# Influence of fulvic acid on the colloidal stability and reactivity of nanoscale zero-valent iron☆

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A B S T R A C T

This study investigated the effect of fulvic acid (FA) on the colloidal stability and reactivity of nano zero-valent iron (nZVI) at pH 5, 7 and 9. The sedimentation behavior of nZVI differed at different pH. A biphasic model was used to describe the two time-dependent settling processes (i.e., a rapid settling followed by a slower settling) and the settling rates were calculated. Generally, the settling of nZVI was more significant at the point of zero charge ($pH_{pzc}$), which could be varied in the presence of FA due to the adsorption of FA on the nZVI surface. More FA was adsorbed on the nZVI surface at pH 5–7 than pH 9, resulting in the varying sedimentation behavior of nZVI via influencing the electrostatic repulsion among particles. Moreover, it was found that there was a tradeoff between the stabilization and the reactivity of nZVI as affected by the presence of FA. When FA concentration was at a low level, the adsorption of FA on the nZVI surface could enhance the particle stabilization, and thus facilitating the Cr(VI) reduction by providing more available surface sites. However, when the FA concentrations were too high to occupy the active surface sites of nZVI, the Cr(VI) reduction could be decreased even though the FA enhanced the dispersion of nZVI particles. At pH 9, the FA improved the Cr(VI) reduction by nZVI. Given the adsorption of FA on the nZVI surface was insignificant and its effect on the settling behavior of nZVI particles was minimal, it was proposed that the FA formed soluble complexes with the produced Fe(III)/Cr(III) ions, and thus reducing the degree of passivation on the nZVI surface and facilitating the Cr(VI) reduction.

## 1. Introduction

Nanoscale zerovalent iron (nZVI) is being increasingly employed for the in-situ remediation of contaminated soil and groundwater sites that contain chlorinated solvent and heavy metals (Zhang, 2003; Quinn et al., 2005; Lowry, 2007; Phenrat et al., 2009; Grieger et al., 2010). Due to the extremely small particle size and the ability to remain in suspension in the aqueous phase, the reactive nZVI particles can be directly injected into contaminated aquifers (Li et al., 2006; Grieger et al., 2010; Dong and Lo, 2013a, 2013b).

Although at appropriate doses, nZVI can effectively eliminate or transform certain pollutants, its reactivity may be limited by its rapid aggregation (Grieger et al., 2010). Bare nZVI particles tend to aggregate, meaning the separate particles cluster together to form larger particles or adhere to soil particles. This decreases the surface area of the nZVI, thereby decreasing the reactivity of nZVI (He et al., 2007; Grieger et al., 2010). Besides, the laboratory and field studies involving the long-term performance of nZVI have shown that contaminant degradation rates decrease with time because of the formation and accumulation of Fe(III) oxides such as maghemite ($\gamma$-$Fe_2O_3$), magnetite ($Fe_3O_4$), hematite ($\alpha$-$Fe_2O_3$), goethite ($\alpha$-FeOOH) and lepidocrocite ($\gamma$-FeOOH) on the outer layer of aged nZVI (Dong et al., 2012; Guan et al., 2015). Passivation of the nZVI surface occurs when reactive sites are covered with the Fe(III) oxides resulting in significant reduction in efficiency of electron transfer from nZVI to the contaminant. Accordingly, a fundamental understanding of the physicochemical processes controlling the colloidal stability and passivation of nZVI particles is essential in estimating the efficiency of contaminant elimination by nZVI in the geochemical environment.

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The stability and passivation of the nZVI particles depends on the geochemical characteristics of groundwater (e.g., ionic strength, natural organic matters (NOM)) (Giasuddin et al., 2007; Saleh et al., 2008; Manciulea et al., 2009; Chen et al., 2011; Dong and Lo, 2013a, 2013b). The influence of NOM (e.g., humic substances (HS)) on the colloidal stability of nZVI has been widely investigated (Ghosh et al., 2011; Dong and Lo, 2013a, 2013b). The interactions between HS and nZVI are complex, resulting in decreased dispersion or increased aggregation of the nanoparticles, depending on conditions, with dispersion caused by charge and steric stabilization and aggregation by the bridging mechanisms, van der Waals attraction, etc. In addition, there are some studies focusing on the investigation of the effects of HS on the contaminant removal by nZVI (Liu and Lo, 2011; Wang et al., 2011). However, the results were controversial, either positive effect or inhibitory effect of HS was found for the nZVI treatment in aqueous solutions. Liu and Lo (2011) reported that humic acid (HA) promoted the removal of Cr(VI) by ZVI. The underlying reason might be that HA enhanced the release of dissolved iron in the forms of soluble Fe—HA complexes and stabilized fine Fe hydroxide colloids, which may suppress the precipitation of iron corrosion products on ZVI surfaces. However, Wang et al. (2011) indicated that the adsorption of HA on the surface of nZVI occupied the active surface sites, thus leading to the decrease in Cr(VI) reduction rates.

