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

Trishikhi Raychoudhury a,1, Nathalie Tufenkji b, Subhasis Ghoshal a,∗

a Department of Civil Engineering, McGill University, Montreal, Quebec, Canada H3A 2K6
b Department of Chemical Engineering, McGill University, Montreal, Quebec, Canada H3A 2B2

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 m, 510 m, 250 m and 150 m and at three different particle concentrations of 0.085 g L/C0, 0.35gL/C0 and 1.70 g L/C0. 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...
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 (Fatson and 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).

\[
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - \frac{v_x}{\partial x} \left( \frac{\partial C}{\partial x} - k_{dep} C - k_{adh} \psi_{rad} C + \frac{\partial k_{dep} S_{dep}}{\epsilon} \right)
\]
\[
\frac{dS_{\text{dep}}}{dt} = e k_{\text{dep}} C - \rho b_{\text{det}} S_{\text{dep}}
\] (2)

\[
\frac{dS_{\text{str}}}{dt} = e k_{\text{str}} \varphi_{\text{str}} C
\] (3)

where \( C \) (ML\(^{-3}\)) is the suspended particle mass concentration and \( \rho \) (ML\(^{-3}\)) is the bulk density of sand, and \( e \) is the porosity of the sand packed column. The particle deposition rate coefficient \( k_{\text{dep}} \) described in Equation (4), is related to the single-collector contact efficiency \( (\eta_{0}) \) which accounts for particle-sand collisions due to particle diffusion, interception and sedimentation (Yao et al., 1971) and the attachment efficiency \( (\alpha_{pc}) \) between a particle and a collector.

\[
k_{\text{dep}} = \left[ \frac{3(1 - e)U}{2d_{c} \alpha_{pc}} \right] \eta_{0}
\] (4)

where \( U \) (LT\(^{-1}\)) is the Darcy velocity, \( d_{c} \) (L) is the average grain diameter and can be calculated using the Tufenkji and Elimelech equation (Tufenkji and Elimelech, 2004).

In Equation (3), \( k_{\text{det}} \) (T\(^{-1}\)) is the detachment rate coefficient, \( k_{\text{str}} \) (T\(^{-1}\)) is the straining rate coefficient, and \( \varphi_{\text{str}} \) is the dimensionless colloid straining function defined by \( \varphi_{\text{str}} = \left( \frac{d_{c}}{D} \right)^{3} \) as described in Bradford et al. (2003). The parameter \( \beta \) describes the spatial distribution of strained particles along the length of the column and \( S_{\text{dep}} \) (MM\(^{-3}\)) is the deposited mass and \( S_{\text{str}} \) (MM\(^{-3}\)) is the strained mass of particles per unit mass of sand.

In this study, the experimental data was analyzed using two colloid transport models. Model 1 accounts for colloid transport due to 1-dimensional advection, dispersion, particle deposition and detachment. The solid phase retention of CMC-NZVI resulting from particle deposition (and detachment) was evaluated by considering Equation (2) which neglects straining of particles (i.e., \( k_{\text{str}} \) (T\(^{-1}\)) was set to zero in Equations (1) and (2)). In Model 2, the solid phase retention due to deposition and detachment and straining was calculated using Equations (2) and (3), respectively. The coefficients \( k_{\text{dep}} \), \( k_{\text{det}} \), and \( k_{\text{str}} \) were simultaneously fitted to the experimentally determined CMC-NZVI breakthrough curves and retention profiles. The Marquardt algorithm for nonlinear least squares optimization was used to determine the best fit parameters for attachment, detachment and straining (Marquardt, 1963). The sum of squares of residuals between experimental data and model calculations for the relative effluent concentration and the solid phase deposition concentration were minimized simultaneously to obtain the least-squares estimates of the parameters.

3. Materials and methods

All chemicals were reagent grade and all solutions were prepared using Milli-Q-UV Plus Ultrapure water (Millipore, MA, USA).

3.1. Synthesis and characterization of CMC-NZVI

The CMC-NZVI preparation method was adapted from He and Zhao (2007). Briefly, an aqueous solution of 0.065 M ferrous sulphate heptahydrate (FeSO\(_4\)-7H\(_2\)O, AlfaAesar, purity greater than 99%) was added to 5 g L\(^{-1}\) of CMC (90K, Sigma–Aldrich) solution prepared in deionised (DI) water and mixed thoroughly for 30 min and then the solution was reduced by the drop-wise addition of sodium borohydride solution (NaBH\(_4\), Sigma–Aldrich) under N\(_2\) atmosphere as described in a prior study. The mixture was then dried overnight under N\(_2\) and stored.

