nZVI is normally limited by their aggregation and settling (Phenratet al., 2007), with mobility in the subsurface being normally less than a few meters as several field applications show(Bennettet al., 2010; Combaet al., 2010; Heet al., 2010). Some strategies have been developed to tackle this limitation, such as coating of the nanoparticles with different polymers (Sunet al., 2007; Yanget al., 2007; Phenratet al., 2008; Tiraferriet al., 2008). Electrokinetics can be used to deliver and activate nZVI in low permeability soils (Pamukcuet al., 2008; Reddyet al., 2011; Yang and Chang, 2011). The electrokinetic process can also provide the electrical supply of energy to drive favorable reduction-oxidation reactions. Pamukcu et al.(2004) demonstrated the feasibility of *in situ* reduction of Cr(VI) to Cr(III) by introducing ferrous iron Fe<sup>2+</sup> to the contaminated soil electrokinetically. This study aims to analyze if coupling electrokinetics and reactive iron nanoparticles can also be an effective method for treating chromium contaminated soils.

## 2. Materials and methods

### 2.1 Electrophoretic cell

A commercially available electrophoretic (EP) (Econo-SubmarineGel Unit, model SGE-020) cell was modified to undertake these experiments (Figure 1). The cell is a rectangular translucent box with a square (20 cm x 20 cm) sample tray. There are two liquid chambers on each side of the sample tray (to hold the electrolyte) and a lid that covers the whole apparatus. The standard cell is equipped with platinum working electrodes and both auxiliary electrodes and a reference electrode were added for this experiment. This modified EP cell allowed direct measurement of the redox potential (ORP) in the soil by use of 0.25 mm diameter platinum wire electrodes fixed in the base plate of the sample tray at equal intervals (3 cm) with conductive glue. ORP measurements were made in the wire electrodes, using a Ag/AgCl reference electrode and a device attached to a low resistance multimeter to facilitate the accurate measurement of soil redox potential (Rabenhorst, 2009) (Figure 1). These electrodes were labeled as E1-E5 starting from the anode end (Figure 1). Compressed fiberglass wool pads were used on both sides to help transport the migrating ions from the electrolyte into the clay and vice versa. The levels of the liquids in the anode and cathode chambers were kept slightly below that of the clay in the sample tray to avoid flooding of the soil cell with excess liquid and any preferential transport of nZVI through water pool at the top.

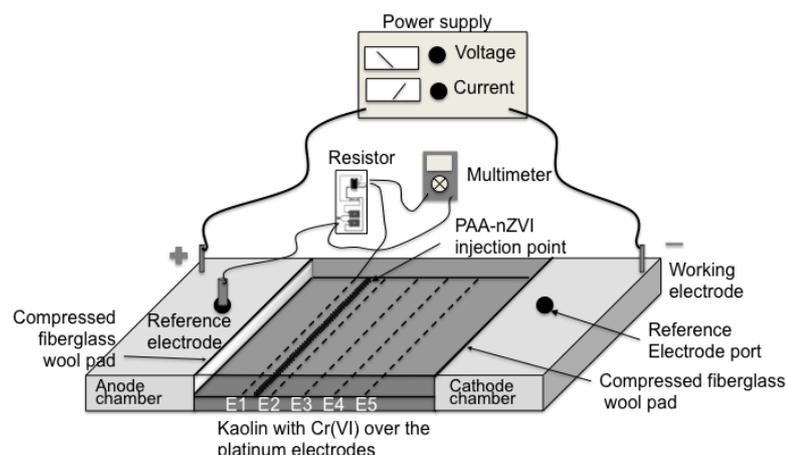


Figure 1: Schematic diagram of the modified electrophoretic cell test setup.

## 2.2 Chemicals

Zero valent iron nanoparticles (nZVI) were prepared with the reduction of ferric chloride (Alfa Aesar) by sodium borohydride (Hydrifin™) and after were stabilized by poly(acrylic acid), sodium salt (PAA) (Polysciences, Inc) following the method described in Jiemvarangkulet al. (2011). A solution with a concentration of  $10 \text{ g L}^{-1}$  of nZVI and 30 % (w/w) of PAA was prepared.

All stock solutions were made from ACS reagent grade materials and distilled de-ionized water. The electrolyte solution used in the electrode chambers, 0.001 M NaCl (Sigma Ultra) was deoxygenated with ultra purified grade nitrogen gas ( $\text{N}_2$ ) for a minimum of 1 h before use. The molar concentration of the potassium dichromate (Aldrich Chemical) solution was 0.005 M.