As discussed above, both the stability behavior and passivation of nZVI can be influenced by NOM, and either stability behavior or passivation determines the reactivity of nZVI towards contaminants. Therefore, it is essential to understand the dual effect of NOM on the colloidal stability and reactivity of nZVI. However, to date, most of studies focused on the individual effect of NOM on the colloidal stability or the reactivity of nZVI (Chen et al., 2011; Dong and Lo, 2013a; Tang et al., 2014), no studies have systematically examined the influence of NOM with both the colloidal stability and the reactivity of nZVI taken into account. Besides, most of the previous studies have employed HA as a model NOM, very few studies have examined the influence of fulvic acid (FA), the predominant humic fraction in dissolved organic matter of groundwater (Manciulea et al., 2009; Mladenov et al., 2015), on the colloidal stability and reactivity of nZVI. Therefore, the objectives of this study were (1) to investigate the influence of FA on the colloidal stability of nZVI, 2) to investigate the influence of FA on the reactivity of nZVI with respect to Cr(VI) reduction and 3) to reveal the dual effect of FA on the colloidal stability and reactivity of nZVI in the common environmental conditions (pH 5, 7, 9).

## 2. Materials and methods

### 2.1. Reagents

The chemical reagents used in this study, including $NaBH_4$, $FeCl_3 \cdot 6H_2O$, $K_2Cr_2O_7$, NaCl, HCl, NaOH, were all of regent grade obtained from Aldrich Chemical, Ltd. The chemical stock solutions were prepared by dissolving chemicals into ultrapure water (Barnstead D11911). Ultrapure water was purged with nitrogen gas for 1 h prior to usage. All the other operating steps were done in a nitrogen-filled glovebox (DECO-VGB-304). HCl and NaOH were applied to adjust the initial pH values of the samples. Suwannee River Fulvic Acid (FA, a well characterized reference material) was purchased from the International Humic Substances Society (USA) and employed as a surrogate organic matter sample. A stock solution (500 mg/L) was prepared by dissolving FA in ultrapure water for 24 h and stored at 4 °C prior to experimental use. FA solutions were prepared by diluting the readymade stock solution with deoxygenated ultrapure water and were stirred overnight (12 h).

### 2.2. Synthesis and characterization of nano zero-valent iron

nZVI was synthesized from borohydride reduction of dissolved Fe(III) in laboratory, following a procedure by Yin et al. (2012). The detailed synthesis procedure is given in the Supporting Information (SI). To avoid the interference caused by aging effects, the nZVI was always freshly made for usage within 2 days.

Morphological analysis of nZVI particles was performed by TEM (JEOL 2010 TEM), which requires the deposit of dispersed particles onto a Cu grid. The average hydrodynamic particle size and particle size distribution of nZVI were determined by using dynamic light scattering (DLS) (Zetaplus, LaborScience S.A.), according to the method mentioned by Chen et al. (2007). The crystals and the elements of nZVI particles were identified by X-ray diffraction (XRD, PW-1830 Philips). Surface charges of the nZVI over the pH range of 4—10 were investigated using a zeta potential analyzer (Zetaplus, LaborScience S.A.).

### 2.3. Sedimentation of nZVI in the absence/presence of FA

The colloidal stability of nZVI particles was evaluated by examining the sedimentation profile of the particle suspensions at pH 5, 7 and 9, respectively. For all sedimentation experiments, the concentrations of nZVI particles were 100 mg $L^{-1}$. The nZVI suspensions in the absence and presence of FA (2, 5, 10 mg $L^{-1}$) were prepared in background solution (1 mM NaCl, representative of typical ionic strength in groundwater (Saleh et al., 2008)) and sonicated for 5 min just prior to measurement. Sedimentation of the nanoparticles was measured by UV scanning ($\lambda = 508$ nm, Ultrospec 4300 Pro, USA) in a drive-time mode for 1 h (Phenrat et al., 2007). Surface charges of the nZVI in the presence of FA (2, 5, 10 mg $L^{-1}$) at pH 5, 7 and 9 were investigated using a zeta potential analyzer (Zetaplus, LaborScience S.A.). The measurements were made at room temperature (25 °C) and all the experiments were run in duplicate or triplicate.

### 2.4. Cr(VI) reduction by nZVI in the absence/presence of FA

The kinetics experiments were conducted using a 100 mg $L^{-1}$ nZVI suspension and 10 mg $L^{-1}$ Cr(VI) in background solution (1 mM NaCl) w/o FA (2, 5, 10 mg$L^{-1}$) at pH 5, 7 and 9, respectively. The solution pH was adjusted using 0.01 N NaOH or HCl, measured by a pH meter (Orion, Model 420A). The final solutions (40 mL) in 41-mL glass vials sealed with Teflon caps were shaken in an end-over-end rotator at 26 rpm, at room temperature (25 °C). At predetermined time interval, one sample (40 mL suspensions) was filtered using 0.45-μm pore size cellulose nitrate filters. To analyze Cr(VI), 50 μL of 1 M acetate buffer was dosed into the samples collected at various pH and the resulting pH was ~4.3. The Cr(VI) concentration of the mixture was determined by measuring the absorbance at 370 nm using 1 cm quartz cells in a Cary 300 UV/ visible spectrophotometer with detection level of 10—20 μg $L^{-1}$ (Guan et al., 2011). All the experiments were run in triplicate. The precipitates in the experiments w/o FA (10 mg $L^{-1}$) were collected, washed with distilled water and then freeze-dried before being subjected to scanning electron microscope (SEM, JEOL-6300F) analysis.

## 3. Results and discussion

### 3.1. Characterization of nZVI

The particle size distribution of the synthesized nZVI is shown in Fig. 1a. The mean hydrodynamic particle size of nZVI was 113 nm. As observed in TEM image (Fig. 1c), the particles are aggregated in