Influence of electrolyte and voltage on the direct current enhanced transport of iron nanoparticles in clay

CrossMark

Helena I. Gomes [a,b,c,*], Celia Dias-Ferreira [c], Alexandra B. Ribeiro [b], Sibel Pamukcu [a]

[a] Department of Civil and Environmental Engineering, Fritz Engineering Laboratory, Lehigh University, 13 E. Packer Avenue, Bethlehem, PA 18015-4729, USA
[b] CENSE, Departamento de Ciências e Engenharia do Ambiente, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal
[c] CERNAS – Research Center for Natural Resources, Environment and Society, Escola Superior Agrária de Coimbra, Instituto Politécnico de Coimbra, Bencanta, 3045-601 Coimbra, Portugal

HIGHLIGHTS

- Direct current can enhance iron nanoparticles transport in clay by 25%.
- Oxidizing conditions and higher ionic strength limit nZVI enhanced transport.
- Ionic strength was significant, promoting nanoparticles aggregation and oxidation.

ARTICLE INFO

ABSTRACT

Zero valent iron nanoparticles (nZVI) transport for soil and groundwater remediation is slowed down or halted by aggregation or fast depletion in the soil pores. Direct electric current can enhance the transport of nZVI in low permeability soils. However operational factors, including pH, oxidation–reduction potential (ORP), voltage and ionic strength of the electrolyte can play an important role in the treatment effectiveness. Experiments were conducted to enhance polymer coated nZVI mobility in a model low permeability soil medium (kaolin clay) using low direct current. Different electrolytes of varying ionic strengths and initial pH and high nZVI concentrations were applied. Results showed that the nZVI transport is enhanced by direct current, even considering concentrations typical of field application that favor nanoparticle aggregation. However, the factors considered (pH, ORP, voltage and electrolyte) failed to explain the iron concentration variation. The electrolyte and its ionic strength proved to be significant for pH and ORP measured during the experiments, and therefore will affect aggregation and fast oxidation of the particles.

1. Introduction

Zero valent iron nanoparticles (nZVI) are considered an emergent solution for *in situ* soil and groundwater remediation due to their high specific surface area and reactivity and because they target a vast number of contaminants, from organochlorines to heavy metals (Masciangioli and Zhang, 2003; Zhang, 2003; Zhang and Elliott, 2006). The growing use of nZVI in pilot and full-scale applications in the last decade is notable (USEPA, 2011; Mueller et al., 2012; Rejeski et al., 2012). However, one of the major limitations is the effective long distance transport without aggregation and loss of their reactivity – the mobility of nZVI in the subsurface is normally less than a few meters (Bennett et al., 2010; He et al., 2010; Comba

et al., 2011; Su et al., 2013). Coated nanoparticles are more mobile than bare nZVI (He et al., 2007; Phenrat et al., 2007; Sun et al., 2007; Kanel et al., 2008; Tiraferri et al., 2008; Lin et al., 2009; Phenrat et al., 2009; Tiraferri and Sethi, 2009; Phenrat et al., 2010; Raychoudhury et al., 2010; Jiemvarangkul et al., 2011; Phenrat et al., 2011), but aggregation remains and can be determined by the particle size distribution and Fe^0 content of nZVI, as well as by soil water ionic strength and composition (Saleh et al., 2008; Lin et al., 2010).

Electrokinetic (EK) remediation is a well-known technology with demonstrated results, especially in low permeability fine-grain soils. Direct current can enhance the transport of iron nanoparticles in sands (Jones et al., 2010; Chowdhury et al., 2012) and clay (Pamukcu et al., 2008) and improve the remediation effectiveness for different contaminants (Yang et al., 2008; Reddy et al., 2011; Gomes et al., 2012a,b; Yuan et al., 2012; Fan et al., 2013). The primary mechanisms for the nZVI enhanced transport are: electrophoresis, towards the anode, and electroosmotic advection, towards the cathode. In sands, with lower surface

* Corresponding author at: Department of Civil and Environmental Engineering, Fritz Engineering Laboratory, Lehigh University, 13 E. Packer Avenue, Bethlehem, PA 18015-4729, USA. Tel.: +351 212948300; fax: +351 212948554.
E-mail address: hrg@campus.fct.unl.pt (H.I. Gomes).

charge, electrophoresis dominates, while in clays, electroosmosis can be the most important transport mechanism, counteracting electrophoresis. The existing studies tested low nZVI concentrations and overlooked parameters such as ionic strength, pH, oxidation–reduction potential (ORP) and electric field strength that can influence the nZVI transport, given that the external supply of electric energy can enhance favorable oxidation–reduction reactions in clay-electrolyte systems (Pamukcu, 2009).

The main objective of the current study was to assess if low direct current can enhance the transport of high nZVI concentrations, typical of field applications, in clay rich soils varying the electrolyte ionic strength and voltage. We used kaolin clay to represent a low permeability medium, and an experimental setup that allowed us to study the variation in the oxidation–reduction potential and pH values in the kaolin during short-term experiments, and estimate the temporal and spatial distribution of the iron oxidation states and hence the reactivity of the nanoparticles.

2. Material and methods

2.1. Chemicals

Before synthesis of the iron nanoparticles, deionized (DI) water was purged with ultra-purified grade nitrogen gas (N_2) for 1 h so that dissolved oxygen would fall to a level below 20%. Iron nanoparticles were prepared reducing $FeSO_4 \cdot 7H_2O$ (MP Biomedicals), dissolved in a polyacrylic acid, sodium salt – (PAA) Mw ~2100 (Polysciences, Inc.) solution, by sodium borohydride (Hydrifin™), using the procedure described by Kanel et al. (2008). The PAA–nZVI suspensions were freshly prepared before each experiment and had a concentration of 4 g L^{-1} of nZVI. The particle size distribution of the nanoparticles had a mean value of particle diameter 62.66 ± 39.6 nm and the median size was 60.2 nm, based on a count of 420 particles in TEM images.

