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EDDS-assisted reduction of Cr(VI) by nanoscale zero-valent iron

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ABSTRACT

In the reduction of Cr(VI) by nanoscale zero-valent iron (nZVI), the reactivity of nZVI drops overtime due to surface passivation, which severely inhibits its effective utilization. This study investigated the effect of EDDS (ethylene diamine disuccinic acid) on the Cr(VI) reduction by nZVI at different pH (5.6, 7.0 and 9.0) and the underlying mechanisms. The removal of Cr(VI) by nZVI increased from around 60–100% as the concentration of EDDS increased from 0 to 4–5 mM at pH 5.6–7.0. It was proposed that the EDDS chelated with the generated Cr(III)/Fe(III) and inhibited their co-precipitation onto nZVI surface. However, under alkaline condition (pH 9.0), the EDDS slightly decreased the Cr(VI) reduction, which was due to the fact that the EDDS facilitated the reaction between nZVI/Fe(II) with dissolved oxygen (DO) in the solution. In the absence of DO, a similar positive effect of EDDS on Cr(VI) reduction was observed at pH 9.0 as that at pH 5.6–7.0. Additionally, it was found that the EDDS could significantly increase the kinetics of nZVI corrosion in deionized water. These results demonstrate that EDDS could be used effectively as a chelating agent for inhibiting the surface passivation and increasing the effective utilization of nZVI.

1. Introduction

Chromium is one of the most common toxic metal ions in water and soil which mainly derive from leather tanning, electroplating, manufacturing, organic syntheses and other industries. Chromium mainly exists in the form of complex of trivalent (Cr(III)) and hexavalent (Cr(VI)) in the aquatic environment. Cr(VI) is considered as one of the most toxic, carcinogenic, mutagenic and teratogenic contaminants to many organisms [1–4]. Therefore, it is vital to remove Cr(VI) from wastewater before discharging into the environment.

There has been many scientific studies and treatment processes employed to remove Cr(VI) successfully from wastewater, including activated carbon, ion exchange, foam flotation, reverse osmosis, photocatalytic reduction, adsorption and chemical reduction [5–9]. Among these methods, nZVI reduction process has achieved more and more attention because of its simple operation and strong reducing reactivity [10–12]. The nZVI particles and the dissolved Fe(II) released from the nZVI reduce carcinogenic Cr(VI) into less toxic insoluble Cr(III) and in return, the nZVI or Fe(II) is oxidized to Fe(III) [6,13–15]. However, there are still some problems needed to get further improvement. The generated Cr(III) and Fe(III) could exist as (hydro)oxides or $Fe_xCr_{1-x}(OH)_3/Fe_xCr_{1-x}(OOH)$ by co-precipitation on the nZVI surface [16]. It occurs as shown in Eqs. (1) and (2) below. As a result, the formation of passive shells decreases the redox reactions rate due to the resistance of electron transfer or mass transfer on the nZVI surface, hindering further reaction of inner nZVI particles and leading to a drop in the reactivity of nZVI [17,18].

$$(1-x)\mathrm{Fe(III)} + x\,\mathrm{Cr(VI)} + 3\mathrm{H_2O} \rightarrow \mathrm{Cr}_x\mathrm{Fe}_{1-x}(\mathrm{OH})_3 + 3\mathrm{H}^+ \quad (1)$$

$$(1-x)\mathrm{Fe(III)} + x\,\mathrm{Cr(VI)} + 2\mathrm{H_2O} \rightarrow \mathrm{Cr}_x\mathrm{Fe}_{1-x}(\mathrm{OOH}) + 3\mathrm{H}^+ \quad (2)$$

To avoid the formation of passivation layer on the external surface of nZVI, one of the approaches is to apply Fe-chelant such as ethylene diamine tetraacetic acid (EDTA) and oxalate, which have been widely investigated to chelate Fe(II) and Fe(III) [18–20]. Zhang et al. [21] demonstrated that the addition of EDTA significantly enhanced the rates and the extent of carbon tetrachloride (CT) removal by microscale ZVI, which was attributed to the elimination of a surface passivation layer of Fe(III) (hydro)oxides on the microscale ZVI through chelating of EDTA with Fe(III), which maintained the exposure of active sites on the ZVI surface to CT. Fu et al. [20] also demonstrated that the oxalate ligands can significantly increase the removal efficiency of Cr(VI) and dye since the ligands

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can accelerate ferrous iron oxidation and increase the generation of hydroxyl radical. The EDTA or oxalate-assisted contaminants degradation by ZVI provides a new approach that could treat the contaminants more efficiently and at a much lower cost. However, EDTA or oxalate ligand is toxic, mobile and with high persistence in the environment, which may pose additional risks of secondary pollution and harmful effects on microorganisms and plants [22]. It may not be practical to discharge high concentrations of EDTA or oxalate ligands to the aquatic environment. Thus, further research should be carried out to find environmentally benign ligands that could be applied in the ZVI or nZVI systems.

EDDS, namely ethylene diamine disuccinic acid, is an aminopolycarboxylic acids (APCAs) which is getting more and more interests in recent years. EDDS could be produced naturally by a number of microorganisms as a novel green chelating agent, chelated Fe(II) (Fe-EDDS) by chelation [23,24]. It has been investigated in bulk on extraction of Zn, Pb, Cu, Ni from metal-contaminated soil [23,24]. Compared with the commonly used EDTA, EDDS do not persist in the environment due to rapid biodegradation while showing considerable metal chelating ability. Therefore, EDDS has a promising future to be an environmentally friendly alternative to EDTA for enhancing metal removal [25–28]. No studies have yet been reported on the effect of EDDS on the nZVI reduction process in the literature. Therefore, the objectives of this study were to investigate the effect of EDDS on the reduction of Cr(VI) by nZVI under different conditions (i.e., solution pH, EDDS concentration and dissolved oxygen) and the underlying mechanisms. The effect of EDDS on the kinetics of nZVI corrosion in deionized water was also studied.

