



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



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## ARTICLE INFO

## Article history:

Received 12 January 2016

Received in revised form 29 March 2016

Accepted 31 March 2016

Available online 1 April 2016

## Keywords:

Chromate reduction

Chelation

EDDS

Nanoscale zero-valent iron

Surface passivation

## 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.

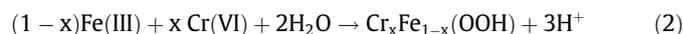
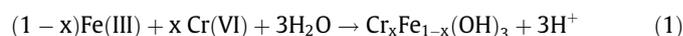
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## 1. Introduction

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  $\text{Fe}_x\text{Cr}_{1-x}(\text{OH})_3/\text{Fe}_x\text{Cr}_{1-x}(\text{OOH})$  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].



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.

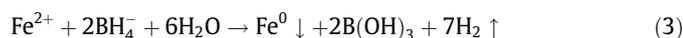
## 2. Materials and methods

### 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:



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  $\mu$ m 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  $K\alpha$  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

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