Aggregation and deposition kinetics of carboxymethyl cellulose-modified zero-valent iron nanoparticles in porous media

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A B S T R A C T
Transport and deposition of carboxymethyl cellulose (CMC)-modified nanoparticles of zero-valent iron (NZVI) were investigated in laboratory-scale sand packed columns. Aggregation resulted in a change in the particle size distribution (PSD) with time, and the changes in average particle size were determined by nanoparticle tracking analysis (NTA). The change in PSD over time was influenced by the CMC-NZVI concentration in suspension. A particle–particle attachment efficiency was evaluated by fitting an aggregation model with NTA data and subsequently used to predict changes in PSD over time. Changes in particle sizes over time led to corresponding changes in single-collector contact efficiencies, resulting in altered particle deposition rates over time. A coupled aggregation-colloid transport model was used to demonstrate how changes in PSD can reduce the transport of CMC-NZVI in column experiments. The effects of particle concentrations in the range of 0.07 g L⁻¹ to 0.725 g L⁻¹ on the transport in porous media were evaluated by comparing the elution profiles of CMC-NZVI from packed sand columns. Changes in PSD over time could reasonably account for a gradual increase in effluent concentration between 1 and 5 pore volumes (PVs). Processes such as detachment of deposited particles also likely contributed to the gradual increase in effluent concentrations. The particle–collector attachment efficiency increased with CMC-NZVI particle concentration due to a rise in dissolved Na⁺ concentration with increased addition of Na-CMC. This inadvertent change in ionic strength led to decreased effluent concentrations at higher CMC-NZVI concentrations.

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1. Introduction

An emerging remediation technique for in situ groundwater remediation of chlorinated solvent and heavy metal-contaminated aquifers is the injection of reactive nanoparticles of zero-valent iron (Tratnyek and Johnson, 2006; Zhang, 2003). Although at appropriate doses, NZVI can eliminate or transform certain pollutants rapidly, its transport to target locations and its reactivity may be limited by its rapid aggregation (Phenrat et al., 2007). Several studies have demonstrated improved colloidal stabilization of NZVI by coating them with polymers or polyelectrolytes (Kanel et al., 2007; Phenrat et al., 2008; Saleh et al., 2007; Schrick et al., 2004). Polyelectrolyte or polymer coatings can inhibit NZVI
aggregation by a combination of electrostatic and steric
repulsion forces when these interactions are large enough to
overcome inter-particle magnetic and van der Waals attrac-
tive forces. The colloidal stabilization of NZVI by polymers
has been shown to reduce the deposition of NZVI on granular
media and thus increase its mobility, relative to that of bare
NZVI (He et al., 2009; Kanel et al., 2007; Phenrat et al., 2008).

Polymeric coatings of NZVI are unlikely to provide
complete stabilization because of incomplete or insufficient
surface coverage (Cirtiu et al., 2011). The extent of colloidal
stabilization is also dependent on the polymer characteris-
tics, the thickness of the polymer layer on the particle surface, and
on the solution chemistry (Phenrat et al., 2008; Saleh et al.,
2008, 2007). Even at g L\(^{-3}\) doses of polymers and poly-
electrolytes there is evidence of incomplete stabilization
within minutes (Phenrat et al., 2008, 2007; Raychoudhury
et al., 2010; Saleh et al., 2007). Thus, it is important to assess
the changes in PSD of polymer-stabilized NZVI due to
aggregation.

The influence of aggregation of polyelectrolyte-modified
NZVI on the deposition and transport of these particles in
granular media has been discussed in recent studies (Petosa
et al., 2010; Phenrat et al., 2010, 2009; Raychoudhury et al.,
2010). Those studies suggested that aggregation of the
nanoparticles will influence their deposition in granular
media and that the particle size determines the magnitude of
the single-collector contact efficiency (\(\eta_0\)), which is defined
as the ratio of the number of collisions between the particle
and the collector and the total number of particles
approaching the collector. The effect of colloid aggregate size
on colloid transport in porous media has been examined by
Chatterjee and Gupta (2009). In their study, injection of
a polydisperse suspension of inert micron-sized particles
composed of silica and metal oxides in a column packed with
borosilicate glass beads resulted in larger particles being
deposited at shallower bed depths compared to the smaller
particles. The observed deposition behavior was quantita-
tively explained by particle-size dependent deposition rate
coefficients. Although those studies have demonstrated that
changes in particle size resulting from aggregation influence
transport, the role of aggregation kinetics or time-varying
PSD on nanoparticle transport behavior has not been
examined.