2. Materials and methods

2.1. Chemical reagents

All chemical reagents used in this study, including $K_2Cr_2O_7$, $FeSO_4{\cdot}7H_2O$, $NaBH_4$, HCl, NaOH and EDDS were analytical reagent grade (Jingkang new material technology co. Changsha) and used without further purification. A stock solution containing potassium dichromate ($K_2Cr_2O_7$) was prepared by dissolving $K_2Cr_2O_7$ with deionized water, and then was diluted to the desired concentration. EDDS was dissolved directly with deionized water to prepare EDDS solution.

2.2. Synthesis of nZVI

The nZVI particles were synthesized using the borohydride reduction method [29,30]. In this method, a prepared 0.072 M sodium borohydride solution ($NaBH_4$) was added dropwise into another prepared 0.036 M ferrous sulfate solution ($FeSO_4{\cdot}7H_2O$) under constant N_2 stripping. The reaction was proceeded at room temperature stirred with an electric rod at the speed of 500 rpm. The borohydride was applied excessively to make Fe^{2+} and BH_4^- react completely. The synthetic reaction occurs according to following step:

$$Fe^{2+} + 2BH_4^- + 6H_2O \rightarrow Fe^0 \downarrow + 2B(OH)_3 + 7H_2 \uparrow \quad (3)$$

After addition of all the $NaBH_4$, the mixture was stirred continuously for another 30 min under a nitrogen atmosphere. The generated materials were collected by vacuum filtration and rinsed twice with deoxygenated DI water. The collected solids (i.e., nZVI) were kept in ethanol–water to help preservation. To avoid the interference caused by aging effects, the nZVI was always freshly made for usage within 2 days. The physicochemical characterizations (i.e., particle size distribution, TEM image, XRD pattern and zeta potential) of the synthesized nZVI were analyzed and the detailed methodologies and results are shown in Supporting Information.

2.3. Batch experiments

To compare the removal efficiency of Cr(VI) by nZVI in the absence and presence of chelants, the kinetics experiments were conducted using a 100 mg/L nZVI suspension and 10 mg/L Cr(VI) in DI water in the absence and presence of EDDS of different concentrations at initial pH 5.6, 7.0 and 9.0, respectively. The final solutions (200 mL) were placed on a rotary shaker at 25 °C and 195 rpm. A reaction time of 60 min was acceptable for most of the batch experiments. The initial pH was adjusted by NaOH or HCl and the final pH was recorded after the reaction using the PHS-3C pH meter. The mixed solutions were sampled at different time intervals and filtered immediately through 0.45 μm membranes to determine the residual concentration of Cr(VI).

To determine the effect of EDDS on the corrosion of nZVI, the kinetics experiments were conducted using a 100 mg/L nZVI suspension in the absence and presence of EDDS of different concentrations at initial pH 5.6 and 9.0, respectively. The procedure was the same as mentioned above. The total soluble iron concentration was analyzed.

The effect of dissolved oxygen (DO) on the reduction of Cr(VI) at pH 9.0 was evaluated. The samples were purged with N_2 for 30 min before addition of nZVI for the experiments in the absence of DO.

The concentrations of residual Cr(VI) were quantified spectrophotometrically using the 1,5-diphenylcarbazide method with a UV-2550 visible spectrophotometer at wavelength of 540 nm. The concentrations of total Fe were determined by 1,10-phenanthroline spectrophotometry. All experiments were undertaken in duplicate.

2.4. Spectroscopic characterizations

The nZVI particles and that after reaction with Cr(VI) in the absence and presence of EDDS were characterized respectively. The morphology of these particles was observed using a scanning electron microscopy (SEM, JEOL-6300F) with an operating voltage of 20 kV. X-ray diffraction (XRD) patterns were operated using a Rigaku D/Max 2500 with Cu Kα radiation at 40 kV/250 mA.

3. Results and discussion

3.1. Cr(VI) reduction by nZVI

The removal of Cr(VI) by nZVI in aqueous solution was investigated at different pH. The results are shown in Fig. 1. At initial pH values of 5.6, 7.0 and 9.0, the removal efficiency of Cr(VI) was 57.5%, 62.6% and 45.5%, respectively. The final pH values were 7.4, 7.7 and 8.3, respectively. The increase in pH (at initial pH 5.6 and 7.0) should be ascribed to the corrosion of nZVI, consuming H^+ or/and releasing OH^- [31]. However, a drop 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 most rapid at pH 5.6 (Fig. 1). It indicates that the nZVI nanoparticles have a high reactivity. Acidic conditions could accelerate the corrosion of nZVI, thus enhancing Cr(VI) reduction. However, the reduction of Cr(VI) to Cr(III) at experimental solution pH 5.6 and pH 7.0 were comparable after 1 h of reaction. The plot for pH 5.6 reached a plateau after 20 min, which was probably due to the rapid passivation of the surface with the consequent loss of reactivity [32–35]. The plot for pH 9.0 shows a less rapid and lower removal than that at pH 5.6

