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Modeling coupled nanoparticle aggregation and transport in porous media: A Lagrangian approach

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ABSTRACT

Changes in nanoparticle size and shape due to particle–particle interactions (i.e., aggregation or agglomeration) may significantly alter particle mobility and retention in porous media. To date, however, few modeling studies have considered the coupling of transport and particle aggregation processes. The majority of particle transport models employ an Eulerian modeling framework and are, consequently, limited in the types of collisions and aggregate sizes that can be considered. In this work, a more general Lagrangian modeling framework is developed and implemented to explore coupled nanoparticle aggregation and transport processes. The model was verified through comparison of model simulations to published results of an experimental and Eulerian modeling study (Raychoudhury et al., 2012) of carboxymethyl cellulose (CMC)-modified nano-sized zero-valent iron particle (nZVI) transport and retention in water-saturated sand columns. A model sensitivity analysis reveals the influence of influent particle concentration (ca. 70 to 700 mg/L), primary particle size (10–100 nm) and pore water velocity (ca. 1–6 m/day) on particle–particle, and, consequently, particle–collector interactions. Model simulations demonstrate that, when environmental conditions promote particle–particle interactions, neglecting aggregation effects can lead to under- or over-estimation of nanoparticle mobility. Results also suggest that the extent to which higher order particle–particle collisions influence aggregation kinetics will increase with the fraction of primary particles. This work demonstrates the potential importance of time-dependent aggregation processes on nanoparticle mobility and provides a numerical model capable of capturing/describing these interactions in water-saturated porous media.

1. Introduction

Stability of nanoparticles (NPs) in aqueous systems is a key factor controlling their transport and ultimate fate in aqueous environments (D. Lin et al., 2010). Changes in particle shape and size resulting from particle–particle interactions (i.e. aggregation) may significantly alter NP transport potential (Solovitch et al., 2010) as well as their reactivity (Klaine et al., 2008). Indeed, there have been numerous reports of the effect of particle aggregation on NP transport in porous media (e.g., Bian et al., 2011; Fang et al., 2009; Klaine et al., 2008; Raychoudhury et al., 2012; Solovitch et al., 2010; Wiesner and Bottero, 2007). In general, aggregation will be controlled by the properties of particles (e.g., size, chemical composition, surface charge, surface roughness and heterogeneity), and chemistry of the aqueous phase (e.g., ionic strength, pH, and NOM) (Bian et al., 2011).

Theoretically, the kinetics of particle aggregation depends on the magnitude of the electrostatic energy barrier. Particles that overcome the energy barrier will aggregate with another particle in a deep primary energy minimum (Elimelech et al., 1995). The height of the energy barrier for NP deposition or aggregation depends on the size of the interacting particles, with smaller particles (i.e. NPs versus micrometer-sized particles) exhibiting much lower energy barriers (Elimelech and O'Meila, 1990;

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Petosa et al., 2010). Thus, it is expected that NPs will aggregate more in the primary minimum (Petosa et al., 2010), implying a higher propensity for aggregation than that observed for larger colloids. It has also been suggested that NPs which aggregate in primary energy minima are less likely to dissociate following changes in solution chemistry, such as ionic strength reduction or changes in pH (Chen and Elimelech, 2006).

Depending upon particle surface and solution chemistry, aggregation can influence particle–collector interactions (i.e. transport and retention) by increasing the effective particle hydrodynamic size. According to colloidal filtration theory (Yao et al., 1971), hydrodynamic size strongly influences the behavior of particles approaching collector surfaces. Thus, consideration of particle–particle interactions is imperative when attempting to predict the transport and retention of NPs in porous media (Petosa et al., 2010). For example, for many metallic particles, such as nZVI, aggregation can be one of the main processes governing the environmental fate of nanoparticles, particularly at high concentrations (Phenrat et al., 2009). The classical clean bed filtration theory however, does not incorporate particle–particle interactions that account for spatial and temporal variations in particle sizes observed during aggregation within a porous medium.

