Journal of Colloid and Interface Science 471 (2016) 7–13

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis

Chromate removal by surface-modified nanoscale zero-valent iron: Effect of different surface coatings and water chemistry

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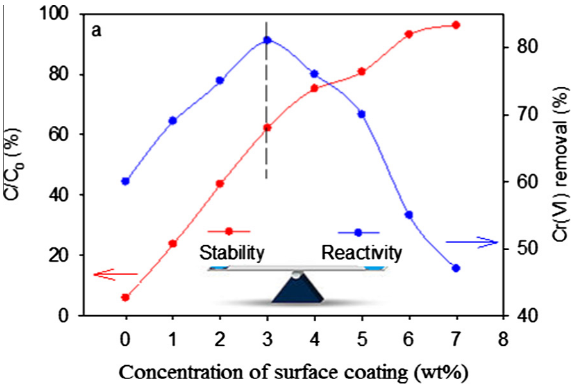
GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 21 January 2016
Revised 4 March 2016
Accepted 4 March 2016
Available online 5 March 2016

Keywords:
Colloidal stability
Chromate removal
Calcium ions
Humic acid
Nanoscale zero valent iron
Surface coating

ABSTRACT

This study investigated the correlation between the colloidal stability and reactivity of surface-modified nano zero-valent iron (SM-nZVI) as affected by the surface coating (i.e., polyacrylic acid [PAA] and starch) under various geochemical conditions. Generally, the colloidal stability of nZVI was enhanced with increasing loading of surface coating, while there is an optimum loading for the most efficient Cr(VI) removal by SM-nZVI. At lower loadings than the optimum loading, the surface coating could enhance the particle stabilization, facilitating the Cr(VI) reduction by providing more available surface sites. However, the over-loaded surface coating on the surface of nZVI particles decreased the Cr(VI) reduction due to the occupation of the reactive sites and the inhibition of the mass transfer of Cr(VI) ions from water to the particle surface by providing the electrostatic or steric repulsion. The effects of Ca^{2+} ions or humic acid (HA) on the colloidal stability and reactivity of PAA-modified nZVI (P-nZVI) and starch-modified nZVI (S-nZVI) were examined. Differing stability behavior and reactivity were observed for different SM-nZVI. It was found that the presence of Ca^{2+} or HA altered surface chemistry of SM-nZVI, the particle-particle interaction and the particle-contaminant interaction, and hence influencing the stability behavior and reactivity of the particles.

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http://dx.doi.org/10.1016/j.jcis.2016.03.011
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1. Introduction

The use of nanoscale zero-valent iron (nZVI) particles to in-situ remediates contaminated soil and groundwater has received increasing amounts of attention over the past two decades, primarily due to its broad application and high degrees of reactivity [1–4]. A large number of studies reported nZVI to be able to degrade a large range of contaminants (e.g., chlorinated solvent and heavy metals) [2,5,6]. Although the high reactivity of nZVI towards contaminants has been proved by these studies, some other important issues, e.g., stability against aggregation and mobility in subsurface, need to be addressed to ensure an effective subsurface remediation [7,8].

To be effective for the in-situ aquifer remediation, iron nanoparticles should be mobile in subsurface to be transported for some extent around the injection point [9]. However, it has been evidenced that the mobility of nZVI in the subsurface environment is quite limited under various conditions [10–13]. The nZVI particles tended to aggregate when dispersed in water, due to the strong magnetic attractive forces among particles. The formed aggregates could significantly limit migration by plugging the pores of the aquifer, and exhibit reduced specific surface area, and consequently reactivity [2,14,15]. To improve both the colloidal stability and mobility of nZVI, modification of particle surface and viscosity of dispersant fluid have been investigated and were shown effective [9,13,16]. Various types of surface coatings, e.g., anionic or nonionic surfactant, polyacrylic acid (PAA), carboxymethyl cellulose, starch, and anionic copolymers, have been used to modify the particle surface [9,10,14,15,17–19]. Applied to nZVI, the electrostatic, steric or electrosteric hindrances provided by such coating molecules counteract the electrical and dipolar attractions among particles and improve the colloidal stability. However, the effective stabilization is only achieved when a sufficient mass of coating material is present on the surface of nZVI. It is generally believed that the reducing aggregation of nZVI particles with the aid of surface stabilizers could lead to the enhancement in the specific surface area and thus the reactivity. Nevertheless, this may be influenced by the loading amount of surface coating on the surface of nZVI. The large amount of coating on the surface of nZVI may occupy the active surface sites, thus leading to the decrease in reactivity towards contaminants. Accordingly, a fundamental understanding of the correlation between the colloidal stability and reactivity of nZVI particles with different surface coatings is essential in estimating the efficiency of contaminant elimination by surface-modified nZVI in the practical application. However, to date, most of studies focused on the individual effect of surface coatings on the colloidal stability of nZVI [9,10,13,14,17], no studies have systematically examined the influence of surface coatings with both the colloidal stability and the reactivity of nZVI taken into account. Therefore, the objectives of this study were to investigate the dual effects of different surface coatings on the colloidal stability of nZVI and the reactivity of nZVI with respect to Cr (VI) reduction. Moreover, previous studies have shown that the colloidal stability of the surface-modified nZVI nanoparticles also depends on the geochemical characteristics of groundwater (e.g., Ca^{2+}, humic acid (HA)) [7,8,16,20–22], which hence may also exert effect on the reactivity of the nanoparticles. Thus, this study further examined the colloidal stability and reactivity of the surface-modified nZVI under various water chemistries (i.e., in the presence of Ca^{2+}, HA).

