



Oxidation of nanoscale zero-valent iron under sufficient and limited dissolved oxygen: Influences on aggregation behaviors



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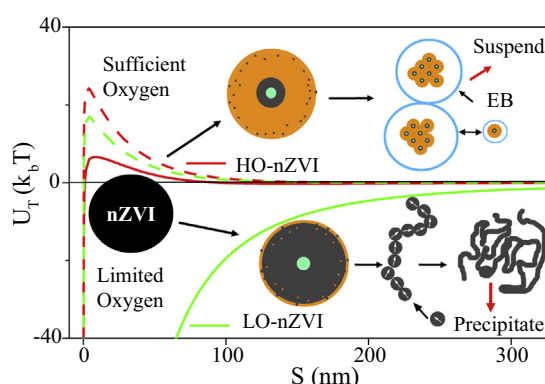
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HIGHLIGHTS

- Two oxidation conditions were designed according to the environmental applications.
- The two oxidized nanoparticles exhibited disparate colloidal behaviors.
- Aggregation formation and aggregation kinetics were elucidated by colloidal theories.
- Dissolved oxygen controlled aggregation by determining composition and magnetization.
- Aggregation morphology decided aggregation kinetics though magnetic.

GRAPHICAL ABSTRACT



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ABSTRACT

Oxidations of nanoscale zero-valent iron (nZVI) under aerobic (dissolved oxygen $\approx 8 \text{ mg L}^{-1}$) and anaerobic (dissolved oxygen $< 3 \text{ mg L}^{-1}$) conditions were simulated, and their influences on aggregation behaviors of nZVI were investigated. The two oxidation products were noted as HO-nZVI (nZVI oxidized in highly oxygenated water) and LO-nZVI (nZVI oxidized in lowly oxygenated water) respectively. The metallic iron of the oxidized nZVI was almost exhausted ($\text{Fe}^0 \approx 8 \pm 5\%$), thus magnetization mainly depended on magnetite content. Since sufficient dissolved oxygen led to the much less magnetite ($\sim 15\%$) in HO-nZVI than that in LO-nZVI ($> 90\%$), HO-nZVI was far less magnetic ($M_s = 88 \text{ kA m}^{-1}$) than LO-nZVI ($M_s = 365 \text{ kA m}^{-1}$). Consequently, HO-nZVI formed small agglomerates ($228 \pm 10 \text{ nm}$), while LO-nZVI tended to form chain-like aggregations ($> 1 \mu\text{m}$) which precipitated rapidly. Based on the EDLVO theory, we suggested that dissolved oxygen level determined aggregation morphologies by controlling the degree of oxidation and the magnitude of magnetization. Then the chain-like alignment of LO-nZVI would promote further aggregation, but the agglomerate morphology of HO-nZVI would eliminate magnetic forces and inhibit the aggregation while HO-nZVI remained magnetic. Our results indicated the fine colloidal stability of HO-nZVI, which might lead to the great mobility in the environment.

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1. Introduction

Nanoscale zero-valent iron (nZVI) exhibited great ability in dechlorinating chlorinated organics (such as trichloroethene, TCE (Elliott and Zhang, 2001)) and immobilizing heavy metals (such

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as Chromium (Liu et al., 2010)) in aquatic environment. Thus nZVI has been widely applied to *in situ* groundwater remediation for more than ten years (Mueller et al., 2012; Yan et al., 2013) and has also been gradually used in wastewater treatment recently (Li et al., 2007, 2013). With the increasing applications of nZVI, there is an urgent need to study the controversial impact of nZVI on its surrounding aquatic environment (Karn et al., 2009). According to toxicology studies, nZVI and iron-related nanoparticle (20–50 mg L⁻¹) would induce oxidative stress and injuries to human cell (Zhu et al., 2011) and fish (Li et al., 2009) as well as introducing risk to environment by acting as the carrier of coexisting contaminations (Sun et al., 2009; Tan et al., 2012). However, some researchers suggested that it was not likely that the use of nZVI for *in situ* remediation could pose significant risk to the environment (Grieger et al., 2010), since nZVI tended to aggregate and precipitate in short duration after introducing into the remediation site, and the mobility of nZVI was asserted to be extremely limited (few centimeters) (Saleh et al., 2008; He et al., 2010).

Nevertheless, oxidation could induce great influences to the colloidal stability as well as the mobility of nZVI. The nZVI would be oxidized if exposed to oxidative matter (e.g. dissolved oxygen), forming an amorphous iron oxide layer (Yan et al., 2010). The oxidized nZVI precipitated slower than fresh nZVI (5 mg L⁻¹ of aged nZVI with “negligible iron content”) (Phenrat et al., 2009) as well as transport further in sandy media (6 g L⁻¹ of nZVI with Fe⁰ ≈ 10 wt%) comparing to the less oxidized nZVI (Fe⁰ = 24 wt% and 50 wt%) (Phenrat et al., 2010). The authors suggested that it was the decrease of magnetization (which induced by the transformation of Fe⁰ to less magnetic oxidizes) which enhanced the particle transport (Phenrat et al., 2010), because magnetic forces acted the crucial role in forming the aggregation of iron-related NPs (Phenrat et al., 2007).