CMC-NZVI suspensions having three different concentrations (0.085, 0.35 and 1.7 gFe L\(^{-1}\)) were prepared in 0.1 mM NaHCO\(_3\) by sonicating with a 40 kHz ultrasonic cleaner (Cole-Palmer 8891) for 10 min to ensure homogeneity of the suspensions and then the suspensions were stirred for 90 min.

Particles sizes were assessed at different time points to ensure that 90 min was sufficient to attain stable particle sizes. The mean hydrodynamic diameter was determined by nanoparticle tracking analysis (NTA, NanoSight LM10). Stock suspension of CMC-NZVI of three different concentrations (0.085, 0.35 and 1.7 gFe L\(^{-1}\)) in 0.1 mM NaHCO\(_3\) was filled in a vial under N\(_2\) atmosphere to zero headspace. Samples of these suspensions were withdrawn after 90 min and were diluted to 5 mg L\(^{-1}\) under an N\(_2\) atmosphere immediately prior to NTA measurement as described elsewhere (Raychoudhury et al., 2012).

3.2. Packed column experiments

A glass column (Konets Chromoflex) of 1 cm i.d. and packed bed length of 9 cm was used. A nylon mesh (100 \( \mu \)m) was placed at the bottom of the packed column to prevent sand grains from being displaced into the end adapters. Two batches of silica sand (Unimin Corp, WI, USA), Unimin 4020 and Unimin 2030, were acid washed with 12 N concentrated HCl, rinsed with DI water and oven-dried for 3 h at 550 °C. The washed sands were sieved using nylon mesh and the average size of the sand grains was determined. The sample labelled as F2025 passed through an 850 \( \mu \)m sieve (F20) and was retained on a 700 \( \mu \)m sieve (F25) sieve, and its average particle diameter was 775 \( \mu \)m. Similarly, the F3040, F5070, and F70140 sample nomenclature refers to the sieve sizes used, and the average diameters for these samples were 510, 250, and 150 \( \mu \)m and

| Table 1 – Experimental conditions and parameters for column experiments. |
|-----------------|-----------------|
| **Column length, L** | 9 cm            |
| **Nano iron concentration of the column feed, \( C_{0} \)** | 0.085, 0.35 or 1.7 g L\(^{-1}\) |
| **Darcy velocity, \( U \)** | 0.445 cm min\(^{-1}\) |
| **Packing density of dry sand in the packed-bed, \( n_{b} \)** | 1.95 g cm\(^{-3}\) |
| **Density of the nanoparticles** | 2.6 \( \times \) 10\(^{3}\) kg m\(^{-3}\) |
| **pH of the CMC-NZVI suspension** | 7.4 ± 0.4 |
| **Ionic strength of electrolyte solution as prepared** | 0.1 mM of NaHCO\(_3\) |
| **Average sand diameter, \( d_{c} \)** | 775 \( \mu \)m, 510 \( \mu \)m, 250 \( \mu \)m and 150 \( \mu \)m |
| **Dispersion coefficient, \( D \)** | 0.16 ± 0.03 cm\(^{2}\) min\(^{-1}\) (for all four sand sizes) |
| **Porosity, \( \epsilon \)** | 0.35 (for 775 \( \mu \)m dia sand), 0.32 (510–150 \( \mu \)m dia sands) |
150 μm, respectively. Details of sand sizes and other properties are given in Tables 1 and 2.

The column was dry-packed with sand and vibrated intermittently to ensure uniform packing and then saturated with CO₂ to ensure removal of air bubbles. The column was conditioned prior to the experiment as described elsewhere (Raychoudhury et al., 2012).

A 20 mg L⁻¹ KNO₃ solution was injected at the same flow rate through all four types of sand packed columns to determine the hydrodynamic dispersion coefficient (D). The porosity (φ) and the value of D, for the columns containing the different sands are presented in Table 1.

The influent CMC-NZVI suspensions were prepared at different particle concentrations of 0.085, 0.35 and 1.7 gFe L⁻¹ in 0.1 mM NaHCO₃ as described earlier and pumped downwards at a velocity of 0.445 cm min⁻¹ using a syringe pump. The particle suspension pH was 7.4. Settlement of the CMC-NZVI in the syringe was prevented by internal stirring. CMC-NZVI suspensions were less than 0.2% on a number basis (Figure S3) and also accounted for a negligible mass fraction.

