



Chromium(VI) removal by mechanochemically sulfidated zero valent iron and its effect on dechlorination of trichloroethene as a co-contaminant

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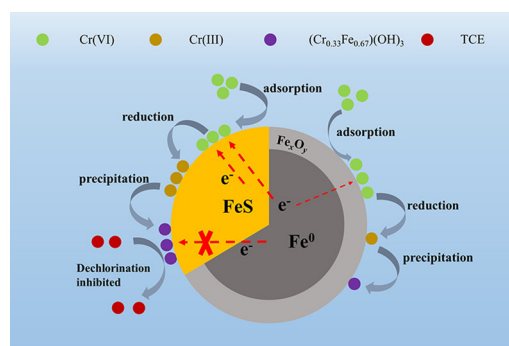
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HIGHLIGHTS

- Cr(VI) removal by S-mZVI^{bm} was mainly a surface reduction and precipitation process.
- Mechanochemical sulfidation enhanced Cr(VI) removal by increasing surface area.
- Electron efficiency of Cr(VI) removal was 100% but particle efficiency was <1%.
- Cr(VI) was an electron sink for TCE dechlorination by S-mZVI^{bm}.

GRAPHICAL ABSTRACT



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ABSTRACT

Mechanochemically sulfidated microscale zero valent iron (S-mZVI^{bm}) is a promising groundwater remediation material as it has been proven to be not only efficient in dechlorinating chlorinated compounds but also amenable to up-scaling. Yet, its efficiency in treating metal contaminants remains barely studied. In this study, we investigated the mechanism and efficiencies of Cr(VI) removal by S-mZVI^{bm} and its effect on TCE dechlorination as a co-contaminant. The Cr(VI) removal by S-mZVI^{bm} was mainly a chemisorption process and its kinetics was well fitted by a pseudo-second-order model. Alkaline pH inhibited Cr(VI) removal while dissolved oxygen slightly depressed the Cr(VI) removal. The Cr(VI) removal rapidly formed a non-conductive layer on S-mZVI^{bm} surface to hinder further electron transfer from Fe⁰ core before H⁺ was able to accept any electrons to produce H₂, which resulted in 100% electron efficiencies of Cr(VI) removal but <1% of Fe⁰ utilization efficiency. The presence of Cr(VI) also dramatically inhibited the dechlorination of TCE and its electron sink efficiency as a co-contaminant by passivating the FeS surface. Therefore, Cr(VI) is likely to be an electron sink if present for remediation of other contaminants in groundwater.

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1. Introduction

Chromium is a priority pollutant and is often found in groundwater due to its widely use in industrial processes such as leather tanning, electroplating and stainless-steel production (Palmer and Wittbrodt,

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1991; Sarin et al., 2006; Yoon et al., 2011). Cr(VI) and Cr(III) are two oxidation states of chromium. Cr(VI) species, such as $\text{Cr}_2\text{O}_7^{2-}$ and HCr_2O_7^- , are harmful to both animals and plants due to their strong toxicity and mobility (Jin et al., 2016a; Jin et al., 2015; Jin et al., 2016b; Myers et al., 2000; Qian et al., 2013; Zhitkovich et al., 2002), whereas Cr(III) species are less hazardous and have low solubility in water (i.e., generally precipitate as hydroxides, $K_{sp}(\text{Cr}(\text{OH})_3) = 6.7 \times 10^{-31}$) (Ai et al., 2008; He et al., 2013; Hoch et al., 2008; Manning et al., 2007; Shen et al., 2013). Therefore, converting Cr(VI) to Cr(III) is a common strategy in remediating Cr-contaminated groundwater.

Zero valent iron (ZVI), considered as an efficient and low-cost reductant, has been widely investigated for the dechlorination of chlorinated compounds and reduction of redox-sensitive heavy metals and anions in groundwater (Feng et al., 2018; Fu et al., 2014; Gao et al., 2015; Guan et al., 2015; He et al., 2010; Lv et al., 2014; Mu et al., 2017; O'Carroll et al., 2013; Tang et al., 2017). Previous studies have proven that ZVI could easily transform Cr(VI) to Cr(III) via coupled oxidation with Fe^0 and Fe^{2+} , and then Cr(III) species precipitated with Fe(III) generated by forming $(\text{Cr}_x\text{Fe}_{1-x})(\text{OH})_3$ (Li et al., 2008; Manning et al., 2007; Ponder et al., 2000).

One of the most challenging aspects of applying ZVI in groundwater remediation is its low selectivity (or electron utilization efficiency) (Fan et al., 2016; Gu et al., 2017; Li et al., 2018). This is due to that the concurrent corrosion of ZVI competes electrons from Fe^0 with contaminants. Our previous research has shown that when microscale ZVI was used for trichloroethene (TCE) dechlorination under simulated plume conditions, only 0.19% of electrons from Fe^0 was used for TCE reduction while the rest was consumed by water corrosion (Gu et al., 2017). Yet, the reaction of Cr(VI) with ZVI is more favorable and the precipitation of Cr(III) species that are poor in conducting electrons would cause the passivation of ZVI surface. Both factors could significantly affect the selectivity of ZVI toward Cr(VI), which remains to be explored.