The objectives of this study were to assess the rates of
aggregation of CMC-NZVI particles, as well as the effects of
aggregation kinetics on CMC-NZVI transport and deposition in
granular porous media at different nanoparticle concentra-
tions. Changes in the equivalent mean diameter of a CMC-
NZVI suspension due to aggregation were measured over
a time period equivalent to the particle residence time during
a transport experiment. An aggregation kinetics model was
fitted to this data to obtain the particle–particle attachment
efficiency (\(\alpha_{pp}\)) and calculations were performed to determine
the change in the PSD with time during the transport experi-
ments. In an effort to better understand the role of nano-
particle aggregation kinetics on nanoparticle transport,
a modified colloid transport model which couples the gov-
erning transport equation to the aggregation kinetics equation
was developed. A schematic of the multiple concurrent
nanoparticle aggregation, deposition and transport processes
occurring in granular porous media is shown in Fig. 1. Column
transport experiments were performed for different nano-
particle concentrations, and the effluent CMC-NZVI concen-
trations over time were fitted to the modified colloid transport
model to assess whether particle-size dependent deposition
rates could account for the observed shape of the experi-
mental breakthrough curves. The potential role of other
nanoparticle deposition mechanisms such as blocking of
deposition sites, detachment of nanoparticles and the
changes in electrolyte composition with CMC-NZVI concen-
tration, were also considered for explaining the observed
breakthrough curves.
2. Materials and methods

2.1. Synthesis of CMC-NZVI

CMC-NZVI was prepared according to the methods described by He and Zhao (2007). Briefly, an aqueous solution of 0.065 M FeSO$_4$
$\cdot$7H$_2$O (AlfaAesar, purity greater than 99%) was added to a 5 g L$^{-1}$ of Na-CMC (90 K, Aldrich) solution and mixed thoroughly for 30 min. The solution was then reduced by the drop-wise addition of a solution of NaBH$_4$ (Sigma-Aldrich) at a rate of 55.5 mg min$^{-1}$ under an N$_2$ atmosphere. The ratio of [BH$_4$]/[Fe$^{2+}$] was set at 2.0. The mixture was then stirred for an additional 30 min before being dried overnight and finally the dry powder was stored under N$_2$. The ratio of [CMC]/[Fe$^{2+}$] was 1.6$	imes$10$^{-3}$. This is the lowest CMC/Fe ratio that provides a unimodal particle size distribution and a mean particle diameter of less than 100 nm. Other details of the synthesis conditions and characterizations are described in our previous study (Cirtiu et al., 2011).

2.2. Particle size analysis of CMC-NZVI for assessment of aggregation kinetics

The above process yielded CMC-NZVI particles with a mean diameter of 70 nm as determined by high resolution (Philips CM200) transmission electron microscopy (TEM) operated at 200 kV and 120 kV. A typical TEM image of CMC-NZVI particles is presented in the Supplementary data (Fig. S1). Samples for TEM analysis were prepared by depositing two droplets of nanoparticle suspension onto carbon-coated 400 mesh copper grids under N$_2$ to avoid oxidation, and the diameters were measured using the General Image Manipulating Software (GIMP Software, GNU) by averaging 100 particles on different TEM grids. From the TEM images, the CMC-layer thickness was approximated to be in the range of 5–10 nm, which is in agreement with CMC-layer thicknesses reported in prior studies (Fatisson et al., 2010; Raychoudhury et al., 2010). For calculating the single-collector contact efficiency ($n_0$) and the particle–particle collision efficiency function ($\beta$), an average CMC-layer thickness of 7 nm was considered.

The particle sizes of CMC-NZVI over time in aqueous suspensions were determined by nanoparticle tracking analysis (NanoSight LM10). Prior to CMC-NZVI size measurement, the NTA accuracy was verified by checking the size of standard NanoSight polystyrene latex particles of 100 nm and 200 nm diameter. For CMC-NZVI size measurement, suspensions of 0.07, 0.2 and 0.725 g L$^{-1}$ CMC-NZVI (as total Fe) were prepared in N$_2$ atmosphere with filtered (0.22 um) degassed 0.1 mM NaHCO$_3$ and sonicated by a 40 kHz ultrasonic cleaner (Cole-Palmer 8891) for 10 min to ensure homogeneity of the suspensions, and the suspension was filled in a vial to zero headspace. The pH of each particle suspension was 7.4 ± 0.4. Aliquots were withdrawn at various time points from vials subjected to slow stirring, and then diluted to 5 mg L$^{-1}$. The mean square displacements of single particles were determined by tracking the path of scattered light using the NanoSight software. With NTA, the diffusion coefficients are determined from a series of single-particle Brownian motion tracks over time, rather than the collective light scattering response from all nanoparticles in dynamic light scattering which results in more biased toward the larger-sized particles in the latter technique (Domingos et al., 2009).

