Numerical prediction of diffusion and electric field-induced iron nanoparticle transport

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ABSTRACT

Zero valent iron nanoparticles (nZVI) are considered very promising for the remediation of contaminated soils and groundwaters. However, an important issue related to their limited mobility remains unsolved. Direct current can be used to enhance the nanoparticles transport, based on the same principles of electrokinetic remediation. In this work, a generalized physicochemical model was developed and solved numerically to describe the nZVI transport through porous media under electric field, and with different electrolytes (with different ionic strengths). The model consists of the Nernst–Planck coupled system of equations, which accounts for the mass balance of ionic species in a fluid medium, when both the diffusion and electromigration of the ions are considered. The diffusion and electrophoretic transport of the negatively charged nZVI particles were also considered in the system. The contribution of electroosmotic flow to the overall mass transport was included in the model for all cases. The nZVI effective mobility values in the porous medium are very low (10^{-7}–10^{-4} cm^2 V^{-1} s^{-1}), due to the counterbalance between the positive electroosmotic flow and the electrophoretic transport of the negatively charged nanoparticles. The higher the nZVI concentration is in the matrix, the higher the aggregation; therefore, low concentration of nZVI suspensions must be used for successful field application.

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1. Introduction

Zero valent iron was used successfully for soil and groundwater remediation in permeable reactive barriers for more than two decades [1–3]. With the development of advanced nanotechnologies since late nineties, due to their size and reactivity that allowed an easy injection, zero valent iron nanoparticles (nZVI) were considered a promising step forward in soil and groundwater clean-up, particularly targeting organochlorines [4–8]. The nZVI transport in porous media was studied in column tests with sand [9–16], glass beads [17–19] and model soils [20,21]. These studies showed that nZVI has a tendency to aggregate quickly and settle in the pores, primarily due to magnetic attractive forces [22]. Results from field scale applications [23–27] confirm this

limited mobility, ranging from 1 m [28] to 6–10 m [26], depending on soil characteristics, test operations, and injection velocities [29].

One of the methods tested to overcome poor nZVI mobility was the use of direct current (DC) [16,30–34], using the same principles of electrokinetic remediation (EKR). In this method, low-level direct current is the "cleaning agent", inducing different transport mechanisms (electroosmosis, electromigration and electrophoresis) and electrochemical reactions (electrolysis and electrodeposition) in contaminated soils [35]. Direct comparison of the results provided in previous studies on nZVI enhanced transport with direct current is limited due to the differences in experimental setups, soils or other solid media used, types of iron nanoparticles, injection places (i.e., directly in the soil, anode or cathode compartments), magnitude and duration of the voltage gradients applied. In general electrophoretic transport of the particles was shown to be predominant in sandy soil [33,36,37], while electroosmotic transport appeared more important in kaolin clay and loamy sand soil [16,32]. The available analytical models of the

Nomenclature

A cross-sectional area (cm^2)
c concentration (mol cm^{-3})
E redox potential (V)
E^0 standard redox potential (V)
F Faraday constant
I current intensity
k_e electroosmotic permeability coefficient
N   mass flux (mol $cm^2 s^{-1}$)
Q reaction quotient
R ideal gas constant
R reaction rate
T temperature (K), assuming a constant room temperature of 25 ºC
t time
U^* effective electrophoretic mobility
V volume (cm^3)
z ionic charge

Greek letters
ϕ electrical potential
η Faradaic efficiency
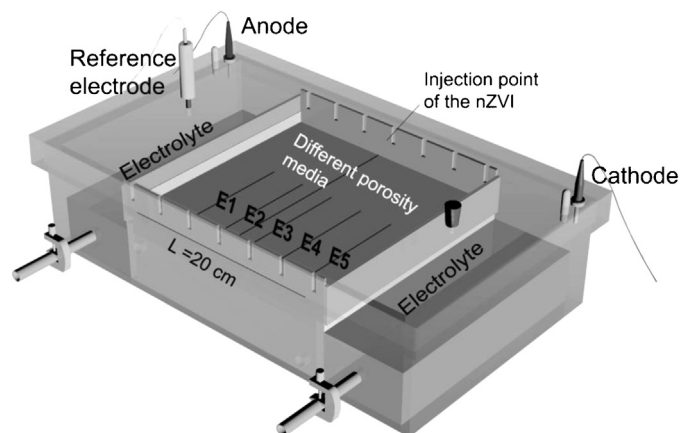
Subscripts
i species
j cell

Fig. 1. Modified electrophoretic cell used in the experiments [30,31]. E1 to E5 are auxiliary platinum electrodes and represent the locations of the solid samples for iron quantification.

nanoparticle transport in literature include only the electrophoretic effect that mostly takes place in sands [33,37].

The numerical modeling of electrokinetic remediation of heavy metals contaminated soils was first implemented by Wilson et al. [38,39], and lately adapted also for organic contaminants [40,41]. Further developments include the electrodialytic and dialytic treatment of a fly ash [42], and also the electrokinetic desalination treatments [43].

In this work, a generalized physicochemical model has been developed to describe the electrically induced transport of nZVI particles through different types of porous media of varying porosity and surface reactivity. The model is sufficiently detailed, including the fundamental processes, and its numerical solution offers a reliable prediction of the nZVI transport. Experimental data using different porosity media and different pore fluid electrolytes were used to validate the model [30,31].

2. Experimental

2.1. Experimental procedure

The experimental data used for the validation of the model have been published previously by Gomes et al. [30,31], where the experimental conditions are described in detail. The experiments were designed so that the transport of nZVI took place in the domain of a layer of porous solid (kaolin and/or glass beads) saturated with an electrolyte.

The experiments were conducted in a modified electrophoretic cell (Econo-Submarine Gel Unit, model SGE-020) as shown in 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. Two liquid chambers hold the anolyte and the catholyte and platinum working electrodes on either side of the sample tray (Fig. 1). In all

experiments, both the anolyte and catholyte compartments were filled with the same electrolyte solution (volume of 650 mL each, Table 1) as that used to saturate the porous specimen. The level of the solutions in the side compartments was kept slightly below the specimen surface, thus preventing preferential transport of nZVI through a liquid pool over the specimen. Compressed fiberglass wool pads, saturated and immersed in the electrolyte solution, helped transport the migrating ions from the solution into the specimen and vice versa. Different porosity and surface reactivity test media, ranging from glass beads (with particle diameter less than 1 mm, previously sieved) to white Georgia kaolinite clay (>2 μm) were used in the transport experiments (Table 1). The polyacrylic acid coated iron nanoparticles (PAA-nZVI) suspensions were freshly prepared before each experiment, according to the method used by Kanel et al. [18] and had a concentration of 4 g L^{-1} of nZVI. The particle size distribution of the nanoparticles had a mean particle diameter value of 63 nm and the median size was 60.2 nm, based on a count of 420 particles in TEM images [30,31]. 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. 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 disperse into a pre-cut shallow channel in the porous specimen between the auxiliary electrodes E2 and E3.

The soil and aqueous samples were analyzed for total iron and ferrous iron concentrations. The iron was extracted from the test medium with the sodium dithionite-citrate-bicarbonate (DCB) method. The iron analyses were conducted using a PerkinElmer AAnalyst 200 flame atomic absorption spectroscopy (AAS) and a Hach DR 2800 spectrophotometer (UV).

2.2. Model description

The analytical model operates in two steps: first the kinetic process is simulated by integrating forward in time the one-dimensional transport equations, including the electrochemical reactions at the electrodes; then the chemical equilibriums are reestablished before the next step of integration. This is done because chemical equilibriums are considered instantaneous when compared with the transport time.