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Modeling and sensitivity analysis on the transport of aluminum oxide nanoparticles in saturated sand: Effects of ionic strength, flow rate, and nanoparticle concentration

Tanzina Rahman, Harry Millwater, Heather J. Shipley *

University of Texas at San Antonio, Department of Civil and Environmental Engineering, One UTSA Circle, San Antonio, TX 78249, USA

HIGHLIGHTS

- Nanoparticle transport was effectively modeled using a two kinetic-site model.
- Fast attachment and blocking were the predominant mechanisms to improve model fit.
- The model does well at predicting nanoparticle breakthrough under varying conditions.
- This study demonstrates the importance of using sensitivity analysis with modeling.

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ABSTRACT

Aluminum oxide nanoparticles have been widely used in various consumer products and there are growing concerns regarding their exposure in the environment. This study deals with the modeling, sensitivity analysis and uncertainty quantification of one-dimensional transport of nano-sized (~82 nm) aluminum oxide particles in saturated sand. The transport of aluminum oxide nanoparticles was modeled using a two-kinetic-site model with a blocking function. The modeling was done at different ionic strengths, flow rates, and nanoparticle concentrations. The two sites representing fast and slow attachments along with a blocking term yielded good agreement with the experimental results from the column studies of aluminum oxide nanoparticles. The same model was used to simulate breakthrough curves under different conditions using experimental data and calculated 95% confidence bounds of the generated breakthroughs. The sensitivity analysis results showed that slow attachment was the most sensitive parameter for high influent concentrations (e.g. 150 mg/L Al_2O_3) and the maximum solid phase retention capacity (related to blocking function) was the most sensitive parameter for low concentrations (e.g. 50 mg/L Al_2O_3).

1. Introduction

Today, nanoscale materials are used in a variety of fields such as electronic, biomedical, pharmaceutical, cosmetic, energy, environmental, and materials. Predominantly, metal oxide nanoparticles are being used in various fields such as water treatment, medicine, cosmetics and engineering (Sadiq et al., 2011). Among them, aluminum oxide nanoparticles are used in fuel production as energetic material, in light bulbs and fluorescent tubes, paints, advanced ceramics, and as a flame retardant agent (Darlington et al., 2009) due to their unique properties such as low melting point, increased light absorption, high heat of reaction, and fast reaction due to their small size (Theodore and Kunz, 2005). Unfortunately, almost no federal or state laws have been specifically established that regulate the manufacturing, transport, use, sale, or disposal of nanomaterials as is the case in many parts of the world (Popovsky, 2011). Due to their widespread application, they will eventually be released into the environment where their fate and behavior are barely known (Sadiq et al., 2011) and could have implications on ecological health. Therefore, understanding the mechanisms of mobility is necessary for the assessment of their risk in the environment.

Traditional colloid filtration theory (CFT) describes three transport mechanisms for colloids: diffusion, interception, and sedimentation for nanoparticle retention in porous media (Tufenkji and Elimelech, 2004). However, research suggests that other physical mechanisms such as straining (Auset and Keller, 2004; Bradford et al., 2005; Auset and Keller, 2006; Xu et al., 2006; Torkzaban et al., 2008) and blocking (Song and Elimelech, 1993; Chowdhury et al., 2011) are important in the removal of nanoparticles from suspension (Bradford et al., 2002, 2004; Jaisi et al., 2008; Li et al., 2008; Jaisi and Elimelech, 2009; Liu et al., 2009). Modeling of nanoparticle transport considering only traditional CFT cannot fully explain the deposition behavior of the

* Corresponding author. Tel.: +1 210 458 7926; fax: +1 210 458 6475.
E-mail address: heather.shipley@utsa.edu (H.J. Shipley).

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nanoparticles in porous media. Therefore, the inclusion of other physical mechanisms (e.g. blocking and straining) in transport modeling is necessary to fully explain the retention of nanoparticles in porous media (Lecoanet et al., 2004; Lecoanet and Wiesner, 2004; Jaisi et al., 2008; Jaisi and Elimelech, 2009; Liu et al., 2009).

Recent studies (Zhang et al., 2012; Mattison et al., 2011; Kasel et al., 2012) show that nanoparticle transport in porous media can be modeled using a two site transport model which considers other physical mechanisms such as blocking and straining. These studies have focused on carbon based nanoparticles, fullerene (nC_{60}) and multi-walled carbon nanotubes (MWCNT). Zhang et al. studied the transport of fullerene nanoparticles in saturated sand and sandy soil. They used the two site model that takes into account both the blocking and straining effect which provided improved agreement between the numerical modeling and experimental results (Zhang et al., 2012). In addition, a study by Mattison et al., looking at the transport of multi-walled carbon nanotubes in four different quartz sands found that the dual deposition model considering fast and slow attachments along with a blocking term significantly improved the agreement between numerical modeling and experimental results (Mattison et al., 2011). Another study with multi-walled carbon nanotubes looked at the effect of input concentration and grain size in high purity quartz sands using a one site kinetic retention model including a blocking term. The breakthrough curves and the retention profiles were simulated using a numerical model that accounts for time- and depth-dependent blocking functions (Kasel et al., 2012).