2. Materials and methods

2.1. Reagents

The chemical reagents used in this study, including $K_2Cr_2O_7$, $CaCl_2$, HCl, NaOH, PAA (average MW ~2000) and potato starch, were all of regent grade obtained from Aldrich Chemical, Ltd. The chemical stock solutions were prepared by dissolving chemicals into ultrapure water. Ultrapure water was purged with N_2 for 1 h prior to usage. All samples, unless otherwise specified, were prepared at pH 7. The solution pH was adjusted using 0.01 N NaOH or HCl, measured by a pH meter (INESA, PHS-3C). Suwannee River Humic Acid (purchased from the International Humic Substances Society, USA) solution was prepared with ultrapure water and its concentration was measured in terms of total organic carbon (TOC) using a TOC analyzer (Shimadzu TOC 5000A, Japan).

2.2. Synthesis and characterization of surface-modified nZVI

Pristine nZVI (Nanofer 25, produced from nanosized ferrihydrite) was purchased from the NANOIRON® Company (Czech Republic, EU). Nanofer 25 (referred to as nZVI in this study) was used for further modification by using PAA or starch. Deoxygenated ultrapure water was used for the preparation of surface-modified nZVI to avoid the oxidation of Fe^0 during the modification process. PAA-modified nZVI and starch-modified nZVI are referred to as P-nZVI and S-nZVI, respectively, in the following.

P-nZVI was prepared by dispersing nZVI particles in aqueous PAA to result in suspensions comprising iron nanoparticles ($1.0\ g\ L^{-1}$) and PAA of various concentrations (1, 2, 3, 4, 5, 6 and 7 wt%) individually, followed by sonication for 30 min. S-nZVI was prepared following a method reported in the previous studies [7,8]. Briefly, a 0.6 wt% starch solution was prepared and introduced into nZVI stock suspensions to result in suspensions comprising iron nanoparticles ($1.0\ g\ L^{-1}$) and starch at different concentrations (0.1, 0.2, 0.3, 0.4, 0.5 and 0.6 wt%), followed by sonication for 30 min. The P-nZVI and S-nZVI suspensions were freshly prepared before each experiment.

P-nZVI (3 wt%) and S-nZVI (0.2 wt%) were chosen for the following characterization, because of their high reactivity for Cr(VI) reduction, as will be discussed in the later section. Surface charges of nZVI before and after surface modification were measured in the pH range of 5–10 with a zeta potential analyzer (Zetaplus, LaborScience S.A.) and the results are shown in Fig. S1 in the Supporting Information (SI). The significant change in the surface charge of nZVI after surface modification indicates the successful coating of the stabilizers on the surface of nZVI. Morphological analysis of nZVI particles was performed by TEM (JEOL 2010 TEM). The individual particles of P-nZVI and S-nZVI appear spherical and have an average diameter of around 5 nm (Fig. S2, SI). The mean hydrodynamic particle sizes of P-nZVI and S-nZVI (measured at $100\ mg\ L^{-1}$) were 190 nm and 340 nm, respectively, and were determined by using dynamic light scattering (DLS) (Zetaplus, LaborScience S.A.). The particle size distributions are shown in Fig. S3 (SI). The hydrodynamic sizes larger than individual particle sizes of P-nZVI and S-nZVI obtained from TEM observations demonstrated that aggregates formed in the suspension at the onset of the DLS measurements [9,23].

