The influence of humic acid and clay content on the transport of polymer-coated iron nanoparticles through sand

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HIGHLIGHTS

- Humic acid enhanced the mobility of bare nZVI.
- The transport of CMC90K-nZVI was not significantly affected by humic acid.
- The impact of kaolinite on nZVI retention was more pronounced at lower pore water velocities.

ARTICLE INFO

ABSTRACT

The introduction of nanoscale zero valent iron (nZVI) into the subsurface has recently received significant attention as a potentially effective method for remediation of source zones of chlorinated solvents present as dense nonaqueous phase liquids (DNAPL). One of the challenges in the deployment of nZVI is to achieve good subsurface nZVI mobility to permit delivery of the nZVI to the target treatment zone. Stabilization of nZVI with various polymers has shown promise for enhancing nZVI subsurface mobility, but the impact of subsurface conditions on nZVI mobility has not been fully explored. In this study, the effect of humic acid and kaolinite on the transport of polymer-stabilized nZVI (carboxylmethyl cellulose-surface modified nZVI, CMC90K-RNIP) in sand was investigated using column experiments. In addition, effects of electrolytes on the stability of CMC90K-RNIP in the presence of humic acid, and the stability of humic acid-coated reactive nanoscale iron particles (HA-RNIP) at various humic acid concentrations were investigated. Humic acid enhanced the mobility of bare RNIP, whereas the transport of CMC90K-RNIP was not significantly affected by humic acid injected as a background solution, except at the highest concentration of 500 mg/L. At lower pore water velocity, the effect of humic acid on the transport of CMC90K-RNIP was greater than that at high water velocity. Adding kaolinite up to 2% by weight to the sand column reduced the retention of CMC90K-RNIP, but further increases in kaolinite content (to 5%) did not significantly affect nZVI retention. The impact of kaolinite on nZVI retention was more pronounced at lower pore water velocities.

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1. Introduction

The transport and deposition of nano-sized zero valent iron particles (nZVI) in porous media are of considerable interest, as subsurface injection of nZVI is being investigated as a remedial technology for chlorinated solvent source zones. Bare nZVI (RNIP-10DS, manufactured by Toda Kyogo Corp.) without surface-modification has been found to rapidly form aggregates of chain-like structures due to the magnetic forces between particles (Phenrat et al., 2007). This aggregation can cause pore plugging, gravitational settling and particle deposition (Phenrat et al., 2007), and results in ineffective in-situ remediation. Therefore, nZVI

suspensions are usually made by surface modification through sorption of macromolecules to enhance the nZVI stability and mobility. The stabilization of nZVI particles with negatively charged polymers is due to electrosteric interactions, a combination of electrostatic and steric interactions (Pincus, 1991). For particles that are only electrostatically stabilized, the electric double layer screening length as a function of ionic strength and ionic composition will be influenced by electrolytes. And the electrostatic double layer repulsive interaction between particles will affect their stability and mobility (Pincus, 1991; Saleh et al., 2008). Steric stabilization is generally produced by adsorbing or grafting a polymer onto the surface of the particles (Friz et al., 2002). End grafting may be achieved by covalently bonding the polymer to the surface with a chemically active end group (Pincus, 1991). Steric stabilization is robust and less sensitive to electrolytes, compared to pure

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electrostatic stabilization (Sung and Piirma, 1994; Friz et al., 2002). Surface-coating of nZVI with polymers (e.g. carboxylmethyl cellulose (CMC), polystyrene sulfonate or polyaspartate) has been shown to enhance the stability of nZVI, producing a more negative zeta potential and decreasing aggregation of nZVI particles (Phenrat et al., 2008; Tiraferri et al., 2008).