All chemicals were reagent grade (NaCl, NaOH, Na_2SO_3, sodium citrate dihydrate – $HOC(COONa)(CH_2COONa)_2 \cdot 2H_2O$ from Sigma Aldrich, $CaCl_2$ from Fisher Science Education, $NaHCO_3$ from Research Organics, and $Na_2S_2O_3 \cdot 5H_2O$ from Amresco ProPure). Water was purified from deionized water in a Barnstead NANO-pure system (18 MΩ cm). In all the tests, the electrolyte solutions were deoxygenated with ultra-purified grade nitrogen gas (N_2) for a minimum of 1 h before each use.

2.2. Enhanced transport experiments

2.2.1. Electrophoretic cell

A commercially available electrophoretic cell (EP) (Econo-Submarine Gel Unit, model SGE-020), originally designed for molecular separation, was modified to undertake these experiments (Fig. 1). The cell is a rectangular translucent box 10 cm height, 40 cm long and 23 cm width, with a square (20 cm × 20 cm) sample tray and a lid that covers the whole apparatus. The left and right sides of the sample tray have a liquid chamber (to hold the anolyte and the catholyte, respectively) with platinum working electrodes.

The modified EP cell allowed direct measurement of the redox potential (ORP) in the clay during the experiments, using auxiliary platinum wire electrodes (0.25 mm diameter; 99.9% metals basis, Alfa Aesar) fixed at the base surface of the sample tray at equal intervals (3 cm) with conductive glue. These measurements were made using an Ag/AgCl reference electrode (Accumet) with 4.0 M KCl solution. The auxiliary electrodes were labeled E1 to E5 starting from the anode side (Fig. 1). An OAKTON pH probe (Model WD-35805-18) was used for measuring pH in the kaolin on the electrodes E1–E5.

In all experiments, both anolyte and catholyte compartments were filled with the same electrolyte solutions (volume of
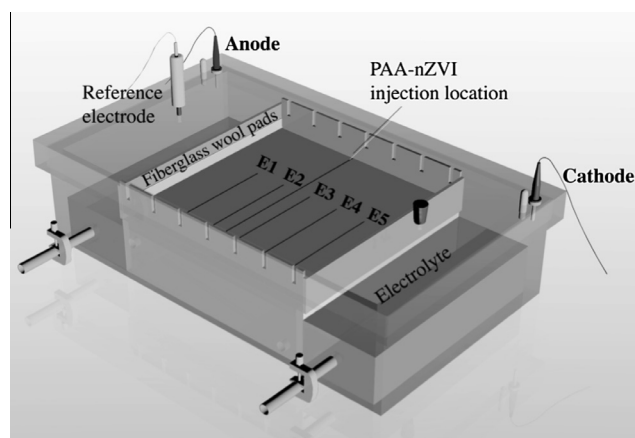

Fig. 1. Schematic diagram of the modified electrophoretic cell test setup.

650 mL each), keeping the level slightly below the clay surface and preventing preferential transport of nZVI through a water pool on top of the kaolin. Compressed fiberglass wool pads, saturated and immersed in the electrolyte solution, helped transport the migrating ions from the electrolyte into the clay and vice versa. The experimental set-up included a power supply, wiring and a multi-meter (Fluke 179).

2.2.2. Experimental conditions

Table 1 shows the experimental conditions used in this study. High-purity (china grade, EMD Chemicals) colloidal kaolinite clay with a nominal particle size of 2 μm, pH 4.97 and with 125.24 ± 13 mg kg^{-1} of extractable iron was used to prepare the test medium. The final water content of the test clay was 60% (by dry weight, before placing it the EP cell) with a mass density of 1.63 g cm^{-3}. The pH_{iep} of this clay is 2.5 (Brosky and Pamukcu, 2013). A more detailed characterization of the kaolin used can be found in Pamukcu et al. (2004). The kaolin mixture was transferred to the tray of the electrophoretic cell and spread uniformly over the wire electrodes to a thickness of 5 mm (200 cm^3).

Two sets of control experiments were conducted for each mixture under the same conditions, one without direct current but with PAA–nZVI, and another with current but without PAA–nZVI. In the experiments with current, a constant potential was applied for 48 h. Table 1 presents the average values of the actual voltage and current measured during the tests. The potentials of 5 V and 10 V resulted in average current densities of 1.12×10^{-4} to 7.24×10^{-4} mA cm^{-2}, respectively. The cell was kept in a dark location to prevent iron photo-oxidation.

The nanoparticle suspension was delivered in the electrophoretic cell using a syringe to inject 2 mL through a tube, which allowed the suspension dispersion into a pre-cut shallow channel in the clay between the auxiliary electrodes E2 and E3 (Fig. 1). The nZVI injection location in the electrophoretic cell was selected in the central area of the clay bed (between E2 and E3) to avoid interference of extreme pH conditions generated in the electrode compartments. Results available in the literature show that the injection of nanoparticles either at the cathode (Yang et al., 2008; Yang and Wu, 2011) or the anode (Chang and Cheng, 2006; Chowdhury et al., 2012) promote the passivation or corrosion of the nZVI, respectively. Recently, a central injection position was used for stabilized nano Pd/Fe for the remediation of pentachlorophenol-contaminated soil (Yuan et al., 2012) with improved results. As such, a central position of nZVI injection was adopted in this study.

Measurements were taken periodically at 0.25 h, 0.50 h, 0.75 h, 1 h, 2 h, 3 h, 5 h, 6 h, 7 h, 10 h, 12 h, 15 h, 24 h, 27 h, 32 h, 36 h and