2.3. Sedimentation of surface-modified nZVI

The colloidal stability of surface-modified nZVI particles was evaluated by examining the sedimentation profile of the particle suspensions. For all sedimentation experiments, the concentrations of nZVI particles were $100\ mg\ L^{-1}$. The nZVI suspensions in the absence and presence of Ca^{2+} ($20, 40\ mg\ L^{-1}$) or HA ($5, 10\ mg\ L^{-1}$) were prepared and sonicated for 5 min just prior to measurement. Sedimentation of the nanoparticles was measured by UV scanning ($\lambda = 508$ nm, UV-2550, SHIMADZU, Japan) in a drive-time mode for 1 h [7]. Surface charges of the surface-modified nZVI in the presence of Ca^{2+} ($20, 40\ mg\ L^{-1}$) or HA ($5, 10\ mg\ L^{-1}$) 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 surface-modified nZVI

The kinetics experiments were conducted using a 100 mg L^{-1} surface-modified nZVI suspension and 10 mg L^{-1} Cr(VI) in the absence and presence of Ca^{2+} (20, 40 mg L^{-1}) or HA (5, 10 mg L^{-1}) at pH 7. 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 pre-determined time intervals, suspensions were filtered using 0.45-μm pore size cellulose nitrate filters. Cr(VI) was measured following a method reported in the previous studies [24]. Briefly, 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}. The detailed procedures of X-ray photoelectron spectroscopy (XPS, PHI 5700 ESCA System, America) analysis of Cr species in the reaction products were presented in the SI.

3. Results and discussion

3.1. Colloidal stability of surface-modified nZVI

In order to investigate the effect of surface coating on the colloidal stability of the nZVI suspensions, the sedimentation rates of nZVI coated with PAA or starch at different concentrations were examined respectively (Fig. 1). As demonstrated in Fig. 1, the settling rate of pristine nZVI was rapid. The absorbance at 508 nm was reduced by almost 80% of the initial absorbance within 20 min. This reduction in absorbance should be attributable to the rapid aggregation and settling of colloidally unstable bare nZVI particles [25]. Pristine nZVI particles aggregated and settled out of the supernatant rapidly due to the higher magnetic and van der Waals attractive forces among particles [16]. In comparison, the settling of P-nZVI (Fig. 1a) and S-nZVI (Fig. 1b) was significantly reduced with increasing PAA/starch concentration from 1 wt% to 7 wt% and 0.1 wt% to 0.6 wt%, respectively.

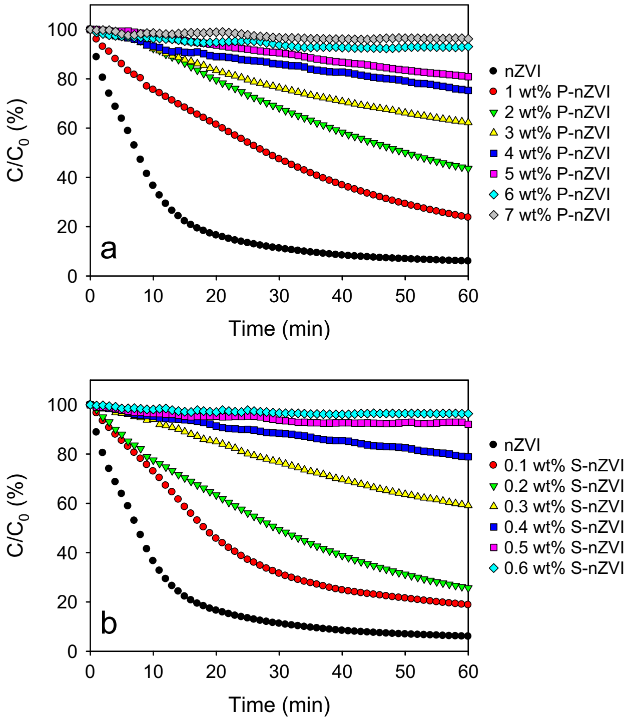

Fig. 1. Sedimentation rates of (a) P-nZVI and (b) S-nZVI under different loadings of surface stabilizer (Fe^0 = 100 mg L^{-1}).