Most of these studies have looked at carbon based nanomaterials and attempted to fit the experimental data of nanoparticle transport in packed columns with one-dimensional transport models. Moreover, fewer studies have dealt with parameter sensitivity analysis on transport models (Cawlfield and Wu, 1993; Corapcioglu and Choi, 1996; Sun et al., 2001) and none to the authors' knowledge have looked at sensitivity analysis and uncertainty quantification for nanoparticle transport. In this study, breakthrough curves (BTCs) for aluminum oxide nanoparticles through saturated packed sand were fitted with a one-dimensional two kinetic site transport model. The model takes into account the blocking phenomenon that was suggested to be a physical mechanism for aluminum oxide nanoparticle removal in sand (Rahman et al., 2013). Experimental BTCs for different ionic strengths, flow rates, and nanoparticle concentrations were fitted with the two-kinetic-site model in this research. The same model was also used to quantify uncertainty in the simulated breakthrough curves. In addition, sensitivity analyses were carried out to determine the most influencing parameter on nanoparticle transport based on the two-kinetic-site model.

2. Materials and methods

2.1. Materials and column transport experiments

The experimental results from the column transport experiments were previously published in Rahman et al. (2013). In general, the aluminum oxide nanoparticles were 99% pure. The primary particle size was measured using SEM to be 18.4 ± 4.1 nm with a dynamic light scattering (DLS) particle size of 81.7 ± 2.5. The surface area was 200 m^2/g and the point of zero charge (PZC) was determined to be at pH 9.38. White quartz sand was used as the porous medium. The principal component of this sand is silicon dioxide, with a particle size between 50 and 70 mesh (237 ± 21.5 μm) and a PZC at pH 3.1. Further details on the materials and methods used can be found in Rahman et al. (2013).

Bromide tracer tests were done to determine the hydraulic properties of the column using potassium bromide (KBr) as a tracer chemical. The experiments were conducted using a glass chromatographic column of 15 mm inner diameter, which was packed with sand to a depth of 70 mm. Aluminum oxide nanoparticles were diluted in background solution according to the desired concentrations before injection. Before the injection of the nanoparticle solution, they were sonicated for 30 min. The sand column was equilibrated with background solution (DI water, 1, 10 or 100 mM NaCl for corresponding experiments) for 40 min before the injection of nanoparticles. The suspension was injected into the column at a constant flow rate (212.2 μL/min, 848.7 μL/min, 1273 μL/min and 2546 μL/min) and different nanoparticle concentrations (50, 150, 400 mg/L). After the injection of the nanoparticle suspension, nanoparticle free solution was injected and the effluents were collected. The solutions were acid digested, diluted and measured on ICP-OES. Breakthrough curves of aluminum as a function of the number of pore volumes passing through the column were used to compare the initial concentration injected with the effluent concentration (C/C_0). At the end of each column experiment, the sand column was cut into seven sections to measure the mass of nanoparticles that remained in the sand. The total mass (mass in the effluent + mass recovered from the sand) ranged between 90 and 100% of the initial mass (Rahman et al., 2013).

2.2. Mathematical modeling

A one-dimensional advection–dispersion equation along with a mass balance equation was used as the nanoparticle transport model where the deposition of nanoparticles was subjected to two different types of attachment sites in the porous media (Mattison et al., 2011):

$$\frac{\partial C}{\partial t}+\frac{\rho_b}{f}\frac{\partial S}{\partial t}+v\frac{\partial C}{\partial t}-v\lambda\frac{\partial^2 C}{\partial x^2}=0 \tag{1}$$

$$\frac{\rho_b}{f}\frac{\partial S}{\partial t}-k_1 C\psi-k_2 C+\frac{\rho_b k_{\mathrm{det}}}{n}S=0 \tag{2}$$

where C is the concentration of nanoparticles suspended in the aqueous phase [M L^{-3}], t is time (T), ρ_b is the bulk density of the solid phase [M L^{-3}], f is the porosity, S is the amount of nanoparticles attached to the solid phase [M M^{-1}] (can be referred to as $S = 1 - C$), v is the pore water velocity [L T^{-1}], x is the spatial dimension in the column [L], k_{det} is the rate constant for detachment of nanoparticles from the surface of collectors [T^{-1}], λ is the longitudinal dispersivity [L] ($v\lambda$ = dispersion coefficient, D [L^2 T^{-1}]), and ψ is a site blocking term.

$$\psi=1-\frac{S}{S_{\max}} \tag{3}$$

where S_{max} is the maximum solid phase concentration, and k_1 and k_2 are the removal rate constants for fast and slow attachments, respectively, where the fast attachment is subject to a site blocking term and the slow attachment is not. These constants are associated with traditional removal mechanisms (interception, sedimentation and diffusion) and adapted as:

$$k_1=\frac{3\alpha_1\eta_0(1-f)v}{2d_c} \tag{4}$$

$$k_2=\frac{3\alpha_2\eta_0(1-f)v}{2d_c} \tag{5}$$

where, d_c is the collector diameter [L], k_1 and k_2 are the attachment efficiencies [T^{-1}] associated with fast and slow depositions respectively, α_1 and α_2 are corresponding sticking efficiencies, and η_0 is the single collector efficiency (calculated from experimental data). The fast and slow attachments are considered corresponding to favorable and unfavorable sites for attachment in sand.