Although the stability of nZVI was increased through adsorption of polymers in laboratory tests, the surface properties and transport behavior of polymer-coated nZVI in the subsurface may be affected by environmental conditions (solution pH, ionic strength, natural organic matter and clay minerals). It is known that natural organic matter (NOM), commonly found in groundwater, readily adsorbs to solid surfaces and nanoparticles. This can change the surface electrochemistry, aggregation and deposition behavior, and therefore the transport of nanoparticles in porous media (Chen and Elimelech, 2008). The major components of NOM include humic acids having carboxylic and phenolic functional groups (Amirbahman and Olson, 1995). Adsorption of humic acid produces both electrostatic and steric stabilization of nanoparticles (Amirbahman and Olson, 1993). For example, the presence of humic acid yielded more negative electrophoretic mobility and reduced aggregation of fullerene nanoparticles due to steric repulsion associated with sorption of humic acid onto the nanoparticle surfaces (Chen and Elimelech, 2007).

Many researchers have investigated the effect of NOM on the stability or transport of iron oxide nanoparticles (Baalousha et al., 2008), carbon nanotubes (Hyung et al., 2007; Hyung and Kim, 2008) and fullerene (C_{60}) nanoparticles (Chen and Elimelech, 2007, 2008; Xie et al., 2008). Johnson et al. (2009) investigated the effect of NOM on the mobility of bare nZVI and Sirk et al. (2009) studied the effect of NOM on the sorption of bare nZVI and polymer-coated nZVI onto silicon dioxide through quartz crystal microgravimetry measurements. Although the effect of NOM on the transport of nanomaterials in porous media including nZVI has been widely studied, it has been limited to bare (unstabilized) nZVI.

Recently, Dong and Lo (2013) investigated the colloidal stability of surface-modified nZVI using polyacrylic acid (PAA), Tween-20, and starch in the presence of humic acid (HA). They found that the adsorption of HA on the surface of PAA-modified nZVI increased the stability of the particles, whereas it stimulated the aggregation of Tween-20-modified nZVI or starch-modified nZVI. Laumann et al. (2014) assessed the mobility of PAA-modified nZVI with co-injection of polyelectrolytes including natural organic matter, humic acid, carboxyl-methyl cellulose, and lignin sulfonate. They found that the co-injection of HA at 50 mg/L did not show any effect on PAA-nZVI transport in quartz sand. Pensini et al. (2013) investigated the interaction between CMC-coated iron particles and magnetite in the presence of humic acid using atomic force microscopy-based force spectroscopy (AFM). They found that the attachment of CMC-coated iron particles onto magnetite was inhibited in the presence of HA at around pH 8 due to repulsive forces.

Investigations of the transport of bare nZVI or polymer-coated nZVI in laboratories have generally been limited to sandy porous media. However, soils in many sites where nZVI injection may be applied will include a fraction of clay minerals. Schrick et al. (2004) investigated the transport of hydrophilic carbon supported nZVI (Fe/C), polyacrylic acid supported nZVI (Fe/PAA), and unsupported nZVI (bare nZVI) in four different soil textural compositions using Fe[BH] (Fe[BH] is nZVI synthesized through reduction of borohydride). The unsupported nZVI eluted most effectively in columns containing clay-rich soils, compared to those containing only sands, while little effect of clay content was observed for supported nZVI. Katsenovich and Miralles-Wilhelm (2009) suggested that the presence of clay minerals resulted in nZVI agglomeration and the formation of clay–iron aggregates ranging between 10 and 100 μm. Üzüm et al. (2009) used kaolinite as a surface modifier to stabilize bare Fe[BH], and demonstrated that the presence of kaolinite resulted in decreased aggregation of bare Fe[BH] (without addition of polymer). Shi et al. (2011) also used clay minerals (bentonite) as a stabilizer and

investigated the effectiveness of bentonite-supported nZVI (B-nZVI) to remove Cr(VI) from aqueous solution. The results showed that bentonite led to an increase of nZVI stability and nZVI specific surface area. However, most studies were limited to the mobility of bare nZVI in the presence of clay minerals or the role of clay mineral as a stabilizer. Recently, Kim et al. (2012) studied the effect of the presence of kaolinite in sand columns on surface-modified nZVI transport. They found that the presence of 2 wt.% kaolinite generally decreased the mobility of surface-modified RNIP in silica sand, but the extent of mobility reduction changed with pH and stabilizer.