2.3. Packed column experiments

A Kontes Chromoflex (Fisher Scientific) column of 1 cm i.d. and bed depth of 9 cm was used. A nylon mesh (100 um opening size) was placed at the bottom of the packed column to prevent sand grains from being displaced into the tubing. The column was packed with graded silica sand (Unimin Corp., #4045) sieved through an F30 sieve and retained on a F50 sieve. The sand was acid-washed with concentrated HCl, rinsed with deionized (DI) water and oven dried for 3 h at 550 °C. The mean size of the graded sand ($d_{50}$) was 375 um. The column was dry-packed with sand at several stages with intermittent vibration to ensure uniform packing and then saturated with CO$_2$ to remove air bubbles. Next, 12 PVs of background electrolyte (0.1 mM NaHCO$_3$) were injected in column using a syringe pump (KDS 200, KD Scientific) for conditioning of the column prior to injecting a suspension of CMC-NZVI. The porosity of the packed granular medium in the column was determined to be 0.32 using methods.

![Fig. 1 – Schematic of concurrent aggregation and particle deposition processes in porous media.](image-url)
Specifications of experimental conditions.

CMC-NZVI suspensions of different nanoparticle mass concentrations (0.07 g L⁻¹, 0.2 g L⁻¹ and 0.725 g L⁻¹ as total Fe) in aqueous solution of 0.1 or 10 mM NaHCO₃ were prepared in a N₂ atmosphere with sonication as described above for the NTA analyses. The column influent suspension was pumped through the column at a rate of 0.445 cm min⁻¹ using a syringe pump. This velocity was chosen as it is intermediate between typical groundwater and NZVI injection velocities. The groundwater velocity beyond the point of injection would be lower than the injection velocity and higher than the background groundwater velocity, and thus an intermediate velocity is relevant. The particle residence time in the reservoir syringe ranged from 0 to 48 min, and the average residence time in the column was 6 min. Settling of the CMC-NZVI in the syringe was prevented by gentle stirring as in the aggregation experiments. The concentration of nanoparticles entering the column was thus maintained constant over time as verified by monitoring of the column influent suspension using flame atomic absorption spectrometry (AAS, Perkin Elmer 3110).

For AAS analyses of Fe, the collected effluent samples were dissolved in concentrated HCl (1:2 v/v ratio), diluted with 5% HNO₃ and analyzed for total Fe at a wavelength of 249.7 nm. The detection limit of AAS for Fe measurement was 0.001 mg L⁻¹ and all the samples have concentrations above the detection limit. The presented data is the average of replicate experiments. The experimental conditions are summarized in Table 1.

### Table 1 – Specifications of experimental conditions.

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column length L</td>
<td>9 cm</td>
</tr>
<tr>
<td>CMC-NZVI concentration</td>
<td>0.07, 0.2 or 0.725 g L⁻¹</td>
</tr>
<tr>
<td>of the column feed C₀</td>
<td></td>
</tr>
<tr>
<td>Interstitial velocity v</td>
<td>0.445 cm min⁻¹</td>
</tr>
<tr>
<td>Packing density of dry sand in the packed-bed, ρₚ</td>
<td>1.95 g cm⁻³</td>
</tr>
<tr>
<td>Column void fraction (or porosity) ϵ</td>
<td>0.32</td>
</tr>
<tr>
<td>Mean diameter of the sand particles dₚ</td>
<td>375 μm</td>
</tr>
<tr>
<td>Longitudinal dispersion coefficient D</td>
<td>0.3 cm² min⁻¹</td>
</tr>
<tr>
<td>Coefficient D</td>
<td></td>
</tr>
<tr>
<td>Electrolyte solution for preparation of particle suspensions</td>
<td>0.1 mM NaHCO₃</td>
</tr>
<tr>
<td>pH</td>
<td>7.4 ± 0.4</td>
</tr>
</tbody>
</table>

The NTA data in Fig. 2a for the 0.2 and 0.725 g L⁻¹ suspension was fitted to particle aggregation kinetics model proposed by Lee et al. (2000) and described in Equation (1).

