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



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ABSTRACT

This study investigated the effect of fulvic acid (FA) on the colloidal stability and reactivity of nano zerovalent 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 (pHpzc), 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.

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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

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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 (γ -Fe₂O₃), magnetite (Fe₃O₄), hematite (α -Fe₂O₃), goethite (α -FeOOH) and lepidocrocite (γ -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 NaBH₄, FeCl₃·6H₂O, K₂Cr₂O₇, 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 $(2, 5, 10 \text{ mgL}^{-1})$ 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 endover-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 μ g L⁻ (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



Fig. 1. Characterization of nano zero-valent iron (nZVI): (a) particle size distribution; (b) XRD analysis of nZVI; (c) TEM image of nZVI; and (d) zeta potential analysis of nZVI at pH 4–10.

chain structures, which might due to both their magnetic properties and their tendency to remain in the most thermodynamically favorable state (Kanel et al., 2007). The crystals and the elements of nZVI particles were identified by XRD (Fig. 1b). The peaks at $2\theta = 45^{\circ}$ and 65° should be assigned to Fe(0) (Hoch et al., 2008). Secondary peaks represent the existence of small amount of magnetite (Rojas et al., 2004). Surface charges of the nZVI over the pH range of 4–10 were investigated and the pH of the point of zero charge (pH_{ZDC}) was determined to be 7.1 (Fig. 1d).

3.2. Effect of FA on the colloidal stability of nZVI at different pH levels

In order to investigate the colloidal stability of the nZVI suspensions, the sedimentation rate of nZVI was examined. Sedimentation kinetics of the nZVI particles were undertaken at different pH levels (5, 7 and 9) w/o FA and the results are shown in Fig. 2a–d.

Fig. 2a shows the sedimentation curve of nZVI in the absence of FA at pH 5, 7 and 9. Generally, the settling kinetic curves can be divided into two stages: a relatively rapid settling of nZVI particles followed by a much slower settling. A biphasic model was used to describe the two time-dependent settling processes and presented as:

$$C_{t}/C_{0} = F_{rapid} \left(e^{-k_{rapid} \bullet t} \right) + F_{slow} \left(e^{-k_{slow} \bullet t} \right)$$
(1)

where C_t is the concentration of suspended nZVI particles at time t, C_0 is the initial concentration of suspended nZVI particles at t = 0, F_{rapid} and F_{slow} are the nZVI fractions in rapidly or slowly settling compartments, k_{rapid} and k_{slow} are the settling rate constants for the compartments (min⁻¹), and t is time (min).

It was found that the biphasic model fitted the data well, with the square of the correlation coefficient of the linear regression (R^2)

>0.99. The calculated settling rate constants (k) and settled fractions (F) based on the biphasic rate model are shown in Table 1. The settlement rate of nZVI at pH 7 was the fastest (F_{rapid} (%) = 92 and k_{rapid} (min⁻¹) = 0.11). Previous studies have revealed that the sedimentation of nanoparticles is directly related to the particle size (refers to the aggregation of nanoparticles) (Yin et al., 2012; Dong and Lo, 2013a, 2013b; 2014). A rapid sedimentation often occur when the size of aggregates reach a critical size (d_c). Settlement of nZVI may presumptively follow two concomitant processes: (1) direct sedimentation of some particles with larger size $(d > d_c)$, and (2) aggregation of the residual particles with smaller size $(d < d_c)$ followed by sedimentation. The particle size distribution of nZVI at pH 5, 7 and 9 were examined (Figure S1, SI). The results show that the mean diameter of nZVI at pH 7 was 351 nm, which was much larger than that at pH 5 (113 nm) and pH 9 (179 nm). This indicates that there were more particles having a diameter larger than d_c at pH 7, which triggered a significant settlement. The aggregation is closely related to the surface charge of the nanoparticles, in which the lower the surface charge, the lower electrostatic repulsion among the particles, and thus the more aggregation (Dong and Lo, 2013a). As demonstrated in Fig. 1d, the surface charge was almost neutral for nZVI at pH 7, and positive and negative for nZVI at pH 5 and 9, respectively. In such a case, the aggregation might occur more efficiently for nZVI at pH 7 due to the lower electrostatic repulsion among the neutrally-charged particles.

