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# Transport of stabilized iron nanoparticles in porous media: Effects of surface and solution chemistry and role of adsorption

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### HIGHLIGHTS

- Iron/aluminum oxides enhance retention of CMC-stabilized ZVI nanoparticles in soil.
- A transport model is proposed to quantify role of adsorption in particle deposition.
- Metal oxide coatings increase adsorptive removal of the nanoparticles by 1.8 times.
- Doubling flow velocity to  $0.076 \text{ cm s}^{-1}$  lowers the filtration rate constant by 74%.
- Neutral stabilizer (starch) increases the nanoparticle retention by 7% than CMC.

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### ABSTRACT

Carboxymethyl cellulose (CMC) stabilized zero-valent iron (ZVI) (CMC-ZVI) nanoparticles have been extensively tested for remediation of soil and groundwater. This study investigated effects of iron oxide and aluminum oxide on retention and transport of CMC-ZVI nanoparticles, which have a mean hydrodynamic diameter of 155 nm. Column breakthrough experiments showed that the metal oxides coatings on quartz sand greatly enhanced particle retention. A mechanistically sounder transport model was proposed by incorporating a Langmuir-type adsorption rate law into the classic convection–dispersion equation with the adsorption parameters derived from independent experiments. The model allows for a quantitative evaluation of the role of adsorption. While filtration is the primary mechanism for particle retention at lower pore velocities, adsorption becomes more significant at elevated velocities. The presence of  $40\text{--}80 \text{ mg-CL}^{-1}$  of natural organic matter and high ionic strength (up to  $200 \text{ mM CaCl}_2$ ) had negligible effect on the breakthrough profiles of the nanoparticles. Starch, a neutral polysugar stabilizer, was also tested as a stabilizer. Starch-stabilized ZVI nanoparticles, with a mean hydrodynamic diameter of 303 nm, displayed a higher particle retention than CMC-ZVI. The information and modeling approach can facilitate our understanding of fate and transport of stabilized ZVI nanoparticles under various geochemical conditions.

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## 1. Introduction

Zero valent iron (ZVI) nanoparticles have received considerable attention for in-situ remediation of contaminated soil and groundwater [1–3]. ZVI nanoparticles hold great potential for diverse remediation applications, from reductive dechlorination [4] to immobilization of metals and radionuclides [5,6] in the subsurface.

Based on a preliminary survey conducted by the U.S. Environmental Protection Agency (USEPA) [7], ZVI had been the most employed particulate materials used for in situ remediation.

ZVI nanoparticles are known to exhibit a core–shell structure, with an iron oxide ( $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$ ) shell surrounding an  $\text{Fe}^\circ$  core [8]. Due to the van der Waals attractive force, dipole interactions and magnetic interactions, synthetic ZVI nanoparticles tend to aggregate rapidly into micro-scale, fractal, and chain-like clusters [9,10]. The particle aggregation not only causes loss in chemical reactivity, but also reduces particle deliverability in soils, which is

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essential for in situ remediation [11]. Non-stabilized or aggregated ZVI nanoparticles are not deliverable in soil [12,13].

To facilitate transport of nZVI nanoparticles in porous media, various surface modification techniques have been investigated using polyelectrolytes, polymers and surfactants as a coating agent or stabilizer [12,14]. The surface coatings introduce electrostatic and/or steric repulsions between nanoparticles and facilitate their transport in porous media. It was found that the type and concentration of the surface coatings greatly affect the particle aggregation, size and transport (He and Zhao [3]). In addition, environmental factors, such as flow conditions [15,16], collector properties [17,18], solution chemistry [19,20] and nanoparticle surface properties [8,21], can affect the stability and mobility of ZVI nanoparticles in porous media. For instances, the mobility of surface-modified ZVI was enhanced with increasing interstitial flow velocities due to reduced gravitational sedimentation and Brownian diffusion [15]. Raychoudhury et al. [17] observed an increased retention of ZVI nanoparticles with finer sands (from 775 to 150  $\mu\text{m}$ ) due to straining and/or wedging at the grain-to-grain contact point. Phenrat et al. [52] reported the ZVI concentration has no effect on the transport behavior of poly(styrene sulfonate)-modified ZVI (PSS-ZVI), while Liang et al. [22] observed an increasing mobility of polyvinylpyrrolidone-stabilized ZVI when the ZVI concentration was increased from 0.5 to 2  $\text{g L}^{-1}$ . The presence of naturally occurring organic molecules was reported to facilitate particle transport by enhancing electrosteric repulsion among nanoparticles [23–25]; however, organics may also serve as an inter-particle bridging agent between nanoparticles, resulting in significant aggregation and sedimentation of surface-modified ZVI nanoparticles [26].

Experimental investigations involving the transport of surface-modified ZVI nanoparticles are often conducted in glass beads or in cleaned quartz sand. There have been very limited studies with heterogeneous media [18,27]. However, common soil minerals, such as iron (hydr) oxides and aluminum (hydr) oxide, may strongly interact with the nanoparticles and the coating agents (which are often strong ligands), thereby strongly affecting the subsurface transport of nanoparticles [28–32]. Zhuang and Jin [33] studied transport of two bacteria-adsorbing agents in a goethite-coated sand column and observed that attachment of bacteria-adsorbing agents was favored with the presence of goethite. Wang et al. [34] observed a similar effect of iron oxyhydroxide coatings on transport of hydroxyapatite nanoparticles. However, the transport of surface-modified ZVI nanoparticles in metal oxides coated sand column has not been investigated.