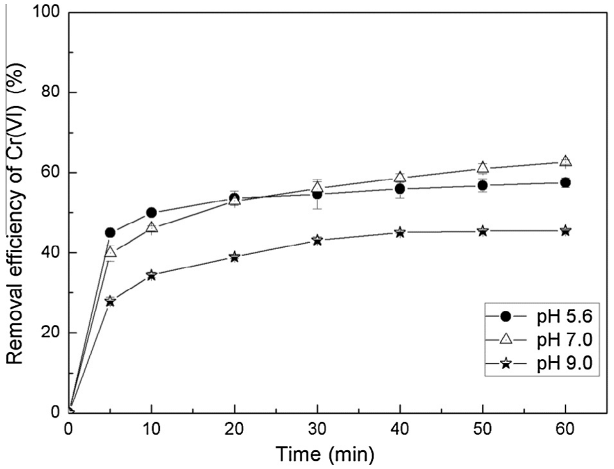

Fig. 1. Removal efficiency of Cr(VI) by nZVI at initial pH values of 5.6, 7.0 and 9.0. (Cr(VI) = 10 mg/L; Fe^0 = 100 mg/L).

and 7.0. This may be because of the rapid precipitation of mixed Fe (III)/Cr(III) oxyhydroxides on the iron surfaces under alkaline conditions and the competing effect of DO [36–38]. The DO in the solution could compete with Cr(VI) for the consumption of reducing agents (i.e., Fe(0) and Fe(II) in this experiment). The effect of DO was further examined and discussed in the following section.

3.2. Effect of EDDS on Cr(VI) reduction

As discussed above, the Cr(VI) reduction by nZVI could be inhibited by the generation of Cr(III)/Fe(III) precipitates and the consequent passivation of nZVI surface [39]. In this section, the effect of EDDS of various concentrations (2–5 mM) on the reduction of Cr(VI) by nZVI was investigated at different pH (Fig. 2a-c).

Fig. 2a and b show that the removal efficiency of Cr(VI) increased as the EDDS concentration increased at pH 5.6 and 7.0. At pH 5.6, it can be observed that the system displayed the highest Cr(VI) removal efficiency for 4 mM EDDS solution (Fig. 2a). The residual concentration of Cr(VI) in the solution was reduced by 100%, which indicates that nZVI could completely reduce all of Cr (VI) in the solution. As shown in Fig. 2a, the removal of Cr(VI) rapidly occurred in the initial 10 min of the reaction and then slightly increased to reach the equilibrium. While at pH 7.0, an initial EDDS concentration of 5 mM was required to achieve the same efficiency of 100% compared with that at pH 5.6 (Fig. 2b). It was obviously illustrated that higher EDDS concentrations were required to attain similar Cr(VI) removal efficiencies for the wastewaters at higher solution pH. The conclusion that acidic conditions facilitate the reduction could be inferred.

After addition of EDDS, the removal efficiency of Cr(VI) was promoted about 40% compared with that using nZVI alone at pH 5.6–7.0. The Cr(VI) removal was interpreted as (1) reduction in the presence of Fe^0 and (2) subsequent precipitation on the surface of the nZVI particles. In all cases of different dosages of EDDS at initial pH 5.6 and pH 7.0, the final pH in the batch experiments was changed to pH around 7.7, because of consumption of H^+ or/and generation of OH^- during the reaction. The formed Cr(III) and Fe (III) ions under neutral or alkaline conditions are unstable and expected to transform into insoluble oxy-hydroxides [1,36]. Nevertheless, it has been proved that EDDS has a high ability to maintain iron in soluble form and plays an important role in stabilizing Fe (III) in a large range of pH (3–9) to prevent its precipitation [40]. Consequently, with addition of EDDS, the presence of Cr(III) and Fe(III) (hydro)oxides could possibly be decreased by forming EDDS-Cr(III) or EDDS-Fe(III) chelating complexes during the reaction. It could prevent the Cr(III)/Fe(III) (hydro)oxides from