The above results indicated that PAA and starch played an important role in stabilizing the nZVI particles. The mechanisms for the stabilization have been investigated in the previous studies [7,14,17,26]. It was reported that the PAA could be adsorbed onto the nZVI surface in the structure of bidentate bridging [26]. The large PAA molecules that bonded onto the nZVI surface could provide the steric stabilization to stabilize dispersions. Besides, the adsorption of PAA imparts substantial negative charge to the particles by chelation of the polyacid to the iron oxide at the particle surface. The primary effect of the large negative charge on the particle surface is to cause electrostatic repulsion between the particles [17]. Accordingly, the adsorption of PAA molecules onto the surface of nZVI nanoparticles results in a layer of physical barrier and negative charges (i.e., the so-called electrosteric stabilization), and thereby preventing the nanoparticles from aggregation. Starch is a branched, hydrophilic polymer that typically contains ~20% amylose. It was reported that the iron-starch interactions and formation of intra-starch Fe clusters play a fundamental role in dispersing and stabilizing the iron nanoparticles. When iron particles are dispersed in the starch matrix, the hydroxyl groups of starch act as the passivating contacts, providing the steric stabilization and thereby preventing the nanoparticles from aggregation [7,14].

As demonstrated, the concentration of surface coating on the surface of nZVI is expected to affect the growth and aggregation of nZVI particles. Higher loading of coating onto the surface of nZVI particles results in more stable nZVI suspensions.

3.2. Cr(VI) removal by surface-modified nZVI

To investigate the effect of surface coating on the reactivity of nZVI particles, the kinetics of Cr(VI) reduction by nZVI with surface coating at various concentrations were examined (Fig. 2). To confirm whether the Cr(VI) was removed by the surface-modified nZVI via reduction, Cr 2p line XPS spectra of the solids collected in the process of Cr(VI) removal by P-nZVI (3 wt%)/S-nZVI (0.2 wt%) have been given in Fig. S4 (SI). Significant bands at binding energy 577 and 586 eV for Cr(III) were observed, which correspond to $Cr2p_{3/2}$ and $Cr2p_{1/2}$ of Cr(III), respectively [27–29]. Meanwhile, no band was observed for Cr(VI), which is expected to appear at binding energies of 579–581 and 588–590 eV [28]. This indicates that the Cr(VI) has been reduced to Cr(III) by either P-nZVI or S-nZVI.

Fig. 2a shows the influence of PAA on the Cr(VI) reduction by nZVI. It was found that the Cr(VI) reduction was increased with the increasing concentration of PAA from 1 wt% to 3 wt%. In association with the effect of PAA on the colloidal stability of nZVI particles (Fig. 1a), it can be presumed that the positive effect of PAA on the Cr(VI) reduction might be ascribed to the enhanced surface area for reaction, resulting from the reduced aggregation and settling of nZVI caused by the stabilization effect of PAA. However, interestingly, even though the presence of 4–7 wt% PAA contributed to the more stable dispersion of nZVI particles in suspension (i.e., lower sedimentation, Fig. 1a), the Cr(VI) reduction was lowered with increasing concentration of PAA. In this case, the colloidal stability of nZVI particles did not positively correlate with the reactivity of the nanoparticles. Lv et al. [30] reported that the adsorption of HA for a limited concentration onto the surface of ZVI–Fe_3O_4 particles could enhance the particle stabilization, facilitating the removal of Cr(VI). However, it was also found that HA could completely surround ZVI–Fe_3O_4 particles when HA

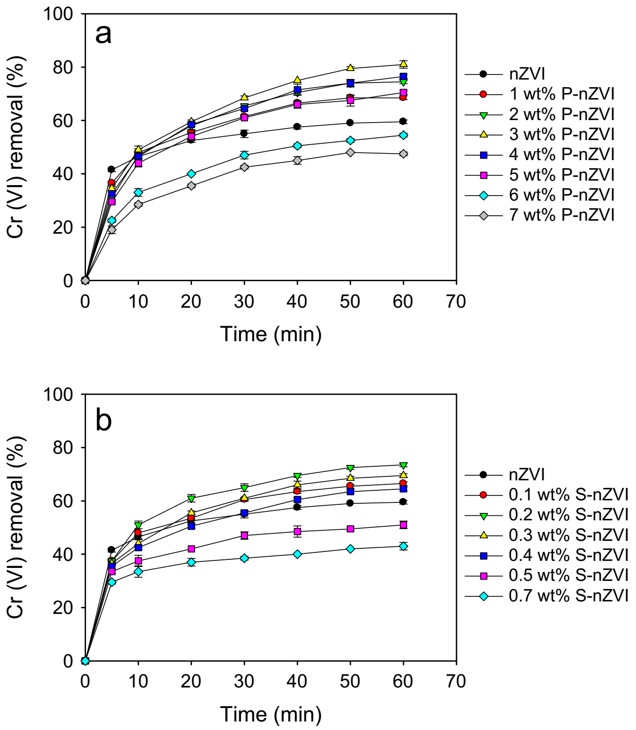

Fig. 2. Cr(VI) removal by (a) P-nZVI and (b) S-nZVI under different loadings of surface stabilizer ($Fe^0 = 100\ mg\ L^{-1}$; $Cr(VI) = 10\ mg\ L^{-1}$).

