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# Straining of polyelectrolyte-stabilized nanoscale zero valent iron particles during transport through granular porous media

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ABSTRACT

In this study, the relevance of straining of nano-sized particles of zero valent iron coated with carboxymethyl cellulose (CMC-NZVI) during transport in model subsurface porous media is assessed. Although deposition of polyelectrolyte stabilized-NZVI on granular subsurface media due to physicochemical attachment processes has been reported previously, there is limited knowledge on the significance of the collector (sand) diameter on the deposition and spatial distribution of the retention of such nanoparticles. Experiments were conducted to assess the transport of CMC-NZVI in columns packed with four different-sized sands of mean diameter of 775 μm, 510 μm, 250 μm and 150 μm and at three different particle concentrations of 0.085 $g\,L^{-1}$, 0.35 $g\,L^{-1}$ and 1.70 $g\,L^{-1}$. CMC-NZVI effluent concentrations decreased with smaller sand diameters. High CMC-NZVI particle retention near the inlet, particularly for the finer sands was observed, even with a low ionic strength of 0.1 mM for the electrolyte medium. These observations are consistent with particle retention in porous media due to straining and/or wedging. Two colloid transport models, one considering particle retention by physicochemical deposition and detachment of those deposited particles, and the other considering particle retention by straining along with particle deposition and detachment, were fitted to the experimental data. The model accounting for straining shows a better fit, especially to the CMC-NZVI retention data along the length of the column. The straining rate coefficients decreased with larger sand diameters. This study demonstrates that CMC-NZVI particles, despite of their small size (hydrodynamic diameters of 167–185 nm and transmission electron microscopy imaged diameters of approximately 85 nm), may be removed by straining during transport, especially through fine granular subsurface media. The tailing effect, observed in the particle breakthrough curves, is attributed to detachment of deposited particles.

## 1. Introduction

The direct injection of reactive nanoscale zero valent iron (NZVI) particles into aquifers is an emerging technology for *in situ* remediation of groundwater contaminated by chlorinated organic compounds (Mueller et al., 2012; O'Carroll et al., 2012; Zhang, 2003). A number of studies have demonstrated that colloidal stabilization of NZVI particles by coating with

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polymers or polyelectrolytes is necessary for facilitating particle transport in subsurface porous media (Phenrat et al., 2008; Raychoudhury et al., 2010). Several potentially biodegradable and non-toxic polyelectrolytes have been identified, which when sorbed or bonded to the NZVI particle surface, provide colloidal stabilization by creating significant electrosteric forces that counter the strong inter-particle magnetic attractive forces (Basnet et al., 2013; Petosa et al., 2010; Phenrat et al., 2008).

The deposition of NZVI particles in subsurface granular porous media is influenced by several factors such as the size and aggregation state of the nanoparticles, the surface chemistry of the nanoparticles, the chemistry of the pore fluid, the fluid velocity (Fatisson et al., 2010; He et al., 2009; Petosa et al., 2010; Phenrat et al., 2009; Raychoudhury et al., 2012). The retention of surface-modified NZVI has been reported to decrease with increasing approach velocities and this is attributed to the significant drag forces at higher velocities that promote detachment of deposited particles (He et al., 2009; Phenrat et al., 2010; Raychoudhury et al., 2010). Significant retention of colloids other than NZVI has been observed, even under unfavourable deposition conditions such as low IS, where there is high electrostatic repulsion between similarly charged colloid and collector surfaces. This observation has been attributed to mechanisms such as straining and wedging of colloids between collector grains and attachment of particles on charge heterogeneities on collector surfaces (Redman et al., 2004; Tufenkji and Elimelech, 2005a).