## 2.3 Enhanced transport experiments

The chromium spiked clay was prepared by adding  $\text{K}_2\text{Cr}_2\text{O}_7$  stock solution to 140 g of white Georgia kaolinite clay, whose properties were described by Pamukcu et al. (2004). The final water content was 60 % by dry weight and the mixture had a density of  $1.63 \text{ g cm}^{-3}$  (Pamukcu et al., 2004). The paste was transferred into the tray and spread uniformly over the wire electrodes to a thickness of 2 mm.

PAA-nZVI were delivered using a pipette to add 0.250 mL solution and spreading it into a pre-cut groove into the clay on the anode side, between E1 and E2 (Figure 1). An acrylic cover (2 mm thick) was then placed over to ensure that the clay saturation is maintained under a thin layer of water, but PAA-nZVI transport in the system occurred through the clay layer only.

A constant potential of 5.0 V was applied across the working electrodes for 24 h. This low potential was selected to remain within the linear range of the power supply used and also prevent excessive gas generation. The 24-h duration was selected to allow adequate time for uniform distribution of iron in the clay based on previously demonstrated results (Pamukcu and Wittle, 1992). The cell was kept in a dark location to prevent iron photo-oxidation. Two control experiments were conducted in the same conditions, without direct current and with current and without nZVI.

Measurements were taken periodically at the following times: 0.25, 0.50, 0.75, 1, 2, 3, 5, 7, 12, 15, 20 and 24 h. At each measurement time voltage, current, ORP, pH and temperature were monitored. At the end of each test, water samples were collected from the electrode chambers, and soil samples were collected in three equidistant locations above the electrodes. The groove where nZVI was injected was not sampled. The soil and water samples were analyzed for total chromium, hexavalent chromium, total iron and ferrous iron concentrations, and pH. All soil and liquid samples were collected, preserved, extracted, and diluted in accordance with the U.S. EPA guidelines (3050B, 3060A, 7196A) or standard methods (APHA, 1992). The iron and chromium analysis were conducted using a Perkin-Elmer Analyst 200 flame atomic absorption spectroscopy (AA) and a Hach DR 2800 spectrophotometer (UV).

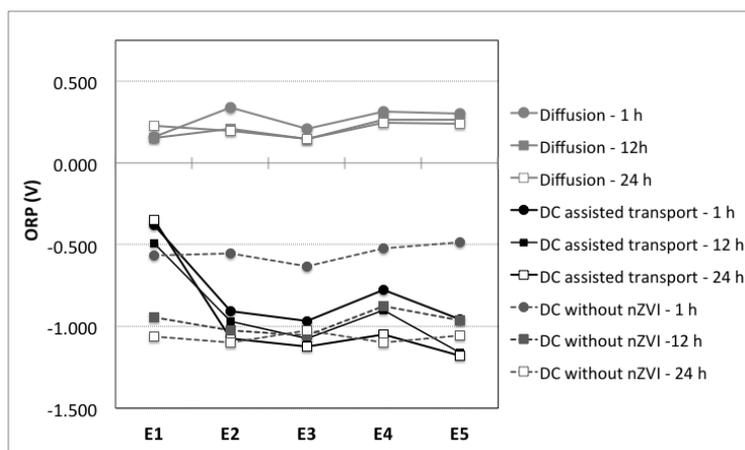


Figure 2: Distribution of ORP in the clay with and without direct current transport and without nZVI.

### 3. Results and discussion

#### 3.1 Redox potential measurements

The redox measurements in soil show the trend of oxidizing to reducing conditions from the anode toward the cathode when the direct current is applied over time in 24 h (Figure 2). When PAA-nZVI was injected between E1 and E2, it caused decrease in the ORP values of 523 mV within the first hour of transport, showing that there is an activation of the nanoparticles as observed by Pamukcu et al. (2008). In the diffusion test, the ORP values maintained a nearly constant value, around 0.222 V, showing no activation of the nZVI. In the experiments where direct current was applied, the current density was  $2.7 \times 10^{-4} \text{ mA cm}^{-2}$  after about 1 h of treatment when no nanoparticles were injected, and  $1.3 \times 10^{-3} \text{ mA cm}^{-2}$  with PAA-nZVI. This shows the increase in the electrical conductivity when PAA-nZVI are used, causing additional current carriers be introduced into the system with the ensuing reactions.

#### 3.2 Chromium and iron distributions

At the end of 24h treatment, no iron or chromium was detected in both the anolyte and the catholyte in all the experiments. The Fe/Cr ratio distribution in soil remained relatively uniform (Figure 3) in the electrodes E1 to E5, throughout the cell as observed by Pamukcu et al. (2004). This is attributed to retarded chromium transport and uniform distribution of the excess iron across the thin cross-section of the kaolin during treatment.