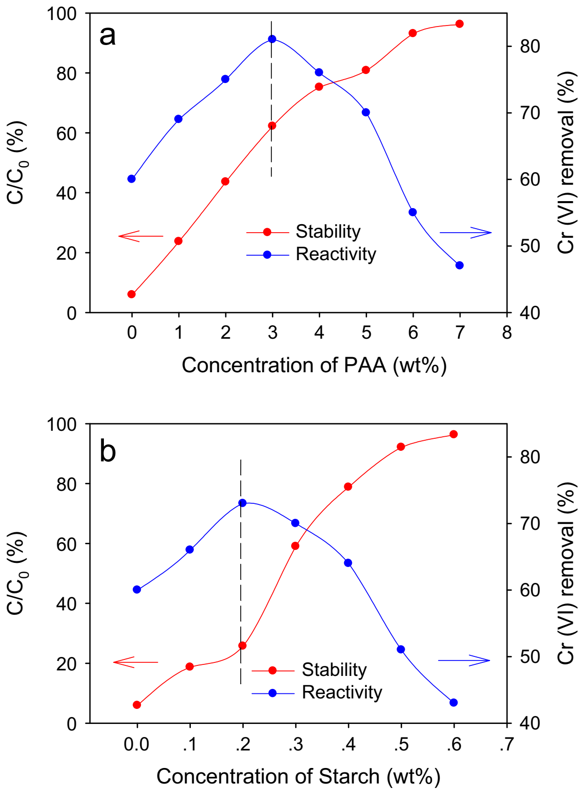

Fig. 3. Correlation between colloidal stability and reactivity of surface-modified nZVI: (a) P-nZVI and (b) S-nZVI.

concentration increased to a certain level, hindering contacts between ZVI–Fe_3O_4 and Cr(VI) ions and gradually offsetting the promoted effect. This inhibitory effect of the adsorbed HA on the Cr(VI) reduction by nZVI particles was also reported by Wang et al. [31]. Thus, it is presumed that the negative correlation between the colloidal stability and reactivity of P-nZVI at 4–7 wt% PAA should be due to the adsorbed PAA on the surface of nZVI occupied the active surface sites for Cr(VI) reduction. The greater the adsorbed PAA was, the more obvious the inhibitory effect was. A similar effect was also observed in the reduction of Cr(VI) by S-nZVI (Fig. 2b). The presence of 0.1–0.2 wt% starch facilitated the Cr(VI) reduction, which is positively correlated with its effect on the colloidal stability of nZVI (i.e., the reduced settling, Fig. 1b). However, the presence of 0.3–0.6 wt% starch inhibited the Cr(VI) reduction, although the starch enhanced the colloidal stability of nZVI (Fig. 1b). Obviously, the surface coating concentration-dependent Cr(VI) reduction reveals that there is a tradeoff between the stabilization and the reactivity of nZVI as affected by the surface coating.

To clear demonstrate the correlation between the colloidal stability and reactivity of surface-modified nZVI as affected by the surface coating, the Cr(VI) removal efficiency and the colloidal stability (represented by C/C_0 after 1 h of settling) as a function of concentration of surface coating was displayed in Fig. 3. It is clear that the most efficient Cr(VI) removal and the best particle stabilization were not occurred at the same concentration of surface coating. The highest Cr(VI) removal by P-nZVI and S-nZVI were achieved at 3 wt% PAA and 0.2 wt% starch, respectively, at which the particle stability (C/C_0) was around 60% for P-nZVI and only 25% for S-nZVI. In the real application, both reactivity and colloidal stability or mobility of the nanoparticles should be taken into account. In such case, the cross point of the two lines in Fig. 3 (the lines indicate the Cr(VI) removal and C/C_0) may indicates a more appropriate concentration of surface coating (around 4.2 wt% for P-nZVI and 0.32 wt% for S-nZVI). This is essential in guaranteeing the injected surface-modified nZVI particles could migrate to the plume zone successfully and remove the contaminants efficiently.