Table 2 – Column transport experiment results and estimated parameters at different experimental conditions.

<table>
<thead>
<tr>
<th>Sand grade</th>
<th>dₚ (μm)</th>
<th>dₚ (NTA)</th>
<th>C₀</th>
<th>C/C₀</th>
<th>ηₒ</th>
<th>M_balance</th>
<th>kₓₑp</th>
<th>kₓₑt</th>
<th>kₓₚ</th>
<th>Mₓₓ, L=0.2-2 (%)</th>
<th>Mₓₓ, L=2.2-9 (%)</th>
<th>a r²/C₀, b r²</th>
</tr>
</thead>
<tbody>
<tr>
<td>F2025</td>
<td>775</td>
<td>167</td>
<td>0.085</td>
<td>0.95</td>
<td>0.0173</td>
<td>88.5</td>
<td>0.0036</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.99</td>
</tr>
<tr>
<td>775</td>
<td>183</td>
<td>0.35</td>
<td>0.97</td>
<td>0.0194</td>
<td>93.5</td>
<td>0.0054</td>
<td>0.16</td>
<td>0.096</td>
<td>3.03</td>
<td>4.36</td>
<td>0.94</td>
<td>0.99</td>
</tr>
<tr>
<td>775</td>
<td>185</td>
<td>1.7</td>
<td>0.89</td>
<td>0.0163</td>
<td>94.8</td>
<td>0.0034</td>
<td>0.16</td>
<td>0.096</td>
<td>3.03</td>
<td>4.36</td>
<td>0.97</td>
<td>0.99</td>
</tr>
<tr>
<td>F3040</td>
<td>510</td>
<td>167</td>
<td>0.085</td>
<td>0.84</td>
<td>0.0222</td>
<td>98</td>
<td>0.0080</td>
<td>0.09</td>
<td>0.33</td>
<td>7.14</td>
<td>9.55</td>
<td>0.98</td>
</tr>
<tr>
<td>510</td>
<td>183</td>
<td>0.35</td>
<td>0.82</td>
<td>0.0209</td>
<td>95.5</td>
<td>0.0076</td>
<td>0.09</td>
<td>0.40</td>
<td>8.52</td>
<td>11.21</td>
<td>0.99</td>
<td>0.95</td>
</tr>
<tr>
<td>510</td>
<td>185</td>
<td>1.7</td>
<td>0.77</td>
<td>0.0208</td>
<td>97.6</td>
<td>0.0075</td>
<td>0.09</td>
<td>0.40</td>
<td>8.52</td>
<td>11.21</td>
<td>0.95</td>
<td>0.85</td>
</tr>
<tr>
<td>F5070</td>
<td>250</td>
<td>167</td>
<td>0.085</td>
<td>0.57</td>
<td>0.0344</td>
<td>98.9</td>
<td>0.0254</td>
<td>0.05</td>
<td>1.13</td>
<td>17.25</td>
<td>19.49</td>
<td>0.92</td>
</tr>
<tr>
<td>250</td>
<td>183</td>
<td>0.35</td>
<td>0.67</td>
<td>0.0322</td>
<td>95.5</td>
<td>0.0238</td>
<td>0.05</td>
<td>1.00</td>
<td>13.71</td>
<td>16.22</td>
<td>0.90</td>
<td>0.99</td>
</tr>
<tr>
<td>250</td>
<td>185</td>
<td>1.7</td>
<td>0.6</td>
<td>0.0319</td>
<td>92</td>
<td>0.0235</td>
<td>0.05</td>
<td>1.00</td>
<td>13.70</td>
<td>16.23</td>
<td>0.96</td>
<td>0.99</td>
</tr>
<tr>
<td>F70140</td>
<td>150</td>
<td>167</td>
<td>0.085</td>
<td>0.55</td>
<td>0.0473</td>
<td>92.8</td>
<td>0.0581</td>
<td>0.43</td>
<td>2.15</td>
<td>20.30</td>
<td>22.39</td>
<td>0.96</td>
</tr>
<tr>
<td>150</td>
<td>183</td>
<td>0.35</td>
<td>0.62</td>
<td>0.0442</td>
<td>92.7</td>
<td>0.0543</td>
<td>0.43</td>
<td>1.97</td>
<td>18.82</td>
<td>21.17</td>
<td>0.92</td>
<td>0.99</td>
</tr>
<tr>
<td>150</td>
<td>185</td>
<td>1.7</td>
<td>0.6</td>
<td>0.0439</td>
<td>86.7</td>
<td>0.0540</td>
<td>0.43</td>
<td>1.97</td>
<td>18.82</td>
<td>21.17</td>
<td>0.93</td>
<td>0.99</td>
</tr>
</tbody>
</table>

a r²/C₀ = r² value for fitted model values and experimental data points for breakthrough curves.
b r²/C₀ = r² value for fitted model values and experimental data points for retention profile along the column length.