\[
\frac{dn_k}{dt} = \frac{1}{2} \alpha_{pp} \sum \beta(i,j)n_i n_j - \alpha_{pp} n_k \sum \beta(i,k)n_i
\]

where, \(n_i, n_j\) and \(n_k\) are the i, j and k-mer particle number concentrations, and \(z\) is the maximum number of size categories. The first term on the right-hand side of Equation (1) accounts for the formation of aggregates of size \(k\) as a result pooled from duplicate experiments conducted for each concentration, with particle diameter measurements taken at different time points. The extent of aggregation of CMC-NZVI over approximately 1 h resulted in an increase in \(d_{Navg}\) of 28 nm (from \(d_{Navg(0\text{~min})}\) to \(d_{Navg(60\text{~min})}\)) for the 0.2 g L⁻¹ CMC-NZVI suspension and 76 nm (from \(d_{Navg(0\text{~min})}\) to \(d_{Navg(60\text{~min})}\)) for the 0.725 g L⁻¹ suspension. The change in particle size with time of the 0.07 mg L⁻¹ CMC-NZVI particle suspension was found to be negligible but there was aggregation at higher particle concentrations. Increasing particle concentrations result in greater number of particle–particle collisions and an increase in the extent of aggregation.

3. Results and discussion

3.1. Aggregation kinetics of CMC-NZVI

The change in the mean diameter (\(d_{Navg}\)) of the CMC-NZVI over time in a 0.07 g L⁻¹, 0.2 g L⁻¹ and 0.725 g L⁻¹ suspension prepared in 0.1 mM NaHCO₃, as determined by NTA, is presented in Fig. 2a. The data points shown in the figure are described elsewhere (Lambe and Robert, 1991). The value of the hydrodynamic dispersion coefficient (D) was estimated to be 0.3 cm² min⁻¹ from breakthrough curves obtained with an inert tracer (KNO₃).

**Fig. 2** – (a) Changes in mean particle size over time for suspensions of CMC-NZVI obtained by nanoparticle tracking analysis (NTA). The lines show the best fit of the aggregation kinetics model to the 0.2 g L⁻¹ and 0.725 g L⁻¹ CMC-NZVI. (b) Change in Na⁺ concentration with increase in CMC-NZVI concentration in suspensions prepared in 0.1 mM NaHCO₃.
of aggregation of particles of size $i$ and $j$. The second term on the right-hand sides account for the loss of particles of size $k$ as a result of collisions that lead to further aggregation. Aggregation kinetics is controlled by the particle–particle attachment efficiency, $\alpha_{pp}$, which is the fraction of particle–particle collisions resulting in attachment and is dependent on solution chemistry, and by the particle–particle collision frequency function, $\beta$. The parameter $\beta$ accounts for Brownian motion, fluid shear and differential sedimentation. In Equation (1), $\beta$ was computed using the Coalesced Fractal Sphere model (Lee et al., 2000), which assumes that only binary collisions occur, and that the shape of the aggregates are defined by their fractal dimension, $D_f$, which remains unchanged during aggregation. The coalesced fractal model is a valid approach for solving the Smoluchowski equation and used to evaluate the coagulation kinetics for a wide range of colloids (Gierczycki and Al-Rashed, 2008; Irapour et al., 2004; Maximova and Dahl, 2006). A generally accepted value of $D_f$ is in the range of 2.0 for reaction-limited aggregation that occurs under conditions of low ionic strength (IS) aqueous solutions and/or inter-particle steric hindrance (Lin et al., 1989; Trinh et al., 2009). The aggregate sizes generated with time, are defined as follows (Lee et al., 2000):

$$d_{p(i)} = \left(N_{i}^{(1)}\right) \times d_{p(i-1)},$$

where $N_i$ is the number of single particles forming an aggregate of diameter $d_{p(i)}$ and $d_{p(i-1)}$ is the diameter of the smallest particle (45 nm) present in the suspension and considered as the primary monomer.