3.3. Effect of Ca^{2+}

Colloidal stability and reactivity of the surface-modified nZVI particles in the presence of Ca^{2+} were examined (Fig. 4). P-nZVI (3 wt%) and S-nZVI (0.2 wt%), having the best reactivity, were chosen in this study. The presence of Ca^{2+} exerted no obvious influence on the settling of P-nZVI (Fig. 4a). However, in the case of S-nZVI (Fig. 4b), the particles settled significantly over time in the presence of 20–40 $mg\ L^{-1}$ of Ca^{2+}. The mechanism for the significant sedimentation of S-nZVI has been investigated in the previous study [8]. Due to the reason that Ca^{2+} can form complexation with the hydroxyl groups of the starch molecules [32,33], the S-nZVI particles could be attached with each other via Ca^{2+} complexation with the starch molecules on the surface of S-nZVI particles, thus enhancing the particle aggregation and sedimentation [8]. In the case of P-nZVI, there are few free carboxylic groups on the surface of P-nZVI for the formation of the Ca^{2+}-carboxylate complexes, due to the reason that the PAA was not only adsorbed on the nZVI surface via bidentate bridging, but also formed a gel network via hydrogen bonding, PAA entanglement and cross-linking [8,26].

Even though the presence of Ca^{2+} exerted no obvious influence on the colloidal stability of P-nZVI, the Cr(VI) removal by P-nZVI was enhanced with increasing concentration of Ca^{2+}. As for S-nZVI, the Cr(VI) removal was decreased with increasing concentration of Ca^{2+}, exhibiting a similar trend with the colloidal stability in the presence of Ca^{2+}. Zeta potential measurements were performed on the two types of particles in the presence or absence of Ca^{2+} to gain insights into the correlation between the surface charges of the particles and the Cr(VI) removal (Fig. 5). Both the two types

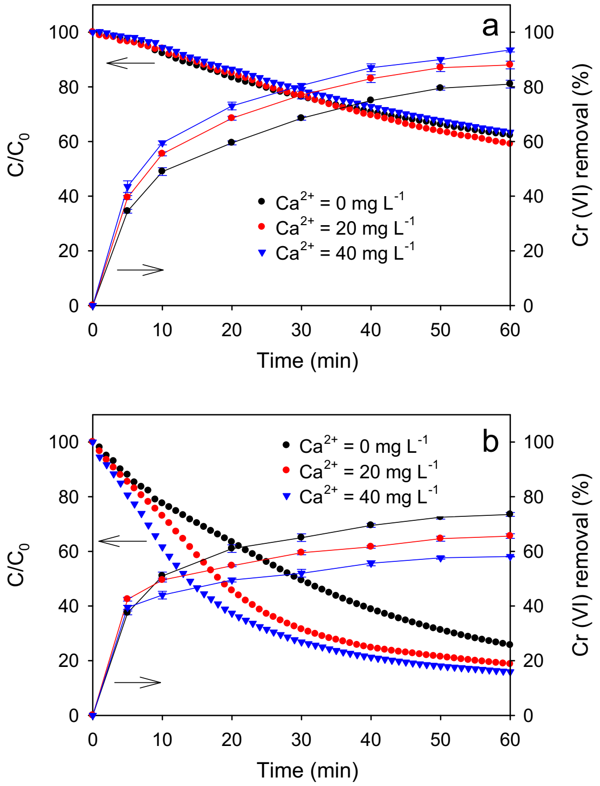

Fig. 4. Effect of Ca^{2+} on the colloidal stability and reactivity of surface-modified nZVI: (a) P-nZVI (3 wt%) and (b) S-nZVI (0.2 wt%). (Fe^0 = 100 mg L^{-1}; Cr(VI) = 10 mg L^{-1}).

of particles exhibited a decrease in surface charge with increasing concentration of Ca^{2+}, which suggests that Ca^{2+} is adsorbed onto the particles. The enhanced Cr(VI) removal by P-nZVI in the presence of Ca^{2+} should be due to the reduced electrostatic repulsion between P-nZVI and the negatively charged Cr(VI) ions, facilitating the mass transfer of Cr(VI) onto the surface of P-nZVI for the reaction. However, even though the surface charge of S-nZVI became less negative in the presence of 20 mg L^{-1} of Ca^{2+} and reached almost zero charge in the presence of 40 mg L^{-1} of Ca^{2+}, which did not enhance but decreased the Cr(VI) removal. In association with the colloidal stability of S-nZVI as affected by the presence of Ca^{2+}, the decreasing Cr(VI) removal should be ascribed to the higher degree of particle settling caused by the presence of Ca^{2+}.