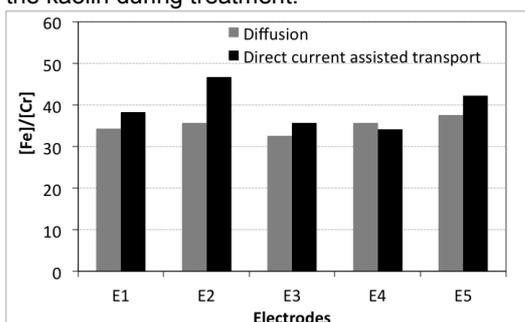


Figure 3: Post-treatment average distribution of total iron to total chromium ratio in the clay.

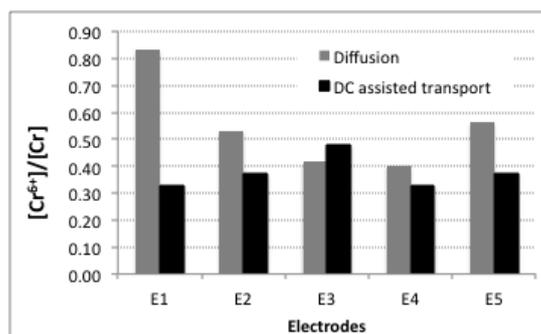


Figure 4: Average mass fraction distribution of Cr(VI) and total chromium measured for each electrode location.

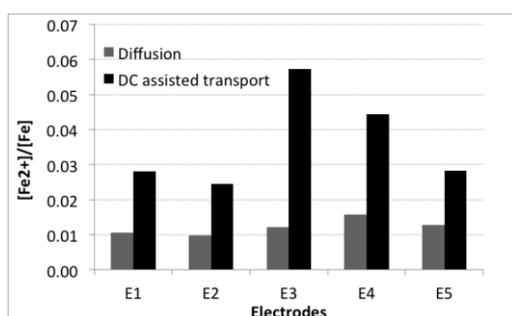


Figure 5: Average mass fraction distribution of  $Fe^{2+}$  and total iron measured for each electrode location.

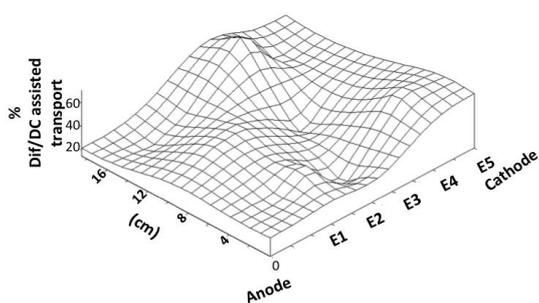


Figure 6: 2D spatial distribution of the %  $[Fe^{2+}]/[Fe]$  observed in the soil comparing the diffusion and DC assisted transport tests of nZVI.

Comparing the ratio between Cr(VI) and total chromium concentrations along the electrodes (Figure 4), it is apparent that less chromium is on this oxidation state, when direct current is used. In this case, across the soil, at the end of 24 h, an average of 62 % of chromium is transformed into the less toxic and less mobile oxidation state Cr(III). Results also show that PAA-nZVI transport is enhanced with direct current, as more  $Fe^{2+}$  was found compared with diffusion (Figure 5). The high value in E3 is consistent with the visual observation of nZVI transport as well. Figure 6 shows the 2-dimensional spatial distribution of the  $[Fe^{2+}]/[Fe]$  percentage between the diffusion and enhanced transport. The overall transformation of Fe to Fe(II) is more than doubled in the enhanced transport case (Figure 5), but the spatial distribution of the species achieved at the end of 24 h is not as uniform as that of the diffusion (Figure 6).

#### 4. Conclusions

According to the experimental results, it can be concluded that the integration of electrokinetics with nZVI is very promising in the cleanup of Cr contaminated soil, enhancing the transport of PAA-nZVI and reducing the target contaminant, even with very low current density. ORP distribution and its temporal variation throughout the tests showed that the electrical field enhances the ORP, creating a synergistic effect of nZVI usage with electrokinetics.

The results show that PAA-nZVI can be transported by electric field even in low permeability clay soils, preventing common issues of agglomeration and settlement, while accelerating *in situ* destruction or immobilization of some contaminating compounds. However, further tests should be done, especially with higher amounts of soil and soils with high surface activity. More detailed analysis of the iron speciation; the competition between the different oxidants present in the media and the stoichiometry should also be considered.

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