In addition, various chemical transformations of iron would occur under different oxidation conditions. Under anaerobic groundwater condition (Reinsch et al., 2010) and in the “deoxygenated water” (Sarathy et al., 2008), the oxide shell of nZVI was mainly composed of magnetite (magnetite content >70%, the left constituent was Fe⁰). Whereas during the wastewater treatment under saturated dissolved oxygen (Li et al., 2007) and the laboratory-scale removal experiment of heavy metal (exposure to oxygen) (Shi et al., 2011), the nZVI would be oxidized into iron oxide and iron oxyhydroxide. Such diverse composition of oxidized nZVI induced by different oxidation processes might also lead to varied magnetization and consequently different aggregation behaviors. Unfortunately, most studies focused on environmental behaviors of nZVI hardly fully considered the varied oxidations under different conditions.

In order to explore the influences of different oxidations on aggregation behaviors, nZVI was oxidized under different dissolved oxygen conditions (sufficient and limited). A series of comparative tests was performed to investigate the chemical composition, physical properties and colloidal behaviors (aggregation and sedimentation) of the two oxidation products. Moreover, the extended Derjaguin–Landau–Verwey–Overbeek (EDLVO) theory was utilized to theoretically elucidate the aggregation behaviors (morphology and aggregation kinetics) of nZVI oxidized under different levels of dissolved oxygen.

2. Materials and methods

2.1. Preparation of oxidized nZVI

nZVI was provided by the group of Prof. Weixian Zhang, Tongji University. It was synthesized by borohydride reduction following the reported procedure (Martin et al., 2008). nZVI slurry

(about 20 g L⁻¹) was kept in 100% ethanol in sealed bottles for any future use.

Fresh nZVI was oxidized in 500 mL of suspensions (323 ± 5 mgFe L⁻¹, which was similarly with the diluted concentration in applications (He et al., 2010; Kocur et al., 2014), fraction concentration (ϕ) ≈ 5.1 × 10⁻⁵) with sufficient (dissolved oxygen ≈ 8 mg L⁻¹, to simulate the aerobic wastewater treatment) and limited dissolved oxygen (dissolved oxygen <3 mg L⁻¹, to simulate the common condition of groundwater) (three parallel bottles for each condition), noted as HO-nZVI (nZVI oxidized in highly oxygenated water) and LO-nZVI (nZVI oxidized in lowly oxygenated water) respectively. Detailed information about producing oxidized nZVI was given in S1, supplementary data. To investigate the influences of magnetization of NPs, magnetite NP and hematite NP (Fe₃O₄, <50 nm, α-Fe₂O₃, <50 nm, Sigma Aldrich Co., St. Louis, MO) were used as contrasts when investigating aggregation behaviors.

2.2. Analysis of composition

Fe⁰ content of nZVI within five days of oxidation was determined using gas chromatography with a thermal conductivity detector (GC-TCD, GC6890, Agilent technologies Ltd., Santa Clara, CA, detailed information for the method was given in S2, supplementary data).

To investigate the chemical composition of the two oxidation products, the X-ray diffraction analysis (XRD, D8 Advance X, Bruker optics Inc., Karlsruhe, German) was performed on powder samples of HO-nZVI, LO-nZVI, hematite and magnetite. Powder samples of HO-nZVI and LO-nZVI were obtained by filtering each suspension with 0.22-μm filter membrane, then dried and stored under nitrogen circumstance prior to test. The samples were scanned from 10° to 90° in glass holders. Powder samples of HO-nZVI and LO-nZVI were then analyzed by X-ray photoelectron spectrum technology (XPS, PH1500C, Ulvac Ltd., Tokyo, Japan) to investigate the surface chemistry.

2.3. Determination of magnetization

The saturation magnetization (M_s) of the five NPs (nZVI, HO-nZVI, LO-nZVI, magnetite and hematite) was determined by superconducting quantum interference device (SQUID, MPMS (SQUID) VSM system, Quantum Design Inc., San Diego, CA) at a temperature of 298 K using the same powder samples in the XRD and XPS analyses (which were stored under nitrogen circumstance).

2.4. Measurement of zeta-potential

A zeta-potential (ζ -potential) analyzer (Zetasizer Nano ZS90, Malvern Instruments Ltd., Worcestershire, the UK) was used to characterize the surface charge of NPs in each suspension. Suspensions were all diluted to 32 ± 3 mgFe L⁻¹ (ϕ ≈ 4.9 × 10⁻⁶, toxic levels reported in toxicology studies (Li et al., 2009; Chen et al., 2011), 0.1 mmol L⁻¹ NaCl, pH 7.1 ± 0.3). Samples were all ultrasonicated for 5 min while aerating nitrogen before analysis. The ζ -potential of nZVI as the function of oxidizing duration under the sufficient and limited dissolved oxygen was also measured.

2.5. Colloidal behavior of NPs

The samples were prepared (32 ± 3 mgFe L⁻¹, 0.1 mmol L⁻¹ NaCl, pH 7.1 ± 0.3) using the same methods in the analyses of ζ -potential. Morphology of aggregations was observed by transmission electron microscopy (TEM, JEM-2010, JEOL Ltd., Tokyo, Japan). The dynamic laser scatter (DLS) instrument (Zetasizer Nano ZS90, Malvern Instruments Ltd., Worcestershire, the UK) was used for

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