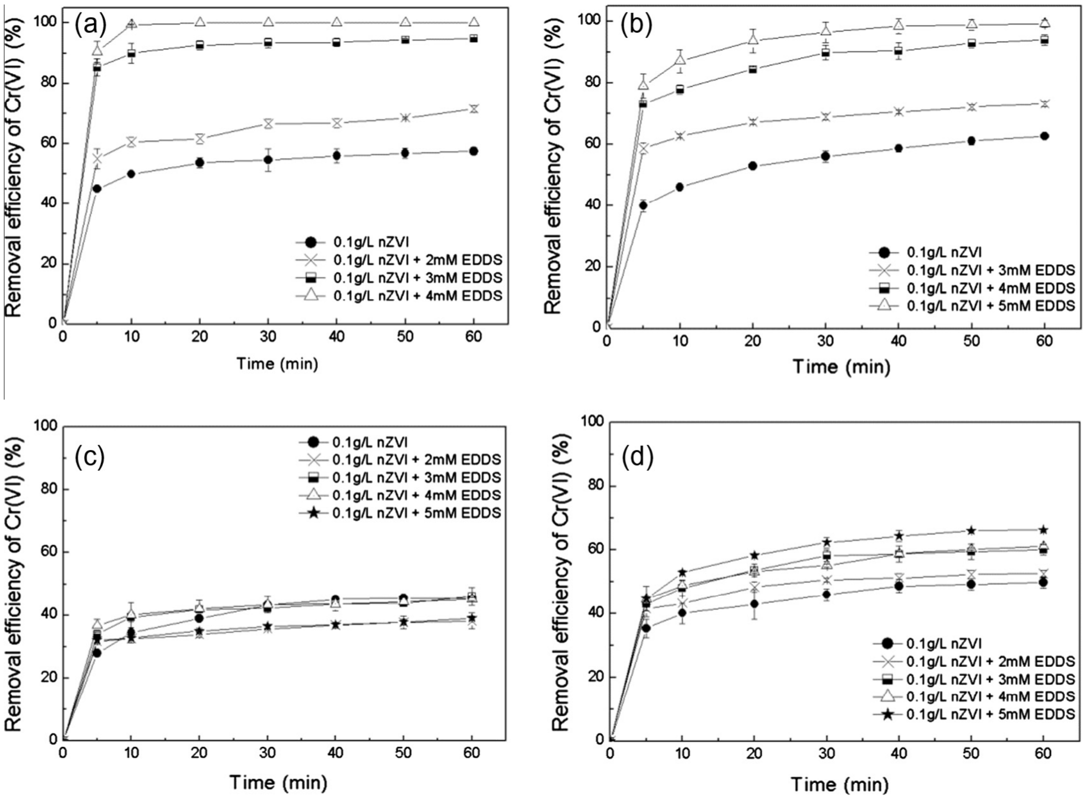

Fig. 2. Removal efficiency of Cr(VI) by nZVI in the presence of EDDS under various conditions: (a) pH 5.6; (b) pH 7.0; (c) pH 9.0; (d) pH 9.0, in the absence of dissolved oxygen.

coprecipitating on the surface of nZVI which inhibited further decomposition of surface iron and lowered nZVI activity. It is clearly demonstrated that the higher the concentration of EDDS, the higher the Cr(VI) removal efficiency. EDDS was effective to maximize the effective utilization of Fe^0 which has been decreased because of the passivation layer formed on its surface.

The results were supported by the XRD patterns of nZVI particles and that after reaction with Cr(VI) in the absence and presence of EDDS (Fig. 3). According to the JCPDS file, two major peaks in Fig. 3a were identified as Fe^0 ($2\theta = 44.64$ and 64.96). Fig. 3b and c obviously show that the characteristic peak of Fe^0 weakened after reaction, which indicates that the nZVI particles had been consumed in the solution. There has a peak "m" in Fig. 3b and c, confirming the existence of magnetite (Fe_3O_4) ($2\theta = 35.45°$), maghemite (γ-Fe_2O_3) ($2\theta = 35.68°$), and Cr_2FeO_4 ($2\theta = 35.50°$) after reaction. The mixture with EDDS has weaker peaks of Fe^0 and "m" compared with that without EDDS, demonstrating that the EDDS increased the amount of nZVI for reaction but produced fewer amounts of precipitates on the surface of nZVI. It should be noted that the chromium peaks could hardly be observed probably due to the small amount of chromium in the solution [41,42]. The SEM images of precipitates collected from the reaction of Cr(VI) reduction by nZVI in the absence and presence of EDDS were examined (Fig. 4). As demonstrated in Fig. 4a, the precipitates assembled together into blocks and a substantial amount of clastic precipitates were observed on the surface of solid phase, which should be ascribed to the accumulation of Fe(III)/Cr(III) precipitates on the surface of nZVI. By contrast, Fig. 4b displays that the precipitates were in the form of smaller-sized debris in the presence of EDDS. This may reveal that the consumption of nZVI was more complete and the EDDS prevented the accumulation of precipitates during the reaction. Thus, it was proposed that the presence of EDDS reduced the degree of passivation on the nZVI surface during the reaction, facilitating the efficiency of electron transfer from nZVI to the contaminant and thus maximizing the utilization of nZVI.

In contrast to the above finding that the presence of EDDS significantly enhanced the reduction of Cr(VI) by nZVI at pH 5.6 and 7.0, the removal efficiency of Cr(VI) at pH 9.0 was not promoted, regardless of the concentrations of EDDS (2–5 mM). Instead, a slight decrease in Cr(VI) removal was observed in the presence of EDDS. Taking consideration of previous results that acid conditions favor the reduction reaction, it could be speculated that there were other factors affecting the reaction under alkaline conditions. The removal of Cr(VI) in aqueous solution at pH 9.0 was further studied in the following.

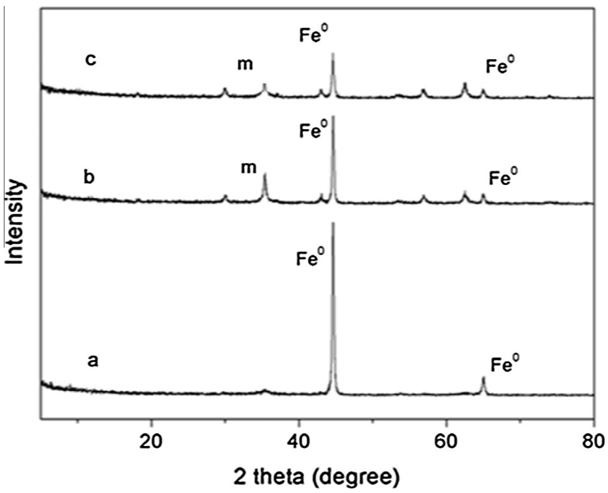

Fig. 3. X-ray diffractograms of nZVI: (a) before reaction with Cr(VI); (b) after reaction with Cr(VI) in the absence of EDDS; (c) after reaction with Cr(VI) with 4 mM EDDS. m = magnetite(Fe_3O_4), maghemite(γ-Fe_2O_3) and Cr_2FeO_4.