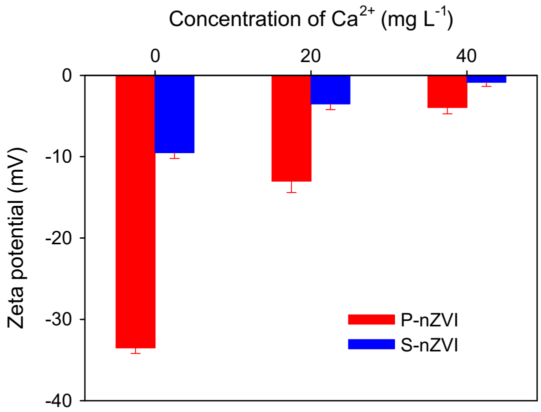

Fig. 5. Zeta potential of P-nZVI (3 wt%) and S-nZVI (0.2 wt%) at various concentrations of Ca^{2+} (pH = 7). Error bars represent the standard deviations of duplicate experiments.

3.4. Effect of HA

The effect of HA on the stability and reactivity of the surface-modified nZVI particles were examined and results are shown in Fig. 6. As demonstrated in Fig. 6a, the increasing concentration of HA (5–10 mg L^{-1}) resulted in a lower degree of settling of the P-nZVI particles. In the case of S-nZVI (Fig. 6b), a higher concentration of HA led to a higher degree of particle settling. Fig. 7 shows the surface charge of P-nZVI in the absence and presence of HA. The increasing negative surface charge of P-nZVI in the presence of HA indicates the adsorption of HA on the surface of P-nZVI. Thus, the lower degree of settling should be ascribed to the adsorption of HA onto the surface of particles, enhancing the electrosteric repulsion effect and thus increasing the dispersion of the particles [7,34]. An increasing negative surface charge of S-nZVI was also observed in the presence of HA. However, the contradictory sedimentation behavior of S-nZVI and P-nZVI at various concentrations of HA indicates that there are other effects influencing the sedimentation behavior of S-nZVI except the effect of electrosteric repulsion exerted by the adsorbed HA. The previous study indicated that the differing effects of HA on the aggregation of P-nZVI and S-nZVI should be associated with different interactions of HA with the two types of surface coatings [7]. HA was adsorbed onto the surface of P-nZVI via complexation with nZVI (instead of the PAA coating) enhanced the electrosteric repulsion effect, increasing the stability of the particles. However, for nZVI modified with starch, HA could interact with the starch molecule on the surface of S-nZVI and play a "bridge" role among the particles, which induced the aggregation and settling of the particles.

Although the presence of HA increased the colloidal stability of P-nZVI, the Cr(VI) removal by P-nZVI was decreased with increasing concentration of HA (Fig. 6a). This is consistent with the findings of the previous section, which shows that further increasing

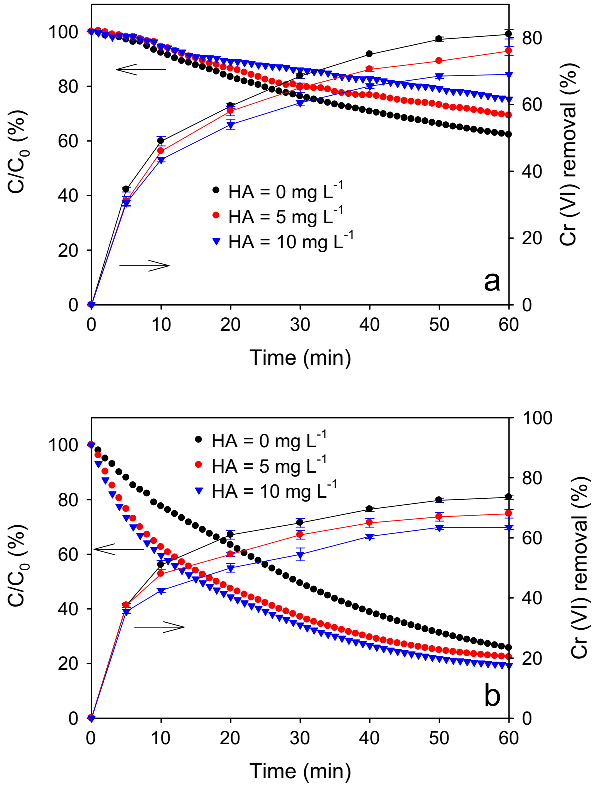

Fig. 6. Effect of HA on the colloidal stability and reactivity of surface-modified nZVI: (a) P-nZVI (3 wt%) and (b) S-nZVI (0.2 wt%). (Fe^0 = 100 mg L^{-1}; Cr(VI) = 10 mg L^{-1}).