Fig. 2b–d demonstrates the sedimentation curve of nZVI in the presence of FA at pH 5, 7 and 9. The calculated settling rate constants (k) and settled fractions (F) based on the biphasic rate model are shown in Table 1. Interestingly, the presence of FA exhibited different influences on the settlement of nZVI at different pH levels. As shown in Fig. 2b, the increasing concentration of FA (2–5 mg L⁻¹) resulted in a larger degree of settling of the nZVI particles, while a lower degree of settling of the nZVI particles was observed in the presence of 10 mg L⁻¹ FA compared to that in the



Fig. 2. Sedimentation kinetics of the nZVI particles (a) in the absence of FA (at pH 5, 7 and 9) and in the presence of FA at pH 5 (b), pH 7 (c) and pH 9 (d). (Fe⁰ = 100 mg L⁻¹).

 Table 1

 Settling rate constants (k) and settled fractions (F) in the rapid and slow compartments of particle sedimentation calculated from the biphasic rate model ($R^2 > 0.99$).

pН	$FA (mg L^{-1})$	F _{rapid} (%)	K_{rapid} (min ⁻¹)	F _{slow} (%)	K_{slow} (min ⁻¹)
5	0	92	0.049	12	3.4e-12
	2	81	0.14	24	0.0094
	5	91	0.11	11	0.0021
	10	97	0.023	1.1	2.0e-10
7	0	92	0.11	8.1	0.0057
	2	66	0.11	27	0.013
	5	32	0.17	66	0.022
	10	44	0.024	52	0.024
9	0	88	0.065	13	5.7e-12
	2	32	0.17	66	0.023
	5	35	0.13	65	0.019
	10	37	0.12	63	0.018

absence of FA at pH 5. However, the presence of FA significantly decreased the degree of settling of the nZVI particles at pH 7 and a higher concentration of FA led to a lower degree of settling (Fig. 2c). In the case of pH 9 (Fig. 2d), the presence of FA only slightly decreased the settling of nZVI particles and the increasing concentration of FA from 2 to 10 mg L^{-1} did not exert any obvious difference.

Previous studies have indicated the aggregation and sedimentation behavior of nZVI nanoparticles in the presence of humic acid (HA) can be explained by the effect of electrostatic repulsion exerted by the adsorbed HA (Dong and Lo, 2013a). The dispersion of the nZVI particles in the presence of HA could be ascribed to the adsorption of HA on the surface of the particles, enhancing the electrostatic repulsion effect. Hence, the zeta potential analysis of nZVI in the presence of FA was carried out. Fig. 3 shows the surface charge of nZVI in the absence and presence of FA at pH 5, 7 and 9. At pH 5, the positive surface charge of nZVI decreased in the presence of 2 mg L^{-1} FA and further decreased to almost neutral at 5 mg L^{-1} FA. However, the surface charge reversed to negative at



Fig. 3. Zeta potential analysis of nZVI in the absence and presence of FA at pH 5, 7 and 9 (Lines are drawn to make it clearer).

10 mg L^{-1} FA. The variation in surface charge of nZVI in the presence of FA indicates the adsorption of FA on the surface of nZVI. Thus, the varving sedimentation behavior observed at different FA concentrations should be ascribed to the adsorption of FA on the surface of particles, influencing the particle-particle electrostatic interaction (Illés and Tombácz, 2006). In the presence of $2-5 \text{ mg L}^{-1}$ FA, the electrostatic repulsion effect among particles reduced due to the decreasing surface charge, and thus leading to more significant sedimentation of nZVI particles. At 10 mg L^{-1} FA, the surface of nanoparticles became negatively charged, increasing the electrostatic repulsion effect and thus increasing the dispersion of the particles. At pH 7, the original almost neutrally-charged particles became more and more negatively charged with increasing concentration of FA from 2 to 10 mg L^{-1} . This reveals that the electrostatic repulsion effect among nZVI particles increased due to the adsorption of FA, which should result in the lower degree of particle settling at a higher concentration of FA. At pH 9, only a slight increase in the negative charge of nanoparticles was observed in the presence of FA, which indicates the adsorption of FA on the surface of nZVI nanoparticles was minimal at pH 9. This is in accordance with the finding that the presence of FA exerted insignificant effect on the sedimentation behavior of nZVI at pH 9 (Fig. 2d). Therefore, the presence of FA can either enhance or decrease the colloidal stability of nZVI particles, depending on the characteristics of nanoparticles (e.g., pH_{pzc}), the geochemical conditions (e.g., pH) and the concentrations of FA.