3.3. Effect of DO on Cr(VI) reduction

Dissolved oxygen (DO) can accept the electrons released from the corrosion of nZVI as an oxidant in aqueous environment and therefore it can be one of typical competitors with contaminants for nZVI utilization. In the presence of DO, the nZVI could consume DO to some extent in the duration of Cr(VI) removal [43–45].

To examine the effect of DO on Cr(VI) removal efficiency, the reaction was performed in absence and presence of DO at initial solution pH 9.0 (Fig. 2d). In the absence of DO, the removal efficiency was higher than that in presence of DO at the same EDDS concentration (e.g., the value was 60.2% and 46.0%, respectively, in the absence and presence of DO with addition of 3 mM EDDS). Moreover, the same trend as observed at pH 5.6 and 7.0 was that the removal of Cr(VI) increased along with the increase of EDDS concentrations in the absence of DO. The results mainly derived from EDDS chelation with Cr(III)/Fe(III) (hydro)oxides as mentioned before. However, it was obvious that the Cr(VI) removal was not promoted by EDDS in the presence of DO and the efficiency even decreased to 38.2% at 5 mM EDDS. The presence of EDDS in alkaline solution with DO exhibited a negative effect on Cr(VI) reduction. This should be associated with the role of EDDS in the oxidation of nZVI in the co-presence of Cr(VI) and DO. Eary and Rai [46] examined the reduction of Cr(VI) with Fe(II) in oxygenated solutions containing phosphate of various concentrations and found the presence of phosphate causes a more significant enhancement in the rate of Fe(II) oxidation by oxygen than that by Cr(VI). Guan et al. [36] reported that the presence of phosphate, humic acid and silicate resulted in an elevation in residual Cr(VI) concentration under alkaline conditions, attributing to the fact that the presence of ligands causes an enhancement in the rate of aqueous Fe(II) oxidation by dissolved oxygen. Keenan and Sedlak [47] also found that the organic ligand (e.g., EDTA) could accelerate the rates of ferrous iron oxidation by oxygen and hydrogen peroxide. Accordingly, it could be inferred that the presence of EDDS might enhance the reaction between DO and Fe(II) (the reducing agent from corrosion of nZVI), leading to the less nZVI consumption on Cr(VI) reduction.

3.4. Effect of EDDS on nZVI corrosion

As discussed above, it was presumed that the presence of EDDS reduced the degree of passivation on the nZVI surface during the reaction, facilitating the utilization of nZVI. Thus, the total iron concentrations were determined to further verify the effect of EDDS on the nZVI corrosion kinetics. Fig. 5 shows the total soluble iron concentrations in nZVI suspension in the absence and presence of EDDS at pH 5.6 and pH 9.0. In the absence of EDDS, the total soluble iron was kept at extremely low concentrations within 1 h at both pH 5.6 and 9.0, indicating that the corrosion of nZVI in DI water was quite slow. In contrast, as the EDDS concentration increased from 0 mM to 5 mM, the total soluble iron concentrations significantly increased. The concentration of total soluble iron achieved 64.75 mg/L when 4 mM EDDS solution was added into the mixture at pH 5.6 (Fig. 5c). It can be concluded that more nZVI participated in the reaction in aqueous solution after addition of the EDDS.

It can be observed that the total soluble iron concentrations were below 30 mg/L at pH 9.0 in the presence of DO (Fig. 5a). However, there is a similar trend as that observed at pH 5.6, i.e., the concentration of total soluble iron increased with increasing concentration of EDDS, which supported that the EDDS enhanced the reaction between nZVI and DO/water at pH 9.0. Considering

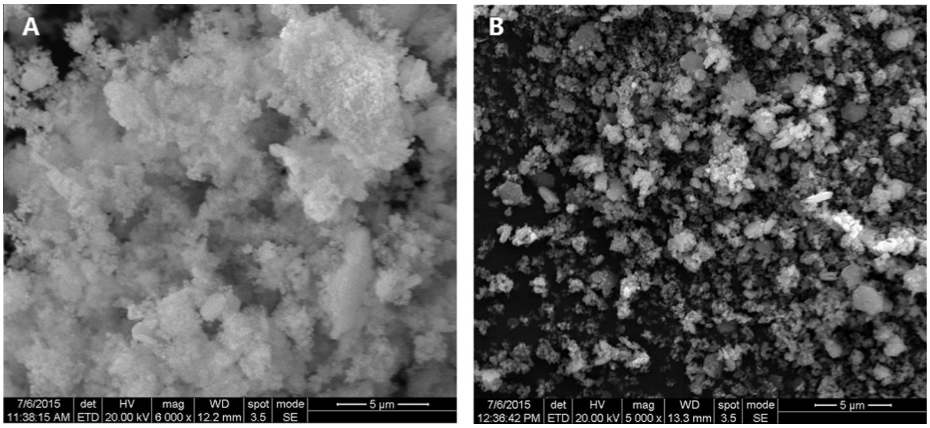

Fig. 4. SEM images of products collected from reaction of Cr(VI) with nZVI at initial pH 5.6 in the absence of EDDS (A) and in the presence of EDDS (B). (Cr(VI) = 10 mg/L; Fe^0 = 100 mg/L; EDDS = 4 mM).