The $\alpha_{pp}$ was determined by fitting the calculated particle number-averaged mean diameter ($d_{n_avg}$) over time predicted by Equation (1) with the number-averaged mean diameter ($d_{n_avg}$) measured over time by NTA. The fit of Equation (1) to NTA data is shown in Fig. 2a. The initial ($t = 0$) PSD was obtained from TEM image analyses of CMC-NZVI in a freshly-prepared suspension, which yielded a $d_{n_avg}$ of 70 nm, and a minimum diameter, $d_{p(45)}$, of 45 nm. The mean particle diameter at $t = 0$ based on NTA was 192 nm. The difference in the mean particle sizes determined by TEM and NTA can be explained by the fact that NTA calculates particle hydrodynamic diameters based on light scattering (Domingos et al., 2009). The difference in mean particle diameters determined from TEM and NTA at the initial time point ($t = 0$ min) was assumed to be constant over time, and the value of $d_{n_avg}$ was adjusted accordingly. The fitting of the 0.2 g L$^{-1}$ and 0.725 g L$^{-1}$ CMC-NZVI suspensions prepared in 0.1 mM NaHCO$_3$ yielded a $\alpha_{pp}$ of $1.7 \times 10^{-4}$ and $3.0 \times 10^{-4}$, respectively. The different values of $\alpha_{pp}$ occurs because it was found that the two suspensions had different IS even though prepared with the same electrolyte solution of 0.1 mM NaHCO$_3$. The effective IS accounting for the increase in Na$^+$ salt concentration for different CMC-NZVI suspensions are reported in Table 2. With an increase in CMC-NZVI concentration, the dissolved Na$^+$ concentration released from NaBH$_4$ added during particle synthesis and from the dissociation of Na-CMC (Shimabayashi et al., 1992) also increases. CMC-NZVI particles were used without washing to prevent excessive loss of particles and to minimize oxidation of these reactive particles and thus any Na added at synthesis remained associated with the particle suspension. A linear increase in Na$^+$ concentration with CMC-NZVI concentration is shown in Fig. 2b. The total Na measured in the aqueous phase, after separating the CMC-NZVI by centrifugation at 10000 rpm for 15 min, was approximated as the Na$^+$ concentration. Thermogravimetric analyses showed that more than 94% of the CMC was bound to the NZVI and thus only a small amount of undissociated Na-CMC could have been present in the CMC-NZVI free solution.

The values of $\alpha_{pp}$ reported above were relatively small, indicating a probability of up to 3 successful collisions out of 10,000. The small values of $\alpha_{pp}$ are not unusual given the low effective IS of less than 10 mM (Petosa et al., 2010) and the predicted high repulsive energy barrier for particle–particle interactions (Fig. S2a in Supplementary data). Saleh et al. (2010) reported $\alpha_{pp}$ of carbon nanotubes coated with humic acid to be in the range of $10^{-3}$ to $10^{-4}$ in 1 mM IS solutions. Hu et al. (2010) also observed particle–particle attachment efficiencies of similar magnitude for humic acid-coated magnetic nanoparticles at IS ranging from 5 to 10 mM.

The particle size distributions of CMC-NZVI suspensions over time were calculated using Equations (1) and (2) with the fitted values of $\alpha_{pp}$. Changes in the PSD with time as calculated by Equation (1) for particle concentrations of 0.2 g L$^{-1}$ and 0.725 g L$^{-1}$ are presented in Fig. S3 in Supplementary data. The results show that at higher particle concentrations, there is a greater abundance of relatively large-sized aggregates.

### 3.2. Framework for assessing effect of aggregation on transport of CMC-NZVI

The effects of aggregation on transport of CMC-NZVI in packed columns were assessed by accounting for the changes in PSD over the course of the transport experiments. The classical colloid transport theory is described in the Supplementary data. The particle deposition rate coefficient ($k_{dep}$) is a function of the attachment efficiency ($\omega$) between suspended particles and the collector surface and the single-collector contact efficiency ($\eta$). The single-collector contact efficiency depends on the porous medium properties (grain size, porosity), fluid properties (fluid velocity and viscosity) and the particle properties (size and density of particles) (Rajagopalan and Tien, 1976; Tufenkji and Elimelech, 2004; Yao et al., 1971). Calculations of $\eta$ using the Tufenkji and Elimelech Equation (Tufenkji and Elimelech, 2004) show that the value of the single-collector contact efficiency decreases rapidly as the particle diameter increases up to 300 nm (Fig. 3a) due to the decreasing contribution of Brownian

### Table 2 — Fitted values of particle–particle attachment efficiency ($\alpha_{pp}$), particle–collector attachment efficiency ($\alpha_{pc}$) and detachment rate constant ($k_{det}$) for different experimental conditions.