3.3. Effect of FA on the reactivity of nZVI at different pH levels

nZVI has been proven to be capable of removing Cr(VI) from groundwater effectively (Yin et al., 2012; Guan et al., 2015). The removal mechanism of Cr(VI) by nZVI mainly involves chemical reduction of Cr(VI) to Cr(III), with subsequent Cr(III) precipitation as Cr(III) hydroxides and mixed Fe(III)/Cr(III) (oxy)hydroxides (Yin et al., 2012). To investigate the effect of FA on the reactivity of nZVI particles, the reduction of Cr(VI) by nZVI was examined in the presence of FA. Removal kinetics were undertaken at different initial pH (5, 7 and 9) w/o FA and the results are shown in Fig. 4a–d.

When Cr(VI) was introduced, the pH was changed quickly with the different initial pH, and remained basically unchanged in the next reaction (Figure S2, SI). The final pH values after the 60 min reaction were 6.4, 7.5 and 8.7, for initial pH of 5, 7 and 9, respectively. The increase in pH should be ascribed to the corrosion of nZVI, releasing OH⁻. However, slight decrease in pH occurred in the case of initial pH 9, which might be attributable to the consumption of OH⁻ via the rapid formation of Fe(III)/Cr(III) oxyhydroxides. In the initial 5 min, Cr(VI) removal was rapid for pH values 5-7 (Fig. 4a). It indicates that the nZVI nanoparticles have a high reactivity. Acidic conditions would accelerate the corrosion of nZVI, thus enhancing Cr(VI) reduction. Under different experimental conditions, the kinetics of Cr(VI) removal by ZVI particles was reported to be zero-order, pseudo first-order or pseudo-second-order (Gheju, 2011; Tang et al., 2014). The kinetic study of Cr(VI) reduction in the absence and presence of FA was fitted using the three

Table 2

Pseudo-second-order rate constants k $(mg^{-1} L min^{-1})$ calculated from the Cr(VI) reduction by nZVI in the absence and presence of FA (R^2 are ranged from 0.82 to 0.89).

$FA (mg L^{-1})$	pH 5	pH 7	pH 9
0	0.0026	0.0022	0.0012
2	0.0018	0.0027	0.0014
5	0.0016	0.0021	0.0017
10	0.0012	0.0016	0.0023

types of models. The pseudo-second-order model provides better fit with the experimental data (R^2 are ranged from 0.82 to 0.89) than the other two models. The pseudo second-order rate constants in the absence and presence of FA are summarized in Table 2. The slight lower removal of Cr(VI) at pH 7 than that at pH 5 should also be ascribed to the higher degree of aggregation and sedimentation of the nZVI particles at pH 7 (as displayed in Fig. 2a). In contrast, the plot for pH 9 shows a less rapid and lower removal (Table 2 and Fig. 4). This may be because of the rapid formation of mixed Fe(III) and Cr(III) oxyhydroxides under alkaline conditions on the iron surfaces (Powell et al., 1995; Lee et al., 2003). The near plateau segment of the plots after 20 min (especially for pH 9) was probably due to the passivation of the surface with the consequent loss of reactivity (Wu et al., 2009).