4. Results and discussion

4.1. Transport of CMC-NZVI at different concentrations through coarse and fine sands

The particle hydrodynamic diameters after 90 min of mixing, dₚ, for the three CMC-NZVI suspensions of 0.085 g L⁻¹, 0.35 g L⁻¹, and 1.70 g L⁻¹ concentrations, as measured by NTA were 167 ± 64, 183 ± 87 and 185 ± 86 nm, respectively. The mean diameter of the NZVI particles from TEM analyses of CMC-NZVI suspensions after 90 min of mixing was in the range of 85 ± 15 nm. Thus, the zero valent iron particles in this study are referred to as nanoparticles. The details of the TEM analyses are given elsewhere (Raychoudhury et al., 2010). For the pregrafted CMC-NZVI used in this study, the CMC is strongly bound with NZVI, which produces more stable particles compared to CMC-NZVI prepared by coating CMC on NZVI particles (post grafted), which results in weaker binding of CMC to the NZVI (Cirtiu et al., 2011). The CMC-NZVI suspension was polydisperse with particle hydrodynamic diameters distributed within a size range of 40–450 nm for 0.085 g L⁻¹ CMC-NZVI and 40–600 nm for the two higher concentrations (Figure S3, Supporting information). The proportion of larger aggregates (400–600 nm) in the two more concentrated CMC-NZVI suspensions were less than 0.2% on a number basis (Figure S3), and also accounted for a negligible mass fraction.

CMC-NZVI transport experiments were conducted using columns packed with clean sand having four different mean grain diameters (150 μm, 250 μm, 510 μm and 775 μm) at three different CMC-NZVI influent concentrations of 0.085 g L⁻¹, 0.35 g L⁻¹ and 1.70 g L⁻¹, in a solution of 0.1 mM NaHCO₃. Fig. 1 shows the breakthrough curves (BTCs) and retention profiles of the solid-phase associated CMC-NZVI for a series of four column experiments conducted with 0.085 g L⁻¹ nanoparticle suspensions using four different-sized sands. Similar results were obtained with the 0.35 and 1.70 g L⁻¹ CMC-NZVI suspensions and are shown in Figures S1 and S2 in Supplementary data.

Fig. 1a demonstrates that for the coarsest sand (775 μm) there was near complete breakthrough of the 0.085 g L⁻¹ CMC-NZVI suspension with a relative effluent concentration (C/C₀)
of 0.95 at 2 PVs. Furthermore, with decreasing average diameter of the sand, the breakthrough value of $C/C_0$ decreased, indicating greater CMC–NZVI retention. The $C/C_0$ decreased from 0.84 for the 510 μm diameter sand to 0.57 for the 250 μm diameter sand and to 0.55 for the 150 μm sand (Table 2). Phenrat et al. (2010) have evaluated the breakthrough patterns of polyelectrolyte modified-NZVI through different sized sand and observed a higher elution ($C/C_0$) with 99 μm diameter sand compared to coarser sands (300 or 880 μm diameter). Those authors have explained such deposition patterns on the basis of higher pore velocities in the finer sands. According to those authors, the higher fluid shear stress acting on aggregates deposited in the finer sands result in breakup or disaggregation of deposited aggregates, leading to higher elution compared to that in coarser sands. In our study, the CMC-NZVI was stabilized for 90 min with a particle diameter of 200 nm (TEM size), suggesting breakup of aggregates is not significant for pre-grafted CMC-NZVI particles used in this study. This is likely because pre-grafted CMC-NZVI did not produce larger, loose aggregates compared to the post-grafted CMC-NZVI.

Fig. 1b (and Figures S1b, S2b in Supplementary data) suggests that retention of CMC-NZVI particles at the column inlet increases as the sand size decreases for all three CMC-NZVI influent concentrations. Tailing of the BTCs with continued electrolyte flushing beyond 3 PVs was observed for all cases except with the coarsest sand receiving lowest CMC-NZVI concentration. The tailing is attributable to particle detachment from the sand surface (Li et al., 2005; Tong et al., 2005a). The mass of CMC-NZVI (measured as total Fe) retained in the column as determined from the sectioning data and the mass of CMC-NZVI eluted based on the BTCs were used to evaluate the mass balances of Fe. The overall mass balances of total CMC-NZVI injected ranged between 87 and 99% for the various experimental conditions, and are presented as $M_{\text{balance}}$ in Table 2.