<table>
<thead>
<tr>
<th>Experimental condition</th>
<th>Effective IS (mM)</th>
<th>$\alpha_{pp}$</th>
<th>$\alpha_{pc}$</th>
<th>$k_{det}$ (min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_0$ = 0.07 g L$^{-1}$</td>
<td>1.2</td>
<td>–</td>
<td>0.05</td>
<td>0.005</td>
</tr>
<tr>
<td>C$_0$ = 0.20 g L$^{-1}$</td>
<td>3.2</td>
<td>1.85 $\times$ 10$^{-4}$</td>
<td>0.07</td>
<td>0.005</td>
</tr>
<tr>
<td>C$_0$ = 0.725 g L$^{-1}$</td>
<td>9.6</td>
<td>3.08 $\times$ 10$^{-4}$</td>
<td>0.12</td>
<td>0.005</td>
</tr>
</tbody>
</table>
with particle size in the range 40 and 500 nm. For particles greater than 500 nm, the value of \( \eta_0 \) again increases due to the contributions of interception and sedimentation to particle deposition. Thus, changes in the nanoparticle suspension PSD with time as a result of aggregation will result in time-varying changes in \( k_{dep} \). The magnitude of the overall attachment efficiency for particle deposition is given by Kuhnen et al. (2000) as

\[
\alpha = \alpha_{pc} B(\theta) + \alpha_{pp} \theta,
\]

where \( \theta \) is the fraction of collector surface coverage and \( B(\theta) \) is the blocking function. The deposition of suspended particles onto previously deposited particles can be deemed negligible based on the small values of \( \alpha_{pp} \) reported in Table 2, and \( \theta \) is the number concentration of the ith sized particles. The expressions for the deposition rate coefficient of ith particle size and the resulting modified colloid transport equations are:

\[
k_{dep,i} = \frac{3(1 - \eta)(\l)_{i}}{2d_{i} \tau} \eta_{i}
\]

(3)

\[
C_i = \text{mass} \times n_i
\]

(4)

\[
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - \frac{\partial C}{\partial x} \sum_{i=1}^{n} k_{dep,i} C(t)
\]

(5)

where \( k_{dep,i} \) is the deposition rate coefficient, \( \text{mass} \) is the mass, \( C_i \) is the mass concentration in the aqueous suspension and \( n_i \) is the number concentration of the ith sized particles.

Calculations using Equations (1) and (3–5), show that the shape of the breakthrough curve (BTC) was influenced by the extent of aggregation. Calculated BTCs for CMC-NZVI suspensions with different values of \( \alpha_{pp} \) are shown in Fig. 3b. These predicted BTCs were computed assuming the initial PSD obtained from TEM image analysis with a \( d_{avg} \) of 70 nm as discussed above, a concentration of 0.3 g L\(^{-1}\), and \( \alpha_{pc} \) of 0.1. This value of \( \alpha_{pc} \) is approximately an average value determined from fitting experimental data obtained in this study (Table 2). The results in Fig. 3b show that aggregation can lead to enhanced transport of CMC-NZVI over time. With a \( \alpha_{pp} \) value of \( 10^{-4} \), there was a 13 nm increase in average particle size over the time period within which transport occurred (from \( d_{avg} = 70 \text{ nm at } t = 0 \text{ min to } d_{avg} = 83 \text{ nm at } t = 60 \text{ min} \)), which resulted in relatively small decreases in \( \eta_0 \) and a corresponding small increase in C/C\(_0\) over time (Fig. 3b). However, with a higher degree of aggregation when \( \alpha_{pp} = 10^{-3} \), the \( d_{avg} \) increased from 70 nm at \( t = 0 \text{ min to } d_{avg} = 162 \text{ nm at } t = 60 \text{ min} \), which resulted in a more extensive decrease in \( \eta_0 \) and a corresponding higher increase in C/C\(_0\) over time. As shown in Fig. 3b, for \( \alpha_{pp} = 10^{-3} \), the value of C/C\(_0\) increased from 0.42 at 1.5 PV to 0.6 at 8 PV. In contrast, for \( \alpha_{pp} = 10^{-4} \), C/C\(_0\) increased from 0.42 at 1.5 PV to 0.48 at 8 PV.

3.3. Breakthrough curves of CMC-NZVI from transport experiments

Column transport experiments were conducted using CMC-NZVI suspensions prepared at concentrations of 0.07 g L\(^{-1}\), 0.2 g L\(^{-1}\), and 0.725 g L\(^{-1}\), in an electrolyte solution of 0.1 mM NaHCO\(_3\). Representative BTCs shown in Fig. 4 indicate that at the highest influent CMC-NZVI concentration of 0.725 g L\(^{-1}\), C/C\(_0\) at 8 PVs is 0.61 which is lower compared to C/C\(_0\) of 0.75 for the experiment conducted at 0.07 g L\(^{-1}\).