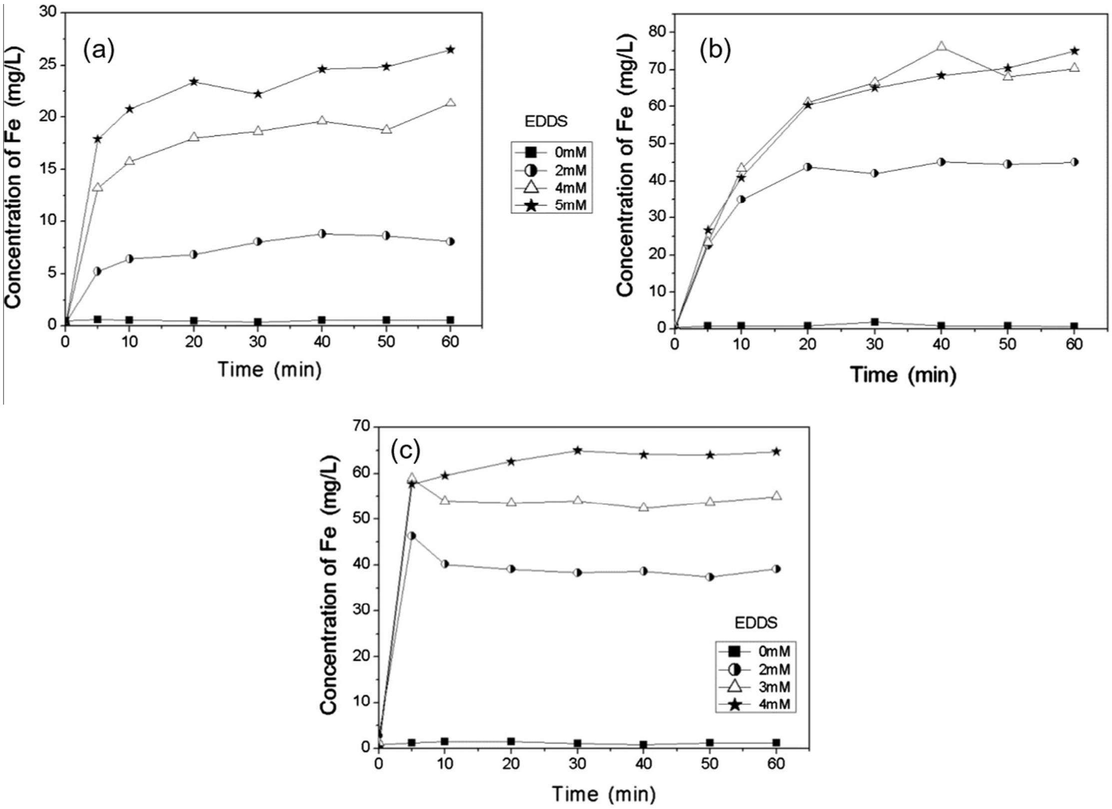

Fig. 5. Kinetics of nZVI corrosion in DI water: (a) at pH 9.0; (b) at pH 9.0 in the absence of DO; (c) at pH 5.6.

the Cr(VI) removal efficiency was not enhanced in the presence of EDDS at pH 9.0 (Fig. 2c), it can be speculated that the reaction mainly proceeded between nZVI and DO. The results verified the speculation about the competing effect of DO on the removal of Cr(VI) in the previous section. In the absence of DO, the value of iron concentration got 75.1 mg/L in the presence of 5 mM EDDS at pH 9.0 (Fig. 5b), which was much higher than that in the presence of DO. This reveals that more nZVI/Fe(II) were transformed to Fe(III) precipitates due to DO oxidation even in the presence of EDDS.

4. Conclusions

The chelant EDDS was proved to be an effective material to enhance reduction in nZVI/Cr(VI) system. EDDS chelated with Cr (III)/Fe(III) ions to reduce Cr(III)/Fe(III) co-precipitation and avoid the formation of passivation layer on nZVI surface, which maximized the utilization of nZVI on Cr(VI) reduction. Batch experiments indicated that the Cr(VI) removal efficiency increased with increasing EDDS concentrations, and decreased as initial pH increased. As a result, the combination of nZVI with EDDS addition was superior to nZVI used alone in removing Cr(VI) from aqueous solution at pH 5.6, with removal efficiencies of 100% and 57.5%, respectively. The presence of DO in the system could also influence the Cr(VI) reduction. The Cr(VI) removal efficiency were 20% higher in the absence of DO than that in presence of DO under alkaline condition when adding the chelant EDDS. Overall, EDDS is an environment-friendly and low-cost chelant, as a consequence, addition of EDDS along with nZVI will be an efficient and promising alternative for the removal of Cr(VI) from wastewater. However, the solution pH and DO are primary factors that could influence the Cr(VI) reduction, which should be taken into consideration in the practical application.

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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.seppur.2016.03.055.