Fig. 4b demonstrates the influence of FA on the Cr(VI) reduction by nZVI at pH 5. It was found that the Cr(VI) reduction was decreased with the increasing concentration of FA from 2 to 5 mg L⁻¹. In association with the effect of FA on the colloidal stability of nZVI particles (Fig. 2b), it can be presumed that the negative effect of FA on the Cr(VI) reduction might be ascribed to the aggregation and sedimentation of nZVI caused by the presence of FA as discussed in the previous section. However, interestingly, even though the presence of 10 mg L⁻¹ FA contributed to the enhanced dispersion of nZVI particles in suspension (i.e., lower sedimentation, Fig. 2b), which still decreased the Cr(VI) reduction.



Fig. 4. Cr(VI) reduction kinetics of the nZVI particles (a) in the absence of FA (at pH 5, 7 and 9) and in the presence of FA at pH 5 (b), pH 7 (c) and pH 9 (d). (Cr(VI) = 10 mg L⁻¹; Fe⁰ = 100 mg L⁻¹).



Fig. 5. SEM images of precipitates collected from the reaction of Cr(VI) reduction by nZVI (a) in the absence of FA and (b) in the presence of FA.

In this case, the colloidal stability of nZVI particles did not positively correlate with the reactivity of the nanoparticles. Ly et al. (2013) reported that HA/FA may have dual effects on Cr(VI) reduction by ZVI nanomaterials. In the presence of HA for a limited concentration, HA served not only as adsorbent for Cr(VI) removal with precipitation on ZVI–Fe₃O₄ particles, but also as a capping agent to stabilize ZVI-Fe₃O₄ particles by providing electrosteric repulsion. Therefore, the removal of Cr(VI) was facilitated. However, if HA concentration increased to a certain level, HA could completely surround ZVI-Fe₃O₄ particles, hindering contacts between ZVI-Fe₃O₄ and Cr(VI) ions and gradually offsetting the promoted effect. In the study of Wang et al. (2011), HA was found to have an inhibitory effect on Cr(VI) removal by ZVI nanoparticles. HA was adsorbed on the surface of ZVI nanoparticles and occupied the active surface sites, thus leading to the decrease in Cr(VI) reduction rates. The greater the adsorbed HA was, the more obvious the inhibitory effect was. Thus, it is presumed that the negative correlation between the colloidal stability and reactivity of nZVI at 10 mg L^{-1} FA should be due to the adsorbed FA on the surface of nZVI, occupying the active surface sites for Cr(VI) reduction. A similar inhibiting effect of FA at higher concentration on the Cr(VI) reduction was also found in the case of pH 7 (Fig. 4c). The presence of 2 mg L^{-1} FA facilitated the Cr(VI) reduction at pH 7, which is positively correlated with its effect on the colloidal stability of nZVI (i.e., the reduced sedimentation, Fig. 2c). However, the presence of 5–10 mg L^{-1} FA inhibited the Cr(VI) reduction although the FA enhanced the colloidal stability of nZVI (i.e., the reduced sedimentation, Fig. 2c). Obviously, the contrasting effect of 2 mg L^{-1} FA and $5-10 \text{ mg L}^{-1}$ FA on the Cr(VI) reduction reveals that there was a tradeoff between the stabilization and the reactivity of nZVI as affected by the presence of FA.

At pH 9, it was interesting to find that the presence of FA increased the Cr(VI) reduction and higher concentration of FA resulted in a higher Cr(VI) reduction (Fig. 4d). As demonstrated in Fig. 3, the zeta potential analysis indicates that the adsorption of FA on the nZVI surface was insignificant at pH 9. Besides, the effect of FA on the settling behavior of nZVI particles was also found minimal (Fig. 2d). Therefore, the enhancement in Cr(VI) reduction in the presence of FA should not be associated with the adsorbed FA on the nZVI surface. Dong et al. (2011) reported that the presence of HA inhibited the Fe(III)/Cr(III) precipitation in the reaction between Fe(II) and Cr(VI) by forming soluble complexes with the newly formed Cr(III) and Fe(III) under alkaline conditions. Liu and Lo (2011) found that the presence of HA may suppress the precipitation of iron corrosion products on ZVI surfaces by enhancing the