Transport experiments conducted at different CMC-NZVI concentrations showed that normalized effluent concentrations did not vary significantly with changes in influent concentration in the range of 0.085–1.70 g L$^{-1}$ (Fig. 1 and Figures S1–S2 in Supplementary data). Phenrat et al. (2009) characterized the transport of polyelectrolyte-coated hematite and NZVI particles. In their study, there was no significant effect of particle concentration on the transport of PSS-coated hematite nanoparticles in the concentration range of 30 mg L$^{-1}$–6 g L$^{-1}$ or for PSS-NZVI in the concentration range of 1–6 g L$^{-1}$. Several studies have reported an effect of concentration on retention of other colloids. For example, Bradford and Bettahar (2006) conducted column transport experiments with micron-sized polystyrene latex particles, and showed that the $C/C_0$ increased with influent concentration. The existence of hindered straining (liberation) at high colloid concentrations resulted in a higher steady-state $C/C_0$ value with increasing influent particle concentrations (Bradford and Bettahar, 2006). Kuhnen et al. (2000) found that with an increase in influent iron oxide particle concentrations, a higher $C/C_0$ was obtained due to blocking of the collector surface. However, our results showed that the normalized effluent particle concentration only varies slightly (less than 10%) with changes in influent concentration suggesting that blocking of collector grain surfaces or hindered straining did not play a significant role in this study.

As discussed earlier, the reasons for increased CMC-NZVI retention with decreasing sand size could be: a) change in single-collector contact efficiency with average sand grain size (e.g., $n_0$ increases ~2.7 fold, from 0.0173 to 0.0473, as the sand size decreases from 775 μm to 150 μm); b) straining and/or wedging at small pores or grain-to-grain contact points; and c) reduced deposition on coarser sands due to blocking. Finer sands have larger specific surface area available for deposition compared to coarser sands, and thus blocking is less likely in finer sands compared to coarser sands. In our study, the sand surface coverage by retained particles were calculated according to methods described elsewhere (Torkzaban et al., 2010), and the fraction of collector surface covered by CMC-NZVI is quite low (in the range of $10^{-5}$–$10^{-4}$) for the different sands. In addition, column experiments conducted at different concentrations suggest that blocking of the collector surfaces is not relevant because there is little variation in relative effluent concentrations with increasing influent concentrations. Thus, in the following section the relevance of the
single-collector contact efficiency during transport through sand packed columns is discussed. In addition, detachment of deposited particles was also incorporated in both models to address the tailing observed in the BTCs.

4.2. Model 1: particle deposition on sand surfaces

The experimental data for the BTCs and mass retention profiles along the column length were compared to results calculated using Model 1, which represents CMC-NZVI retention by deposition on collector surfaces and detachment of deposited particles, without consideration of straining. The model calculations are presented in Fig. 1 (and Figures S1, S2 in Supplementary data). In this model, particle deposition rate coefficients \( k_{dep} \) vary with sand size due to the change in the single-collector contact efficiency \( \eta_0 \). Single-collector contact efficiencies \( \eta_0 \) for the four different sands at three different CMC-NZVI concentrations (which produced three different \( d_p \)) were calculated using the Tufenkji and Elimelech equation (Tufenkji and Elimelech, 2004) and are presented in Table 2. Krol et al. (2013) have suggested that reductions in aqueous phase viscosity with time due to dilution (or bypassing) of CMC in the subsurface porous media is responsible for changes in the deposition rate of NZVI over time. In our study, the amount of free CMC available in the solution was very low at approximately 6% (Cirici et al., 2011) and much higher doses of dissolved CMC are needed to increase the solution viscosity. Thus the solution viscosity of the CMC-NZVI suspension was taken to be that for water in calculations of the \( \eta_0 \). A value of \( \alpha_{pc} = 0.013 \) was obtained by fitting Model 1 to the BTC and retention profile corresponding to the lowest CMC-NZVI concentration (0.085 g L\(^{-1}\)) in the coarsest sand (775 \( \mu m \)). Detachment \( k_{det} \) of deposited particles for this case was ignored as no tailing in the BTC was observed. Fig. 1 shows that the calculated BTC and retention profile for 0.085 g L\(^{-1}\) CMC-NZVI \( (d_p = 167 \text{ nm}) \) transported through the 775 \( \mu m \) diameter sand fitted well with the experimental data with \( r^2 > 0.99 \) (Table 2). The fitted value of \( \alpha_{pc} \) (0.013) obtained in this study is in the same order of magnitude reported in different studies (0.05–0.072), conducted with similar experimental conditions (Phenrat et al., 2008; Raychoudhury et al., 2012; Saleh et al., 2008). The same value of \( \alpha_{pc} = 0.013 \) was employed for fitting the model to the data for all other experimental conditions, given the fact that \( \alpha_{pc} \) is influenced by aqueous chemistry, which was unchanged in the different experimental systems. The detachment coefficient, \( k_{det} \), was fitted simultaneously to the BTC and retention profiles for the various sand sizes.

