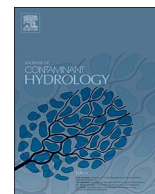




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Transport of polymer stabilized nano-scale zero-valent iron in porous media

Pulin K. Mondal^a, Paul D. Furbacher^a, Ziteng Cui^a, Magdalena M. Krol^b, Brent E. Sleep^{a,*}^a Department of Civil Engineering, University of Toronto, 35 St. George Street, Toronto, ON, M5S1A4, Canada^b Department of Civil Engineering, York University, 4700 Keele St., Toronto, ON, M3J1P3, Canada

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ABSTRACT

This study presents a set of laboratory-scale transport experiments and numerical simulations evaluating carboxymethyl cellulose (CMC) polymer stabilized nano-scale zero-valent iron (nZVI) transport. The experiments, performed in a glass-walled two-dimensional (2D) porous medium system, were conducted to identify the effects of water specific discharge and CMC concentration on nZVI transport and to produce data for model validation. The transport and movement of a tracer lissamine green B[®] (LGB) dye, CMC, and CMC-nZVI were evaluated through analysis of the breakthrough curves (BTCs) at the outlets, the time-lapsed images of the plume, and retained nZVI in the sandbox. The CMC mass recovery was > 95% when injected alone and about 65% when the CMC-nZVI mixture was used. However, the mean residence time of CMC was significantly higher than that of LGB. Of significance for field implementation, viscous fingering was observed in water displacement of previously injected CMC and CMC-nZVI. The mass recovery of nZVI was lower (< 50%) than CMC recovery due to attachment onto sand grain surfaces. Consecutive CMC-nZVI injections showed higher nZVI recovery in the second injection, a factor to be considered in field trials with successive CMC-nZVI injections.

Transport of LGB, CMC, and nZVI were modeled using a flow and transport model considering LGB and CMC as solutes, and nZVI as a colloid, with variable solution viscosity due to changes in CMC concentrations. The simulation results matched the experimental observations and provided estimates of transport parameters, including attachment efficiency, that can be used to predict CMC stabilized nZVI transport in similar porous media, although the extent of viscous fingering may be underpredicted. The experimental and simulation results indicated that increasing specific discharge had a greater effect on decreasing CMC-nZVI attachment efficiency (corresponding to greater possible travel distances in the field) than increasing CMC concentration.

1. Introduction

Groundwater resources are threatened by a large number of contaminated sites worldwide. In the USA alone, the Office of Solid Waste and Emergency Response (OSWER) tracks over 530,000 contaminated sites that occupy almost 23 million acres land (EPA, 2013). An earlier report showed that clean-up of about 355,000 contaminated sites in the USA would require between \$174 and 253 billion (EPA, 2005). Across Europe, 340,000 sites have been detected as contaminated (JRC, 2014). Cost-efficient and reliable techniques are required to remediate these sites. In-situ methods of remediation, particularly passive systems, may help fulfill this demand. One of the earliest passive in-situ methods was the zero-valent iron (ZVI) permeable reactive barrier (Mueller et al., 2012). ZVI is capable of treating chlorinated compounds through reductive dichlorination, and metal removal through surface-mediated mechanisms (Barnes et al., 2010; Gillham and O'Hannesin, 1994; Liu et al., 2005; O'Carroll et al., 2013; Sakulchaicharoen et al., 2010; Zhan

et al., 2008; Zhou et al., 2011). This has generated a widespread interest in the use of nanoscale zero-valent iron (nZVI) as a direct improvement of the technique through the application of nanotechnology. The specific surface area of an nZVI particle can be 30 times greater than a micron scale ZVI particle, increasing the rate of contaminant removal by one to two orders of magnitude (Wang and Zhang, 1997). Furthermore, nZVI particles can be directly injected into the subsurface and are small enough to migrate through many porous matrices. However, the particles rapidly aggregate due to magnetic and van der Waals interparticle forces, reducing the advantages of a nanoscale particle and resulting in deposition and filtration (Farrell et al., 2000; Phenrat et al., 2007).