References

[1] H.R. Dong, X.H. Guan, D.S. Wang, J. Ma, Individual and combined influence of calcium and anions on simultaneous removal of chromate and arsenate by Fe(II) under suboxic conditions, Sep. Purif. Technol. 80 (2011) 284–292.
[2] A.S.K. Kumar, R. Ramachandran, S. Kalidhasan, V. Rajesh, N. Rajesh, Potential application of dodecylamine modified sodium montmorillonite as an effective adsorbent for hexavalent chromium, Chem. Eng. J. 211 (2012) 396–405.
[3] J. Nemecek, O. Lhotski, T. Cajthaml, Nanoscale zero-valent iron application for in situ reduction of hexavalent chromium and its effects on indigenous microorganism populations, Sci. Total Environ. 485 (2014) 739–747.
[4] L. Yang, Y. Xiao, S. Liu, Y. Li, Q. Cai, S. Luo, G. Zeng, Photocatalytic reduction of Cr(VI) on WO_3 doped long TiO_2 nanotube arrays in the presence of citric acid, Appl. Catal. B Environ. 94 (1–2) (2010) 142–149.
[5] V. Achal, X. Pan, D.-J. Lee, D. Kumari, D. Zhang, Remediation of Cr(VI) from chromium slag by biocementation, Chemosphere 93 (7) (2013) 1352–1358.
[6] F. Fu, J. Ma, L. Xie, B. Tang, W. Han, S. Lin, Chromium removal using resin supported nanoscale zero-valent iron, J. Environ. Manage. 128 (2013) 822–827.
[7] F. He, D.Y. Zhao, Preparation and characterization of a new class of starch-stabilized bimetallic nanoparticles for degradation of chlorinated hydrocarbons in water, Environ. Sci. Technol. 39 (9) (2005) 3314–3320.
[8] F. He, D.Y. Zhao, J.C. Liu, C.B. Roberts, Stabilization of Fe-Pd nanoparticles with sodium carboxymethyl cellulose for enhanced transport and dechlorination of trichloroethylene in soil and groundwater, Ind. Eng. Chem. Res. 46 (1) (2007) 29–34.
[9] P. Miretzky, A.F. Cirelli, Cr(VI) and Cr(III) removal from aqueous solution by raw and modified lignocellulosic materials: a review, J. Hazard. Mater. 180 (1–3) (2010) 1–19.
[10] H.R. Dong, I.M.C. Lo, Influence of humic acid on the colloidal stability of surface-modified nano zero-valent iron, Water Res. 47 (1) (2013) 419–427.
[11] H.R. Dong, I.M.C. Lo, Transport of surface-modified nano zero-valent iron (SM-NZVI) in saturated porous media: effects of surface stabilizer type, subsurface geochemistry, and contaminant loading, Water Air Soil Pollut. 225 (2014) 2107–2118.
[12] H.R. Dong, G.M. Zeng, C. Zhang, J. Liang, K. Ahmad, P. Xu, X.X. He, M.Y. Lai, Interaction between Cu^{2+} and different types of surface-modified nanoscale zero-valent iron during their transport in porous media, J. Environ. Sci. 32 (2015) 180–188.
[13] C. Noubactep, S. Care, R. Crane, Nanoscale metallic iron for environmental remediation: prospects and limitations, Water Air Soil Pollut. 223 (3) (2012) 1363–1382.
[14] L.N. Shi, Y.M. Lin, X. Zhang, Z.L. Chen, Synthesis, characterization and kinetics of bentonite supported nZVI for the removal of Cr(VI) from aqueous solution, Chem. Eng. J. 171 (2) (2011) 612–617.
[15] L.N. Shi, X. Zhang, Z.L. Chen, Removal of chromium (VI) from wastewater using bentonite-supported nanoscale zero-valent iron, Water Res. 45 (2) (2011) 886–892.
[16] M. Hou, H. Wan, T. Liu, Y. Fan, X. Liu, X. Wang, The effect of different divalent cations on the reduction of hexavalent chromium by zerovalent iron, Appl. Catal. B Environ. 84 (1–2) (2008) 170–175.
[17] H. Dong, X. Guan, I.M. Lo, Fate of As(V)-treated nano zero-valent iron: determination of arsenic desorption potential under varying environmental conditions by phosphate extraction, Water Res. 46 (13) (2012) 4071–4080.
[18] X. Guan, Y. Sun, H. Qin, J. Li, I.M. Lo, D. He, H. Dong, The limitations of applying zero-valent iron technology in contaminants sequestration and the corresponding countermeasures: the development in zero-valent iron technology in the last two decades (1994–2014), Water Res. 75 (2015) 224–248.
[19] D.Y.S. Yan, I.M.C. Lo, Removal effectiveness and mechanisms of naphthalene and heavy metals from artificially contaminated soil by iron chelate-activated persulfate, Environ. Pollut. 178 (2013) 15–22.
[20] F.L. Fu, W.J. Han, B. Tang, M. Hu, Z.H. Cheng, Insights into environmental remediation of heavy metal and organic pollutants: Simultaneous removal of hexavalent chromium and dye from wastewater by zero-valent iron with ligand-enhanced reactivity, Chem. Eng. J. 232 (2013) 534–540.
[21] X. Zhang, B. Deng, J. Guo, Y. Wang, Y. Lan, Ligand-assisted degradation of carbon tetrachloride by microscale zero-valent iron, J. Environ. Manage. 92 (4) (2011) 1328–1333.
[22] S. Tandy, R. Schulin, B. Nowack, Uptake of metals during chelant-assisted phytoextraction with EDDS related to the solubilized metal concentration, Environ. Sci. Technol. 40 (8) (2006) 2753–2758.