Smoluchowski (1917) first provided a mathematical foundation for the description of aggregation kinetics. In the past few decades, the various processes governing particle transport in porous media have been subject to extensive investigation (Chen and Elimelech, 2006; Elimelech and O'Meila, 1990; Li et al., 2008; Yao et al., 1971). A coupling of the mathematical formulations representing aggregation kinetics and particle transport is complicated by the fact that conventional Eulerian models employ a single particle to represent an entire population of particles and do not address non-uniform particle characteristics. Thus, very few modeling investigations have explored the coupling of NP transport and aggregation. Chatterjee and Gupta (2009) attempted to overcome the limitation of an Eulerian formulation by solving a separate transport equation for each family of aggregates (i.e. "n" separate partial differential equations (PDEs) for colloidal monomers, dimers, trimers, and "n"-mers) with second order production/decay terms estimated from the Smoluchowski equation. However, in their numerical implementation, they neglected particle–particle interactions that may occur during transport through a porous medium. More recently, using a similar multiple transport equation formulation, Raychoudhury et al. (2012) developed and applied an Eulerian finite difference-based model to simulate the transport of carboxymethyl cellulose (CMC)-modified nanometer sized particles of zero-valent iron (nZVI) in laboratory-scale, water-saturated sand columns. Their approach, unlike that of Chatterjee and Gupta (2009), incorporates particle–particle interactions during transport through porous medium, however, it is subject to two limitations: (1) the assumption of binary collisions, and (2) a finite number of primary particles for the largest cluster.

In this work, a more general Lagrangian approach for coupling particle–collector and particle–particle interactions is presented that does not share the limitations of the Eulerian approaches noted above. This approach, based upon the random-walk particle tracking (RWPT) method, can be easily coupled with any flow model because of the simplicity of the explicit equations. In addition, through the implementation of particles as discrete mass parcels, global mass conservation is readily satisfied (Salamon et al., 2006). Model development and implementation are described below, followed by a comparison of model simulations with those from an existing Eulerian model (Raychoudhury et al., 2012) to verify the accuracy of the Lagrangian model. A model sensitivity study is then presented to demonstrate model capabilities and to explore the effects of changes in physicochemical properties on particle–particle and, subsequently, particle–collector interactions.

2. Mathematical model

A general one-dimensional mass balance equation describing the transport of NPs in porous media is given as (Elimelech and O'Meila, 1990):

$$\frac{\partial}{\partial t}\left(\theta_w C_w^{NP} + \rho_b \omega_s^{NP}\right) + \frac{\partial}{\partial x}\left[\theta_w\left(v_w C_w^{NP} - D_{w_{NP}}^h \frac{\partial C_w^{NP}}{\partial x}\right)\right] = r^{NP} \quad (1)$$

where C_w^{NP} [mg/L] and ω_s^{NP} [mg/kg dry soil] are the aqueous and solid phase concentrations of NPs, respectively; θ_w [–]and ρ_b [kg/m^3] are the medium moisture content and bulk density, respectively; and v_w [m/s] and $D_{w_{NP}}^h$ [m^2/s] are the pore-water velocity and hydrodynamic dispersion coefficient of the NPs, respectively. The sink/source term r^{NP} [mol/m^3 s] is the net molar rate of consumption/production of NPs in the aqueous phase per unit bulk volume. The second term on the left hand side of Eq. (1) represents particle–collector interactions (i.e. NP attachment) and is here represented by a modified form of the clean-bed filtration theory (CFT) (Yao et al., 1971):

$$\frac{\rho_b}{\theta_w}\frac{\partial \omega_s^{NP}}{\partial t} = k_{att}\,\psi_{att} C_w^{NP} - \frac{\rho_b}{\theta_w} k_{det}\,\omega_s^{NP}. \quad (2)$$

Here $\psi_{att} = 1 - \frac{\omega_s^{NP}}{\omega_{s,max}^{NP}}$ [–], with $\omega_{s,max}^{NP}$ [mg/kg dry soil] denoting the retention capacity of the porous medium, is a site blocking function and k_{att} [1/s] and k_{det} [1/s] are first-order attachment and detachment constants. Note that, if $\psi_{att} = 1$, Eq. (2) is consistent with the classical CFT model which assumes an unlimited capture capacity for the collector surfaces.

According to the CFT, particles are removed from the suspension by three processes, interception, diffusion to the collector surface, and sedimentation. The particle attachment rate constant is typically expressed as (Yao et al., 1971):

$$k_{att} = \frac{3(1-\theta_w)v_w}{2d_c}\alpha_{PC}\cdot\eta_0 \quad (3)$$

where d_c [m] is a representative collector (sand grain) diameter, α_{PC} [–], the attachment efficiency, represents the fraction of collisions that result in attachment of particles to the collector surface, and, η_0 [–], the single-collector contact efficiency, is a measure of the frequency of particle collisions with soil collector surfaces. η_0 is a function of physical characteristics of the system, which include particle diameter, d_p [m]. In this work, η_0-values are estimated from an empirical correlation presented by Tufenkji and Elimelech (2004).