release of dissolved iron in the forms of soluble Fe–HA complexes and stabilized fine Fe hydroxide colloids. The presence of free FA in aqueous phase, with more binding sites (e.g., carboxylic and phenolic groups) than HA (Mak and Lo, 2011), would strongly complex with the produced Fe(III) and Cr(III) ions, forming soluble Fe(III)/Cr(III)-FA complexes, and thus inhibiting their precipitation on the surface of nZVI surfaces. The SEM images of precipitates collected from the reaction of Cr(VI) reduction by nZVI in the absence and presence of FA were examined (Fig. 5). As demonstrated in Fig. 5a, a substantial amount of clastic sediments were observed on the surface of solid phase. Fig. 5b displays that less precipitates formed on the surface of nZVI in the presence of FA. Thus, it was proposed that the presence of FA reduced the degree of passivation on the nZVI surface during the reaction, facilitating the efficiency of electron transfer from nZVI to the contaminant.

4. Conclusions and environmental implications

Fulvic acid (FA) is an important composite that affects the physicochemical performance of nZVI particles in groundwater. This research provides a context for understanding the colloidal stability and reactivity of nZVI particles in FA-containing water and the correlation between the two properties of nZVI. The results indicate that FA has complex effects on the stability of nZVI particles and the performance of Cr(VI) reduction by nZVI under various pH levels (5, 7 and 9).

Dissimilar sedimentation behavior was observed for nZVI at different pH levels in the presence of FA. Generally, the settling of nZVI was more significant at the point of zero charge (pH_{pzc} = 7.1), which could be varied in the presence of FA of various concentrations due to the adsorption of FA on the surface of nZVI. At pH 5 (<pH_{pzc}), nanoparticles exhibit a positively charged surface whereas FA is negatively charged. Fast adsorption of FA at the nZVI particles occurs, promotes surface charge neutralization and sedimentation. By increasing further FA concentrations charge inversion and stabilization of nZVI particles are obtained. At pH 7 (\approx pH_{pzc}), nZVI nanoparticles are rapidly settled down. Adsorption of FA on nZVI enhanced their stabilization in suspension. However, when nanoparticles and FA are both negatively charged (at pH 9), only a small amount of FA is adsorbed on nZVI surface, causing no obvious effect on the sedimentation behavior.

At certain concentrations of FA, the adsorption of FA on the nZVI surfaces (at pH 5 and 7) could enhance the particle stabilization, and thus facilitating the Cr(VI) reduction by providing more surface sites due to the reduced particle aggregation. However, when the

concentrations of FA were too high to saturate the active sites on the surface of nZVI, even though the presence FA enhanced the dispersion of nZVI particles in suspension, it would lead to the decrease in Cr(VI) reduction rates. Obviously, the results reveal that there was a tradeoff between the stabilization and the reactivity of nZVI as affected by the presence of FA. At pH 9, the presence of FA improved the performance of Cr(VI) reduction by nZVI and higher concentration of FA resulted in a higher Cr(VI) reduction. Given the adsorption of FA on the nZVI surface was insignificant and its effect on the settling behavior of nZVI particles was minimal, the underlying reason for the facilitating effect was proposed that the FA would complex with the produced Fe(III) and Cr(III) ions during the reaction, forming soluble Fe(III)/Cr(III)-FA complexes, and thus reducing the degree of passivation on the nZVI surface.

Overall, the results show that the presence of FA can either enhance or decrease the colloidal stability and reactivity of nZVI particles, depending on the characteristics of nanoparticles (e.g., pH_{pzc}), the geochemical conditions (e.g., pH) and the concentrations of FA. The results from this study are based on a single type of FA in simplified water system (1 mM NaCl). Such studies are a necessary first step toward understanding the behavior of nZVI in natural systems. However, these studies should be extended to a wider and more representative range of conditions, such as FA of different origins, nZVI modified with different surface stabilizers and other constituents (e.g., divalent cations) in groundwater.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2016.01.017.

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