The fitted BTCs for the coarsest sand \( (d_c = 775 \mu m) \) with higher CMC-NZVI concentrations of 0.35 and 1.7 g L\(^{-1}\) \( (d_p = 183 \text{ nm and 185 nm}) \), compared well with the experimental C/C\(_0\) steady-state values; however, the tailing effect was not captured (Figures S1a, S2a). The best fit values of \( k_{det} \) were approximately zero (Table S1), suggesting that the Model 1 is not effective for describing tailing. Furthermore, the measured particle retention near the column inlet was considerably higher compared to Model 1 predictions (Figures S1b, S2b). For sands of smaller diameters \((d_c = 510 \mu m, d_c = 250 \mu m \text{ and } d_c = 150 \mu m)\), the calculated BTCs, considering the same \( \alpha_{pc} \) as the coarsest sand, exceed the measured normalized effluent particle concentration and the tailing in the BTC was not captured in the calculations for all of the experimental conditions (Fig. 1a, Figures S1a and S2a). Furthermore, for these sands of smaller diameters, the measured particle retention near the column inlet for all CMC-NZVI suspension conditions was very high (Fig. 1b and Figures S1b and S2b in Supplementary data), which cannot be explained only by particle deposition.

Overall, Model 1, which accounts for particle attachment on different-sized collectors and subsequent detachment, does not adequately account for the BTCs and the retention profiles observed for the three different CMC-NZVI suspensions.

Earlier studies (Tufenkji and Elimelech, 2005a; Tufenkji et al. 2003) suggest that a wide distribution in the interactions (or interaction energy profiles) between particles and collectors can lead to a distribution in particle deposition rates which can give rise to a non-exponential retention profile. Although heterogeneity in the surface properties of the particle population drives the overall observed non-exponential behavior, charge heterogeneity on collector surfaces due to the presence of different metal oxides and hydroxides can magnify this effect (Tufenkji and Elimelech, 2005b). However, in this experiment the sand grains were acid washed to remove all metal oxides and organic content. Thus, collector heterogeneity is an unlikely cause of the high particle retention at the column inlet.

Hosseini and Tosco (2013) observed that surface modified bimetallic Fe/Cu nanoparticles were retained extensively at the column inlet during the injection period. However the deposited particles were mobilized along the column length during flushing. In our study, the hyper-exponential particle retention profile even after flushing with several PVs of electrolyte indicates that CMC-NZVI particles were retained at the column inlet in a more stable manner. The discrepancy in the mobility patterns of retained particles along the column length may be attributed the coarser sand of an average diameter of 830 \( \mu m \) and higher concentrations of nanoparticles (of 8 g L\(^{-1}\)) used by Hosseini and Tosco (2013).

An increase in particle retention with decreasing sand size and high particle retention near the column inlet is typically attributed to straining and/or wedging. Therefore, in Model 2, straining of CMC-NZVI was incorporated along with particle deposition and detachment as described earlier.

4.3. Model 2: particle deposition and straining

Model 2, which accounts for straining, deposition and detachment of CMC-NZVI was in good agreement \( (r^2 > 0.9) \) with the experimental BTCs and retention profiles for all experimental scenarios (Figs. 2–4). The increasing trend of CMC-NZVI retention in finer sands, particularly near the column inlet was effectively accounted for in Model 2. In general, the tailing in the BTCs was better captured with Model 2. However, for coarse sand the tailing effect was not perfectly captured, possibly due to other processes occurring in this sand, such as to reversible attachment and detachment of CMC-NZVI (Shang et al., 2010).