[23] I.M.C. Lo, D.C.W. Tsang, T.C.M. Yip, F. Wang, W. Zhang, Influence of injection conditions on EDDS-flushing of metal-contaminated soil, J. Hazard. Mater. 192 (2) (2011) 667–675.
[24] D.Y.S. Yan, I.M.C. Lo, Pyrophosphate coupling with chelant-enhanced soil flushing of field contaminated soils for heavy metal extraction, J. Hazard. Mater. 199 (2012) 51–57.
[25] N. Finzgar, A. Zumer, D. Lestan, Heap leaching of Cu contaminated soil with S,S-EDDS in a closed process loop, J. Hazard. Mater. 135 (1–3) (2006) 418–422.
[26] E. Meers, A. Ruttens, M.J. Hopgood, D. Samson, F.M.G. Tack, Comparison of EDTA and EDDS as potential soil amendments for enhanced phytoextraction of heavy metals, Chemosphere 58 (8) (2005) 1011–1022.
[27] T. Suzuki, M. Niinae, T. Koga, T. Akita, M. Ohta, T. Choso, EDDS-enhanced electrokinetic remediation of heavy metal-contaminated clay soils under neutral pH conditions, Coll. Surf A Physicochem. Eng. Asp. 440 (2014) 145–150.
[28] S. Tandy, A. Ammann, R. Schulin, B. Nowack, Biodegradation and speciation of residual SS-ethylenediaminedisuccinic acid (EDDS) in soil solution left after soil washing, Environ. Pollut. 142 (2) (2006) 191–199.
[29] B.A. Manning, J.R. Kiser, H. Kwon, S.R. Kanel, Spectroscopic investigation of Cr(III)- and Cr(VI)-treated nanoscale zerovalent iron, Environ. Sci. Technol. 41 (2) (2007) 586–592.
[30] Y.P. Sun, X.Q. Li, J.S. Cao, W.X. Zhang, H.P. Wang, Characterization of zero-valent iron nanoparticles, Adv. Colloid Interface Sci. 120 (1–3) (2006) 47–56.
[31] Y. Ruey-Fang, C. Fung-Hwa, C. Wen-Po, C. Jen-Chieh, Application of pH, ORP, and DO monitoring to evaluate chromium(VI) removal from wastewater by the nanoscale zero-valent iron (nZVI) process, Chem. Eng. J. 255 (2014) 568–576.
[32] Y. Wu, J. Zhang, Y. Tong, X. Xu, Chromium (VI) reduction in aqueous solutions by Fe_3O_4-stabilized Fe^0 nanoparticles, J. Hazard. Mater. 172 (2–3) (2009) 1640–1645.
[33] P. Feng, X.H. Guan, Y.K. Sun, W. Choi, H.J. Qin, J.M. Wang, J.L. Qiao, L.N. Li, Weak magnetic field accelerates chromate removal by zero-valent iron, J. Environ. Sci. 31 (2015) 175–183.
[34] H.R. Dong, Q. He, G.M. Zeng, L. Tang, C. Zhang, Y.K. Xie, Y.L. Zeng, F. Zhao, Y.N. Wu, Chromate removal by surface-modified nanoscale zero-valent iron: effect of different surface coatings and water chemistry, J. Colloid Interface Sci. 471 (2016) 7–13.
[35] H.R. Dong, K. Ahmad, G.M. Zeng, Z.W. Li, G.U. Chen, Q. He, Y.K. Xie, Y.N. Wu, F. Zhao, Y.L. Zeng, Influence of fulvic acid on the colloidal stability and reactivity of nanoscale zero-valent iron, Environ. Pollut. 211 (2016) 363–369.
[36] X. Guan, H. Dong, J. Ma, Influence of phosphate, humic acid and silicate on the transformation of chromate by Fe(II) under suboxic conditions, Sep. Purif. Technol. 78 (3) (2011) 253–260.
[37] T. Lee, H. Lim, Y. Lee, J.-W. Park, Use of waste iron metal for removal of Cr(VI) from water, Chemosphere 53 (5) (2003) 479–485.
[38] R.M. Powell, R.W. Puls, S.K. Hightower, D.A. Sabatini, Coupled iron corrosion and chromate reduction mechanisms for subsurface remediation, Environ. Sci. Technol. 29 (1995) 1913–1922.
[39] C. Noubactep, S. Care, On nanoscale metallic iron for groundwater remediation, J. Hazard. Mater. 182 (1–3) (2010) 923–927.
[40] W. Huang, M. Brigante, F. Wu, C. Mousty, K. Hanna, G. Mailhot, Assessment of the Fe(III)-EDDS complex in Fenton-like processes: from the radical formation to the degradation of bisphenol A, Environ. Sci. Technol. 47 (2013) 1952–1959.
[41] O. Celebi, C. Uezuem, T. Shahwan, H.N. Erten, A radiotracer study of the adsorption behavior of aqueous Ba^{2+} ions on nanoparticles of zero-valent iron, J. Hazard. Mater. 148 (3) (2007) 761–767.
[42] S.-S. Chen, B.-C. Hsu, L.-W. Hung, Chromate reduction by waste iron from electroplating wastewater using plug flow reactor, J. Hazard. Mater. 152 (3) (2008) 1092–1097.
[43] D. O'Carroll, B. Sleep, M. Krol, H. Boparai, C. Kocur, Nanoscale zero valent iron and bimetallic particles for contaminated site remediation, Adv. Water Resour. 51 (2013) 104–122.
[44] C. Uzum, T. Shahwan, A.E. Eroglu, I. Lieberwirth, T.B. Scott, K.R. Hallam, Application of zero-valent iron nanoparticles for the removal of aqueous Co^{2+} ions under various experimental conditions, Chem. Eng. J. 144 (2) (2008) 213–220.
[45] L. Wu, L. Liao, G. Lv, F. Qin, Y. He, X. Wang, Micro-electrolysis of Cr (VI) in the nanoscale zero-valent iron loaded activated carbon, J. Hazard. Mater. 254 (2013) 277–283.
[46] L.E. Eary, D. Rai, Chromate removal from aqueous wastes by reduction with ferrous ion, Environ. Sci. Technol. 22 (1988) 972–977.
[47] C.R. Keenan, D.L. Sedlak, Ligand-enhanced reactive oxidant generation by nanoparticulate zero-valent iron and oxygen, Environ. Sci. Technol. 42 (2008) 6936–6941.