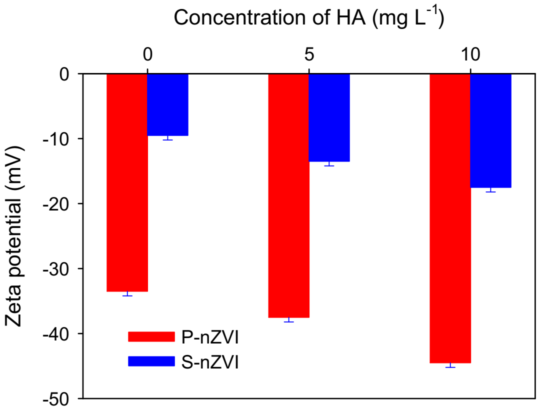

Fig. 7. Zeta potential of P-nZVI (3 wt%) and S-nZVI (0.2 wt%) at various concentrations of HA (pH = 7). Error bars represent the standard deviations of duplicate experiments.

concentration of the surface coating (i.e., PAA) could enhance the particle stability but decrease the reactivity (Fig. 3a). As discussed above, the adsorption of HA onto the surface of P-nZVI increased the negatively charge of P-nZVI. Therefore, it was presumed that the decreased Cr(VI) removal might be ascribed to the following two reasons: on the one hand, the adsorbed HA occupied the reactive sites for the Cr(VI) reduction; on the other hand, the adsorbed HA enhanced the electrosteric repulsion effect, inhibiting the mass transfer of the negatively charged Cr(VI) ions onto the surface of P-nZVI. In the case of S-nZVI, the Cr(VI) removal was decreased with increasing concentration of HA, exhibiting a similar trend with the colloidal stability as affected by the presence of HA. The decreased reactivity should be associated with the increased settling of the S-nZVI particles.

4. Conclusions and implications

This research provides a context for understanding the colloidal stability and reactivity of surface-modified nZVI particles and the correlation between the two properties of nZVI as affected by the surface coating. Both the colloidal stability and reactivity of P-nZVI/S-nZVI particles could be influenced by the concentration of surface coating (i.e., PAA or starch). Generally, the colloidal stability (i.e., dispersion) of nZVI could be enhanced with increasing concentration of surface coating. However, there is an optimum concentration of surface coating for the best Cr(VI) removal by P-nZVI/S-nZVI. Below the optimum concentration, the higher concentration of surface coating led to the higher reactivity, resulting from the more dispersed particles in water (i.e., more reactive sites for reaction). Above the optimum concentration, the Cr(VI) removal was decreased with increasing concentration of surface coating. The over-loaded surface coating on the surface of nZVI particles could not only occupy the reactive sites but also inhibit the mass transfer of Cr(VI) ions from water to the particle surface by providing the electrostatic or steric repulsion.

This study further examined the colloidal stability and reactivity of surface-modified nZVI in the presence of Ca^{2+} or HA. The presence of Ca^{2+} exerted no obvious influence on the colloidal stability of P-nZVI, but enhanced the Cr(VI) removal, which should be due to the reduced electrostatic repulsion between P-nZVI and the negatively charged Cr(VI) ions. The presence of Ca^{2+} decreased the Cr(VI) removal by S-nZVI, which should be due to the higher degree of particle settling caused by the presence of Ca^{2+}. Although the presence of HA increased the colloidal stability of P-nZVI, the Cr(VI) removal by P-nZVI was decreased with increasing concentration of HA due to the occupation of the reactive sites and the provided electrosteric repulsion effect. In the case of starch-nZVI, the Cr(VI) removal was decreased with increasing concentration of HA, which should be associated with the increased settling of the S-nZVI particles.

In the practical application, both reactivity and colloidal stability of the nZVI particles should be evaluated to choose the appropriate concentration of surface coating. This is essential in guaranteeing the successful transportation of the injected surface-modified nZVI particles to the contaminated sites and the efficient contaminant removal. The results also suggest that groundwater geochemistry (e.g., Ca^{2+}, HA) should be taken into account in choosing the suitable surface coating for the modification of nZVI for a particular application.

Acknowledgments

This research was supported by the Fundamental Research Funds for the Central Universities, the National Natural Science Foundation of China (51409100, 51521006, 51378190) and the Program for Changjiang Scholars and Innovative Research Team in University (IRT-13R17).

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcis.2016.03.011.

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