As with Model 1, the value of \( \alpha_{pc} = 0.013 \) obtained from fitting the BTC and retention profiles for the coarsest sand injected with 0.085 g L\(^{-1}\) CMC-NZVI was used for Model 2. For
this experimental condition, particle deposition alone can fit the experimental data (Table 2, Fig. 1) and the fitted \( k_{str} \) value is 0. The fitted values of \( k_{str} \) vary within a range of 0.05–0.43 for all other experimental conditions as presented in Table 2. Similar values of detachment rate coefficients relative to the attachment rate coefficients has been reported for studies conducted under unfavourable deposition conditions (Shang et al., 2010; Smith et al., 2008; Tong et al., 2005b). Our calculations show that although the detachment rate is high, the net deposited mass (\( S_{dep} \)) at any location is non-zero over the duration of the experiment.

Two fitting parameters are introduced by incorporating straining; namely, the straining rate coefficient \( (k_{str}) \), which is dependent on the relative size of particles and sands, and \( \beta \). A single value of \( \beta \) was fitted for all the experimental conditions to describe the spatial distribution of strained particles over a wide range of colloid and collector sizes. The fitted value of \( \beta = 0.609 \) in this study is close to that \( (\beta = 0.43) \) reported elsewhere (Bradford and Bettahar, 2006; Bradford et al., 2003). All parameter values are presented in Table 2. In this study, straining is observed for a \( dp/dc \) ratio ranging between \( 2.24 \times 10^{-4} \) to \( 1.23 \times 10^{-3} \). The straining rate coefficients determined in this study vary from 0.09 min\(^{-1} \) to 2.15 min\(^{-1} \), and are within the range of previously reported values (Bradford et al., 2003; Tosco and Sethi, 2010; Xu et al., 2006). Bradford et al. (2003) reported a \( k_{str} \) value of 0.007 min\(^{-1} \) for carboxyl functionalized latex particles of 0.45 µm diameter through Ottawa sand of 150 µm in diameter (\( dp/dc \) ratio of 0.003). A similar range of \( k_{str} \) of \( 4 \times 10^{-3} \)–\( 7.9 \times 10^{-3} \) min\(^{-1} \) was reported by Xu et al. (2006) for 0.5 µm latex particles transported through 98 µm diameter sand with a \( dp/dc \) ratio of 0.0051. We have observed three orders of magnitude higher straining coefficients in the range of 0.12–0.94 min\(^{-1} \) for NZVI particles of 70 nm diameter (TEM size), stabilized in xanthan gum suspensions, at a \( dp/dc \) ratio of \( 1.01 \times 10^{-4} \). For a similar \( dp/dc \) ratio of \( 2.24 \times 10^{-4} \) given by the CMC-NZVI of 183 nm size and the 775 µm sand we have estimated a \( k_{str} \) of 0.096 min\(^{-1} \) in this study. Thus the rate and extent of straining for nanoparticles are higher than those reported for latex particles by Bradford et al. (2003) and Xu et al. (2006) even at lower \( dp/dc \) ratios. Tosco and Sethi (2010) have reported that formation of a large brush layer of xanthan gum around the NZVI might enhance straining of nanoparticles. Hong et al. (2009) have
also demonstrated straining for hematite, magnetite and magnetite/nickel nanoparticles of size 15–50 nm with a \(d_p/d_c\) ratio range of \(5.5 \times 10^{-6}–1.8 \times 10^{-4}\). Those authors have suggested formation of aggregates of 400–550 nm in diameter enhance the extent of straining. In our study, similar sized aggregates were present at low concentrations, and may have contributed to straining. In general, latex particles such as those used by Bradford et al. (2003) and Xu et al. (2006), are significantly more mono-disperse than the CMC-NZVI particles used in this study (Figure S3). Thus it is likely that a larger CMC-NZVI aggregate can initiate straining and/wedging at the pore throat, which can lead to further straining as mentioned above and in the illustration (Figure S4). The mass of CMC-NZVI retained by straining may alternatively have been retained by wedging between grain to grain contact points. Given that the number of sand grains packed within a unit volume of granular packed media increase with finer sand diameter, the number of grain to grain contact points would also increase with finer sands. Therefore, as with straining, more CMC-NZVI particles are expected to be retained due to wedging with decrease in sand diameter.