The BTCs indicate that even after 2 PVs, steady state concentrations were not achieved as the effluent concentrations slowly but continuously increase with time. The tracer (KNO\(_3\)) BTC showed steady state effluent concentrations after 2 PVs and thus the particle effluent concentrations were not influenced by artefacts arising from column packing. The CMC-NZVI BTCs are typical of blocking of collector surfaces, where deposited particles inhibit additional particle deposition once they have extensively covered collector surfaces (Bradford and Bettahar, 2006; Brown, 2007; Johnson and Elimelech, 1995; Kuhnen et al., 2000; Song and Elimelech, 1993). However, blocking is unlikely in this system given that: (i) the surface coverage of the collector grain surfaces was comparatively small in the range of 0.015–0.24% (at 8 PV), as calculated from the mass of particles eluted based on the BTC and the mass injected, and (ii) effluent concentrations decreased with increasing CMC-NZVI influent concentrations. Blocking generally requires more collector surface coverage by deposited particles than observed in our study. Ko et al. (2000) observed blocking with as low as 5% surface coverage for sub-
particle suspensions of concentrations of 0.07 g L\(^{-1}\), 0.2 g L\(^{-1}\) and 0.725 g L\(^{-1}\). The BTCs were obtained using transport but no detachment, and (b) Particle aggregation, with model fit considering (a) particle aggregation and transport model. Hence, the observed increase in effluent CMC-NZVI suspensions shown in Fig. 4a is slightly greater for the 0.725 g L\(^{-1}\) suspension. This is because the increase in CMC-NZVI suspension, compared to the 0.2 g L\(^{-1}\) suspension, is likely to influence CMC-NZVI transport behavior.

In addition, blocking results in higher effluent concentrations over time, and the corresponding decrease in the net effect is a gradual increasing trend in effluent concentrations up to 5 PVs. The increase in the effluent concentrations over time is greater for the BTC for the 0.725 g L\(^{-1}\) suspension than that for the 0.2 g L\(^{-1}\) suspension. This is because the increase in \(d_{\text{Navg}}\) over time, and the corresponding decrease in \(\eta_0\), was greater for the 0.725 g L\(^{-1}\) suspension compared to the 0.2 g L\(^{-1}\) suspension. The particle-collector attachment efficiency \(\alpha_{\text{pc}}\) was determined by fitting Equations (3)–(5) to the experimentally determined effluent concentrations, and the fitted values are presented in Table 2. Beyond 5 PVs, the observed gradual increase in effluent concentrations for the different CMC-NZVI suspensions shown in Fig. 4a is slightly greater than what is obtained from fitting of the modified colloid transport model. Hence, the observed increase in effluent particle concentrations (beyond 5 PVs) cannot be attributed to aggregation or blocking as described above.

The increasing effluent concentrations beyond what can be accounted for by aggregation may be attributable to detachment of deposited particles. Several studies have demonstrated detachment of colloids, including nanoparticles, when deposited on silica surfaces (Bradford et al., 2007; Phenrat et al., 2009; Quevedo and Tufenkji, 2009; Tong and Johnson, 2006). The results of extended Derjaguin–Landau–Verwey–Overbeek (XDLVO) (de Gennes, 1987; Gregory, 1975) calculations (Fig. S2b in Supplementary data) for the interaction between a CMC-NZVI particle and a sand surface indicate a very high energy barrier with a secondary energy minimum (on the order of 2.7 kT) where particles might be retained under this unfavorable condition for deposition (Chen and Elimelech, 2008; Phenrat et al., 2009). For particles deposited under unfavorable conditions, detachment may occur when the applied torque \(T_{\text{applied}}\) exceeds the adhesive torque \(T_{\text{adhesive}}\). The \(T_{\text{adhesive}}\) acts on a deposited particle due to particle-collector XDLVO total interaction energy, and was calculated for different-sized particles in this study according to Torkzaban et al. (2007). The \(T_{\text{applied}}\) arises from the shear force and hydrodynamic drag acting on deposited particles and was calculated based on the method described by Bergendahl and Grasso (2000). Our calculations show that even for the smallest size particle (45 nm), \(T_{\text{applied}} > T_{\text{adhesive}}\) and with increasing particle size, \(T_{\text{applied}}/T_{\text{adhesive}}\) increases (Fig. S4 in Supplementary data). Therefore detachment of deposited particles due to hydrodynamic drag is likely to influence CMC-NZVI transport behavior.