In this study, commercial nZVI (RNIP-10DS) manufactured by Toda Kogyo Corp. was used and carboxylmethyl cellulose, sodium salt (CMC90K, M.W. = 90 kg/mol) was selected as the stabilizer polymer. The transport of CMC90K-surface modified RNIP-10DS in sand columns was studied to determine the effects of, humic acid (HA) content, and clay minerals on its mobility. The settling of carboxylmethyl cellulose coated RNIP-10DS (CMC90K-RNIP) in the presence of humic acid and electrolytes, and of humic acid-modified RNIP (HA-RNIP) at various humic acid concentrations was also measured. Classical and extended DLVO theory was used to explain the enhanced transport of polymer-coated RNIP. The attachment efficiency was also calculated by the colloid filtration theory (CFT) model refined by Tufenkji and Elimelech (2004). These laboratory column tests provide useful information on the transport of CMC90K stabilized zero valent iron nanoparticles in porous media where humic acids are present, or where soils have significant clay content.

2. Methods

2.1. Preparation of polymer or humic acid-surface modified nZVI suspension

The bare nZVI obtained from Toda Kogyo Corp. (Schaumberg, IL) was RNIP-10DS. The RNIP-10DS was stored in deionized water at pH 10.6 at a concentration of approximately 300 g/L (Tiraferri and Sethi, 2009) and kept in an anaerobic glovebox (Coy) after being received. A portion of the slurry received was diluted in 1 mM $NaHCO_3$ with deionized Milli-Q water (Millipore Corporation, Bedford, MA) purged with N_2 gas (deionized deoxygenated water) to obtain a 15 g/L stock suspension. It was subsequently agitated in a sonication bath (FS20, Bath Sonicator, 42 kHz ± 6%, Fisher Scientific) for 30 min, and then stored in an anaerobic chamber. Deionized deoxygenated water (DDW) was used in all stock solution preparations. The polymer (sodium salt of carboxylmethyl cellulose (Sigma-Aldrich)) stock solutions were prepared using analytical grade reagents dissolved in 1 mM $NaHCO_3$ (99.7–100.3%, Sigma-Aldrich, Oakville, ON). The nZVI stock solution of 15 g/L was diluted in polymer solution to produce polymer-stabilized nZVI aqueous suspensions at concentrations of nZVI and polymer of 3 g/L and 2 g/L, respectively. The polymer-stabilized nZVI suspensions were sonicated for 30 min in a sonicator bath and then the slurry was equilibrated by end-over-end mixing for 48 h. The nZVI suspension was sonicated for an additional 15 min immediately before stability or mobility tests.

Humic acid (sodium salt form) was purchased from Sigma-Aldrich (St. Louis, MO, USA). The humic acid stock solution was prepared at 1 g/L in deionized water and stirred for 1 h and then filtered with a 0.45 μm PTFE syringe filter (Acrodisc®, HPLC certified) before use. For settling curves of CMC90K-RNIP suspension including humic acid (HA) and electrolytes, HA and electrolytes were added at the time of mixing of CMC90K and nZVI. Sodium chloride (99.5%, Sigma-Aldrich) and calcium chloride (93% granular anhydrous, Sigma-Aldrich) were selected as electrolytes, and all stock solutions were prepared in 1 mM $NaHCO_3$ (99.7–100.3%, Sigma-Aldrich). After mixing, the suspension was sonicated for 30 min and then mixed for 48 h before measuring absorbances for settling curves. The initial particle concentration of nZVI suspension was measured immediately before measuring the absorbance. Table 1 includes the experimental conditions in stability tests for CMC90K-RNIP in