The change in the straining rate coefficient as a function of the ratio of the mean CMC-NZVI particle hydrodynamic diameter (based on NTA) and the mean sand diameter is presented in Fig. 5. The straining rate coefficient shows a linear relationship with the \(d_p/d_c\) ratio \((r^2 = 0.97)\). In this study, the CMC-NZVI particle hydrodynamic diameters fall within a limited range for all transport experiments and the results in Fig. 5 suggest that the straining rate coefficient increases linearly with the diameter of the sand grains. Correlations between the straining rate coefficient and the \(d_p/d_c\) ratio have also been reported elsewhere. Xu et al. (2006) found that the straining rate coefficient varies linearly within a \(d_p/d_c\) range of 0.008–0.052, whereas Bradford et al. (2003) reported a power relationship of \((d_p/d_c)^{1.42}\) with the straining rate coefficient.

### 4.4. Spatial distribution of CMC-NZVI in porous media

Our calculations suggest that retained mass in the sand packed column is governed primarily by straining. To demonstrate this, the percentage of strained mass relative to the total injected CMC-NZVI at the inlet (within 2 cm of column length) and beyond was calculated using Model 2. The mass percentage at the column inlet was denoted by \(M_{str,L<2}\) and beyond this point it was denoted by \(M_{str,L=2}\) (Table 2). The data presented in Table 2 shows that with decreasing sand size, the percentage of strained mass increases steadily. It is interesting to note that the percentage of strained mass reduces after 2 cm of column length for all sand sizes and...
concentrations. Within the first 2 cm of the inlet, approximately 19% of the CMC-NZVI mass injected was retained due to straining with the finest sand and 0.35 g L\(^{-1}\) CMC-NZVI. In the remaining 7 cm of the column, only an additional 21% was retained by straining. Similarly, approximately half of the CMC-NZVI was retained within 2 cm of column length for the other sand sizes and CMC-NZVI concentrations.

High particle retention due to straining at the column inlet could result in changes in porosity, permeability and eventually in the flow rate. Hosseini and Tosco (2013) have demonstrated that an increase in pressure drop over time resulted from pore clogging during injection of modified Fe/Cu nanoparticle at high concentrations of 5–12 g L\(^{-1}\). Several studies have reported that polymer-stabilized NZVI, when injected in the field at g L\(^{-1}\) concentrations, are retained within few centimetres to 2.1 m from the point of injection (He et al., 2010; Johnson et al., 2013; Su et al., 2013). Furthermore, NZVI particles may be transformed into micron-sized aggregates in natural systems (Johnson et al., 2013; Su et al., 2013). Thus straining would be even more prevalent under field scenarios.

5. Conclusion

In this study, the significance of straining as a retention mechanism during the transport of a polyelectrolyte-stabilized NZVI particle was investigated systematically for the first time. The results demonstrate that straining can be an important retention mechanism for the transport of polymer-stabilized NZVI in granular porous media. There was a higher extent of CMC-NZVI retention, primarily due to straining, in finer sands (150 and 250 μm diameter) than in coarser sands (510 and 775 μm diameter). A change in the CMC-NZVI influent concentration from 0.085 to 1.7 g L\(^{-1}\) had little impact on the mass of CMC-NZVI retained by straining. Approximately 50% of the strained mass of CMC-NZVI was present in the first 2 cm of the column inlet. It should be noted that physicochemical deposition also contributed to particle retention, however, a fraction of the CMC-NZVI mass deposited was subsequently released back into the pore fluid. The numerical model incorporating particle deposition, detachment and straining exhibited a significantly better fit to the BTCs and retention profiles, compared to the model that did not account for straining. The values of the deposition, detachment and straining rate coefficients obtained from fitting of the model to experimental data, were in the range of values reported in other studies. Although polyelectrolyte or polymer coatings can significantly improve NZVI mobility in granular porous media, our results suggest that with finer sands there will be significant retention of CMC-NZVI closer to the point of injection due to straining. Such spatial distributions of particle retention need to be accounted for in delivering target doses of NZVI to various locations in contaminated aquifers. It should be noted however, that the ionic strength of 0.1 mM for the electrolyte medium used in this study is lower than that typically encountered in groundwaters. At higher groundwater ionic strengths, enhanced aggregation and particle deposition (Raychoudhury et al., 2012; Saleh et al., 2008) would intensify straining.

Acknowledgements

The research was funded by the Strategic Project Grant Program of the Natural Sciences and Engineering Research Council of Canada, by Golder Associates Ltd., and by the Fonds de recherche du Québec - Nature et technologies. T.R. was supported by a McGill Engineering Doctoral Award.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.watres.2013.11.038

REFERENCES