Transport and deposition of nanoparticles in saturated porous media is typically interpreted using the classic convection–diffusion equation coupled with the filtration theory [15,16,21,22,35,36]. According to the filtration theory, particles are retained in porous media through Brownian diffusion, interception, and gravitational sedimentation. Apparently, this theory does not distinguish adsorption (i.e., accumulation of particles on the collector surface through direct particle–collector interactions) from other filtration removal mechanisms. Consequently, the role of nanoparticle adsorption on the collector grains has not been addressed. Prior work [37] revealed that CMC-stabilized ZVI nanoparticles can be strongly adsorbed to a sandy soil. Yet, quantitative information remains missing on how adsorption affects the particle deposition and transport in porous media.

The overall goal of this study was to investigate the effects of surface metal oxides and solution chemistry on transport of CMC-stabilized ZVI nanoparticles and determine the role of particle adsorption. The specific objectives were to: (1) examine the breakthrough behaviors of CMC-stabilized ZVI nanoparticles through quartz sand, iron oxide-coated sand (IOCS), and aluminum oxide-coated sand (AOCS); (2) elucidate the effects of surface metal oxide coatings on particle transport; (3) simulate the particle transport

using a modified mathematical model that quantifies contributions of adsorption and filtration to the overall particle deposition; and (4) determine the effects of particle concentration, ionic strength, natural organic matter (NOM) and polymer stabilizers on the transport of ZVI nanoparticles.

## 2. Material and methods

### 2.1. Chemicals

Chemicals used are presented in Section 1 of the Supplementary material (SM). Dissolved NOM was obtained by extracting a potting soil (HYPONEX®, OH, USA) following the method described in Ref. [37]. In brief, 63 mL of deionized (DI) water was mixed with 36 g of the potting soil for 3 days. Upon centrifugation, the supernatant was filtered through a 0.45  $\mu\text{m}$  cellulose membrane and then the filtrate was stored in a refrigerator at 4 °C. The concentration of dissolved NOM was determined to be 860  $\text{mg L}^{-1}$  as total organic carbon (TOC) using a ultraviolet–persulfate TOC analyzer (Tekmar-Dohrmann Phoenix 8000, Mason, OH). Bromide in the tracer tests was measured using an Ion Chromatograph (DX-120, Dionex, Sunnyvale, CA) with an AS14 analytical column.

### 2.2. Preparation of stabilized ZVI nanoparticles

CMC- or starch-stabilized ZVI nanoparticles were prepared following the particle stabilization technique [3,12]. In each batch, a nanoparticle suspension was first prepared at 1.0  $\text{g L}^{-1}$  as Fe in the presence of 0.8% CMC or starch, the stock suspension was immediately diluted to 0.2  $\text{g L}^{-1}$  using deoxygenated DI water, and then used freshly in the subsequent tests. The hydrodynamic particles size was determined through the dynamic light scattering (DLS) measurements and the  $\zeta$ -potential of the nanoparticles was obtained using a Zetasizer Nano analyzer (Malvern, Southborough, MA). The concentration of the ZVI nanoparticles was determined as follows: first, the nanoparticles were completely dissolved using concentrated HCl at a HCl-to-ZVI suspension volume ratio of 1:4 and then analyzed for total Fe using an inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Liberty-Series II, Varian, Palo Alto, CA).

### 2.3. Preparation of porous media

Quartz sand (Accusand 40/60) (0.21–0.42 mm) was purchased from Unimin Corporation (Le Sueur, MN, USA). Prior to use, the sand grains were cleansed as described in Ref. [15] and Section 2 of SM. IOCS was prepared based on a modified precipitation method [38,39]. In brief, 150 g of the washed quartz sand was first mixed with 80 mL of 2.1 M  $\text{Fe}(\text{NO}_3)_3$ . The pH of the slurry was raised to 12 by drop-wise addition of a 10 M NaOH solution and then oven-dried at 110 °C for 14 h. Upon cooling, the resultant material was repeatedly washed with DI water, and oven-dried at 110 °C for 3 h, and then air-dried for 21 h at room temperature; the wash–dry process was repeated until no iron leached off from the sand. AOCS was prepared based on the method by Kuan et al. [40]. Briefly, 150 g of the quartz sand was soaked with 100 mL of a 1 M of  $\text{AlCl}_3$  solution. Then, a 4.0 M NaOH solution was added drop-wise to raise the pH to 11. After mixing for 15 min, the suspension was oven-dried at 70 °C for 2 days. The sand was then repeatedly washed with DI water followed by oven-drying at 70 °C for 3 h until the rinse-off was free of aluminum. There was no appreciable change in the size of the sand grains upon the coatings per standard sieve measurement. The total amount of iron and alumina loaded on the sand was determined to be 0.074 and 0.13  $\text{mmol g}^{-1}$ , respectively, per EPA Method 3050b using the ICP-AES.

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