To better understand the potential influence of particle detachment on the shape of the particle BTC, the aggregation-based transport model described by Equation (5) was extended to incorporate particle detachment from the collector surface (Bradford et al., 2003) as follows:

\[ \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - u \frac{\partial C}{\partial x} - \sum_{i=1}^{n} k_{\text{dep},i} C_i(t) + \frac{\rho k_{\text{det}} S_{\text{dep}}}{\epsilon} \]  

where \(k_{\text{det}}\) is the detachment rate coefficient, \(S_{\text{dep}}\) is the concentration of particles deposited on the solid phase (mg kg\(^{-1}\)) and \(\rho\) is the bulk density of the porous medium.

As shown in Equations (6) and (7), the cumulative CMC-NZVI mass deposited increases over successive PVs, and so does the detachment of this deposited mass (Bradford and Bettahar, 2006; Phenrat et al., 2010; Torkzaban et al., 2007). The net effect is a gradual increasing trend in effluent concentrations over time. Fig. 4b shows that the transport model that accounts for aggregation kinetics as well as particle detachment can be fitted well \((r^2 > 0.95)\) to the experimental data obtained from column experiments. The fitted parameters in Equations (6) and (7) are \(k_{\text{det}}\) and \(\alpha_{\text{pc}}\), and the values are presented in Table 2. The single fitted value of \(k_{\text{det}}\) of 0.005 min\(^{-1}\) in this study is within the range (0.001–0.015 min\(^{-1}\)) reported in other studies conducted with latex particles of submicron to micron-sized spheres (Bradford et al., 2003; Li et al., 2005; Tong and Johnson, 2006). Additional experimental data confirming detachment of CMC-
NZVI are however needed to demonstrate particle detachment, and will be addressed in future work.

The value of \( \alpha_{pc} \) is expected to be constant for different concentrations of the CMC-NZVI suspensions. However, the observed increase in \( \alpha_{pc} \) with particle concentration suggests enhanced deposition at higher influent concentrations and can be attributed to the effective increase in IS with increasing CMC-NZVI concentrations as explained in Section 3.1. The values of \( \alpha_{pc} \) obtained in this study range from 0.05 to 0.12 as reported in Table 2, and are in the range of values of 0.065–0.072 reported in other studies conducted at a similar IS (Phenrat et al., 2009; Saleh et al., 2008).

The effect of Na\(^+\) concentration on transport and deposition was assessed by additional column transport experiments where particle suspensions of 0.2 g L\(^{-1}\) CMC-NZVI were prepared in electrolyte solutions of 0.1 mM and 10 mM NaHCO\(_3\) and all other experimental parameters unchanged. The IS of 10 mM was chosen as it was similar to the effective IS of the 0.725 g L\(^{-1}\) suspension based on Na\(^+\) concentrations (Table 2). Fig. 5 shows that the relative effluent CMC-NZVI mass concentrations (\(C/C_0\)) at 8 PVs are 0.66 and 0.40 for IS of 0.1 mM and 10 mM, respectively. Indeed, the deposition of CMC-NZVI increased in the presence of higher amounts of Na\(^+\) in the electrolyte.

4. Conclusion

The effects of particle concentration on aggregation and transport of CMC-NZVI was investigated. With increases in particle concentration, more rapid increase in average particle size with time was observed because of increased particle–particle attachment efficiency and number of collisions. A coupled aggregation–transport model demonstrated that the initial particle size distribution of a CMC-NZVI suspension determines the magnitude of the single-collector contact efficiency as a result of aggregation and leads to a time-dependent deposition rate coefficient. Column experiments with CMC-NZVI at different concentrations showed a gradual increase in effluent particle concentration over eight pore volumes, and the non-steady state change in effluent concentration was more rapid with increasing particle concentrations. The increases in effluent concentrations beyond approximately 5 PV were however higher than what was accounted for by fitting the coupled aggregation-transport model and it is proposed that detachment of deposited particles contributed to the increasing effluent concentrations, especially at higher PVs. Particle deposition increased with higher CMC-NZVI influent concentrations and was attributable to increases in Na\(^+\) in solution from the higher doses of Na-CMC and NaBH\(_4\) present in more concentrated particle suspensions. Such effects of CMC concentration on aqueous chemistry and transport have not been reported to date.

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Appendix Supplementary material


References