The aggregation tendency of nZVI particles has been counteracted through the use of polymers, polyelectrolytes or surfactants that provide electro-static and steric repulsion (Fatisson et al., 2010; He and Zhao, 2007, 2008; Johnson et al., 2009; Laumann et al., 2014; Phenrat et al., 2008, 2009; Wang et al., 2013). Stabilization can be conducted

* Corresponding author.

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pre- or post-nZVI synthesis. Generally, pre-stabilization includes the stabilizing agent in the synthesis reaction to immediately control particle aggregation, whereas post-stabilization disaggregates nZVI while introducing the stabilizer. Post-synthesis stabilization has been found to be more cost effective, but also more laborious and produces less stable particles (O'Carroll et al., 2013). Carboxymethyl cellulose (CMC) is a water-soluble organic polymer which interacts strongly with nZVI particles and has been widely studied for use as a stabilizer. CMC consists of a cellulose molecule modified by the replacement of the CH₂OH group with a carboxymethyl group. As CMC is a polyelectrolyte that contains both carboxylate and hydroxyl groups CMC can strongly interact with and stabilize nZVI particles. In addition, CMC is low-cost and environmentally friendly making it attractive for use in remediation applications (He et al., 2007). CMC stabilized nZVI particles (CMC-nZVI) are most commonly prepared through the reduction of aqueous Fe(II) or Fe(III) using sodium borohydride (He et al., 2007) with CMC added to interact with the nanoparticles as they are formed (Fatisson et al., 2010). CMC-nZVI particles show promise for use in groundwater remediation applications but require further investigation to fully understand transport behavior in porous media.

The transport behavior of polymer-nZVI and CMC-nZVI in one-dimensional flow columns has been well studied (He et al., 2009; Kocur et al., 2013; Li et al., 2015; Mystrioti et al., 2015; Raychoudhury et al., 2010, 2012, 2014; Saleh et al., 2008; Tiraferri and Sethi, 2009; Tosco and Sethi, 2010). Colloid filtration theory (CFT) has been applied to model CMC-nZVI transport behavior; however, work in this area has suggested that CFT requires coupling with straining, aggregation and settling mechanisms for better model results (He et al., 2009; Kocur et al., 2013; O'Carroll et al., 2013; Raychoudhury et al., 2012, 2014). Furthermore, one-dimensional column studies do not provide the level of detail required to assess the transport performance of nZVI at site conditions, as flow is limited to a single direction and porewater velocities are typically far higher than those encountered in typical field applications (O'Carroll et al., 2013). Bennett et al. (2010) studied CMC stabilized nZVI mobility and reactivity in shallow aquifer at field scale for treatment of chlorinated ethenes. Their results indicated that nZVI particles were mobile in the aquifer. However, due to interactions between the particles and aquifer sediments the mobility declined significantly in a short time (in ~13 h). Krol et al. (2013) studied nZVI mobility at the field scale, using a 3D compositional simulator with CFT to model CMC-nZVI transport in the field studies of Bennett et al. (2010). Their findings showed that the increase in viscosity due to the CMC solution affected mobility by altering the hydraulic properties of the system and by decreasing nZVI attachment. These effects were especially noticeable during push-pull tests, suggesting the need to further investigate CMC-nZVI transport behavior across varying porewater velocities at conditions comparable to those in the field.

Recent work has attempted to more closely mimic field conditions at the lab scale through the use of two-dimensional experiments. Kanel et al. (2008) investigated poly acrylic acid stabilized nZVI in a 2D system, presenting transport visualization and demonstrating that a density-coupled groundwater flow model may be used to simulate density effects in the two-dimensional system. Phenrat et al. (2010) studied the effects of nZVI particle concentrations on the transport of polymer-modified Fe⁰ nanoparticles in a lab-scale 2D heterogeneous porous media system. They demonstrated that heterogeneity significantly impacted the nZVI deposition pattern, where polymer-modified nZVI movement followed the preferential flow pathways, and the particle transported better at lower particle concentration. Chowdhury et al. (2012) studied CMC-nZVI transport in a lab-scale 2D system in low permeability porous media enhanced by electrokinetics. Busch et al. (2014) studied the transport of carbon colloid supported nZVI in a 2D system, presenting a visualization and transport behavior of the particles. Li et al. (2016) studied CMC-nZVI transport behavior in a 2D environment, varying the injection solution CMC concentration, injection velocity, and media grain size to observe the effects on transport.