There are limited reports on the effects of collector size on NZVI or other nanoparticle transport. The collector (sand) size can have a significant effect on nanoparticle transport through porous media because it influences the surface area available for deposition of colloids as well as the pore size and fluid velocities encountered by the colloids. Decreases in pore size can lead to retention of nanoparticles by straining. To the best of our knowledge, Phenrat et al. (2010) is the only study that has investigated the effects of sand size on polymer stabilized-NZVI transport. In that study a reduction in $C/C_0$ with increase in sand size was observed, which is contrary to the classical colloid filtration theory that suggests more particle deposition with an increase in the single-collector contact efficiency with decrease in sand size (Tufenkji et al., 2004). Furthermore, the observation does not match with previous studies on the transport of latex colloids in different sized sands (Bradford et al., 2003; Xu et al., 2006).

A few studies have suggested that nanoparticles, such as those of hematite, maghemite and maghemite/nickel of diameters in the range of 15–50 nm, and single-walled carbon nanotubes of hydrodynamic diameters of 122 nm can be retained in packed columns of sand or soil due to straining (Hong et al., 2009; Jaisi and Elimelech, 2009). These studies have not assessed the elution and retention of nanoparticles along the column length in a range of sand sizes. The relevance of straining was concluded from observations that the steady-state effluent concentration of those nanoparticles decreased under conditions favourable to aggregation. A more robust approach to assessment of straining requires evaluation of the effects of sand size on particle retention profile along the column length in conjunction with the breakthrough curves (Bradford et al., 2003). Straining of colloids is characterized by significantly higher deposition near the injection point than what can be ascribed to physicochemical deposition, as well as by decreasing effluent concentrations in finer sands.

A few recent studies have demonstrated that polymer stabilized-NZVI particles, when injected in the field, were retained close to the point of injection (He et al., 2010; Johnson et al., 2013; Su et al., 2013). It is thus important to understand the various colloid retention mechanisms contributing to the spatial distribution of polymer stabilized-NZVI in granular porous media, and the role of sand size in such retention behaviour.

The objectives of this study are to assess the extent of deposition and the spatial patterns of deposition of CMC-NZVI during transport in a packed sand column, and to assess whether straining can be a dominant retention mechanism during transport of CMC-NZVI in subsurface granular media. Column transport experiments were conducted where the CMC-NZVI effluent breakthrough patterns were assessed during CMC-NZVI injection and subsequent flushing with the background electrolyte solution. The size of CMC-NZVI particles in the suspensions injected in the column was stable with time. Following each transport experiment, the packed columns were sectioned and the CMC-NZVI retention profile along the column length was analyzed. Because straining is dependent on pore throat size and thus on sand grain size, four different sand sizes were selected for this study. The application of NZVI for remediation requires its injection into aquifers at concentrations up to several g $L^{-1}$. Thus, the column experiments were conducted with CMC-NZVI concentrations ranging up to 1.7 g $L^{-1}$. Two colloid transport models considering 1) particle deposition and detachment of deposited particles, and 2) straining along with deposition and detachment of deposited particles were fitted to the experimental data to evaluate the role of straining in CMC-NZVI retention.

## 2. Theoretical approach

Nanoparticle transport in granular porous media is often described by the colloid transport model that accounts for advection, dispersion and deposition of colloids onto collector surfaces (Kuhnen et al., 2000; Tufenkji and Elimelech, 2005a). Detachment of deposited particles is also accounted for in certain cases, especially, when the particles are deposited under unfavourable conditions. Detachment is most likely when the torque acting on a deposited particle due to hydrodynamic drag is greater than the torque acting on it due to adhesive forces (Bergendahl and Grasso, 2000; Torkzaban et al., 2007). Our calculations reported elsewhere (Raychoudhury et al., 2012) suggests that applied torque on the deposited CMC-NZVI particles due to hydrodynamic drag is greater than the adhesive torque under these experimental conditions, which makes detachment from the sand surfaces feasible. Particle retention due to straining can be represented by modifications to the colloid transport equations as shown in Equations (1)–(3) (Bradford et al., 2003).

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - \upsilon_x\frac{\partial C}{\partial x} - k_{\mathrm{dep}}C - k_{\mathrm{str}}\psi_{\mathrm{str}}C + \frac{\rho k_{\mathrm{det}}S_{\mathrm{dep}}}{\varepsilon} \quad (1)$$