Their results indicated that nZVI retention in the sandbox was not influenced by straining, and change in nZVI recovery and reduction in media hydraulic conductivity depended on the CMC concentration and solution injection velocity.

The work done to date on CMC-nZVI transport in 2D experimental systems has not yet combined the transport visualization experiments with the CFT based numerical simulation, and showed the effects of specific discharge and CMC concentration on nZVI transport. The objective of this study was to address this need, and to improve the understanding of the transport behavior of CMC stabilized nZVI in porous media through laboratory scale 2D experiments and CFT-based numerical modeling. The effects of solution viscosity due to change in polymer concentration and effects of specific discharge on the transport of CMC and CMC-nZVI were identified as these are key control variables in field applications.

2. Materials and methods

2.1. Glass-walled sandbox

A laboratory-scale two-dimensional (2D) glass-walled sandbox was used for the transport experiments (shown in Fig. S1 and described in Section S1.1 in Supplementary Information, SI). This sandbox was also used in the studies of O'Carroll and Sleep (2007) and Ye et al. (2009). Two glass plates (0.019 m thick) were sealed to a 0.013 m thick rectangular aluminum frame with Viton® rubber gaskets and silicone glue. The inside dimensions of the space created for porous media were 0.55 m in length and 0.45 m in height. The distance between two glass plates was 0.014 m. There was a clear-well at the left end of the box (with volume of 20 mL) that acted as a continuous inlet for the injected fluid. In addition, there was a well (3 mm OD SS tube) installed from the top of the box for point injections. The location of the point injection was at 0.05 m from the left end and 0.23 m from the top of the box. On the outlet end of the box there were three clear-wells (each with 2 mL volume and 0.02 m length) centered at distances of 0.035 m, 0.23 m and 0.435 m from the top of the box. The sandbox was wet-packed as uniformly as possible in layers with silica sand of grain size ranging from 425 to 600 µm. Each layer of sand packing was 0.01 m thick. The sand was acid washed with 5% HNO₃ and rinsed with distilled water several times. The packed sand bulk density was 1710 kg/m³ and the porosity was 0.35. The sand was saturated with de-aired distilled water. Hydraulic tests resulted an average permeability of the sand of $1.01 \times 10^{-12} \text{ m}^2$.

2.2. Experimental set-up

A schematic diagram of the experimental set-up is shown in Fig. 1. The experimental system included: (a) the glass-walled sandbox, (b) a dual-head peristaltic pump (MasterFlex® L/S with Easy-Load® II pump heads, 77201-60) to feed the system, (c) an inlet manifold and an outlet sample collection manifold, both consisting of SS tubes (3.2 mm OD), PTFE tubes (3.2 mm OD), and SS tube fittings, (d) two pressure transducers (0–5 psi), one connected to the inlet manifold and one connected to the sandbox at the top near inlet clear-well, (e) PTFE tube piezometers (2 mm ID) connected to the inlet and outlet manifolds for water head measurement, (f) Pyrex® glass feed containers (500 mL and 2 L), (g) nitrogen gas (N₂) tank with regulator, (h) a light source, (i) a computer controlled digital camera (Canon EOS) on a tripod support, and (j) a dark box enclosure (0.7 m × 0.6 m × 2 m) to house the digital camera for image collection.

The Pyrex® feed bottles, 500 mL for injection of test solutions (LGB, CMC, and nZVI solutions) and 2 L for injection of flushing distilled water (DW), were connected to a N₂ gas tank keeping them under positive pressure (~1 psi) to maintain anaerobic conditions in the bottles. The peristaltic pump injected either the test solution or DW into the sandbox. A 3-way valve (valve-1) was used to control the switching

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