In recent years, one modification of ZVI called sulfidation—defined as ZVI modified by sulfur compounds—has emerged as a promising approach in enhancing both the particle reactivity but also the selectivity in dechlorinating TCE, one of the most detected contaminants in groundwater (Fan et al., 2016; Han and Yan, 2016; Li et al., 2017; Rajajayavel and Ghoshal, 2015). Until now, researches on sulfidated ZVI have been primarily focused on nanoscale ZVI (Cao et al., 2017; Dong et al., 2018; Fan et al., 2017; He et al., 2018; Li et al., 2016; Tang et al., 2016; Wu et al., 2018). However, nanoscale ZVI (nZVI) is expensive and only likely to be used at modest quantity for targeted application (Crane and Scott, 2012). In addition, the reported nZVI sulfidation processes were typically carried out in aqueous phase using dissolved, low-valent sulfur species that are readily oxidized by oxygen, which makes the process hard to be scaled up (Fan et al., 2016; Li et al., 2017). To solve these problems, our group recently reported the synthesis of sulfidated microscale ZVI (S-mZVI^{bm}) with ZVI and elemental sulfur using mechanochemical method (Gu et al., 2017; Huang et al., 2017). The obtained S-mZVI^{bm} could dechlorinate TCE with at least an order magnitude faster rates and greater electron efficiencies than the unsulfidated counterparts (mZVI^{bm}) and the process is highly amenable to up-scaling. Yet, its efficiencies in treating heavy metal contaminants such as Cr have not been fully determined.

Several studies on Cr(VI) removal by S-ZVI have been reported (Du et al., 2016; Gong et al., 2017; Li et al., 2018; Shao et al., 2018). Du et al. (2016) prepared a nanoscale FeS@Fe^0 material using a two-step method. Nanoscale ZVI was firstly synthesized through reduction of ferrous salts by borohydride and then dispersed in ferrous iron solution followed by adding sulfide. The FeS@Fe^0 showed much higher reactivity than the unsulfidated nZVI toward Cr(VI) sequestration by forming Fe-Cr hydroxides. This was attributed to the coverage of FeS accelerating the electron transfer from Fe^0 core to the sorbed Cr(VI). Dissolved oxygen (DO) was found to negatively affect Cr(VI) removal. Gong et al. (2017) fabricated S-nZVI particles through “one-pot” synthesis by adding dithionite during nZVI synthesis. The FeS coating on the Fe^0

surface effectively inhibited the aggregation of Fe^0 and resulted in larger specific surface area and consequently higher Cr(VI) removal efficiency than nZVI. More recently, Shao et al. (2018) showed that oxygenation, however, significantly enhanced Cr(VI) removal by sulfidated microscale ZVI, which was attributed to enhanced Fe(II) production that resulted from accelerated corrosion of $\text{Fe}(0)$, in contrast to that reported by Du et al. (2016). Nonetheless, the electron selectivity of S-ZVI toward Cr(VI) was not determined and how sulfidation affects particle selectivity was not studied under typical anoxic conditions in groundwater. In addition, as a strong passivation agent, Cr(VI) can significantly affect the interaction of ZVI or S-ZVI with its typical co-contaminants such as TCE in groundwater. Yet, this effect has not been explored in previous studies.

The overall objective of this study is to understand the interfacial reaction between S-mZVI^{bm} and Cr(VI) and its effects on dechlorination of TCE as a co-contaminant. The specific objectives are to (i) quantify and compare the removal rate of Cr(VI) and the electron selectivity by S-mZVI^{bm} and mZVI^{bm} under various conditions, (ii) gain insights into the mechanism of Cr sequestration by S-mZVI^{bm}, and (iii) determine the effect of Cr passivation on TCE dechlorination by S-mZVI^{bm}.

2. Materials and methods

2.1. Chemicals

All chemicals used in this study were of analytical grade or better unless otherwise mentioned. Microscale ZVI (reagent grade), elemental S powder, FeS, NaCl, NaOH and HCl (reagent grade) were provided by Aladdin (Shanghai, China). Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$, 99.8%) was purchased from Wuxi Haishuo Biological Co., LTD (Jiangsu, China). TCE (99%, GC grade), methanol (>99%, GC) and liquid chlorinated ethene standards in methanol including TCE (1000 ppm), cis-DCE (1000 ppm), trans-DCE (1000 ppm), 1,1-DCE (1000 ppm), and VC (1000 ppm) were obtained from Aladdin (Shanghai, China). Gaseous alkane, alkene, and alkyne standards (1000 ppm of methane, ethene, ethane, acetylene, propene, propane, butene, butane, pentene, pentane, hexene, and hexane) were purchased from Dalian Special Gases Co. (Dalian, China). Ultra-high purity nitrogen, hydrogen and air were supplied by Hangzhou Special Gas Co. (Hangzhou, China) for GC measurements. Solutions were typically prepared with deionized (DI) water, which was deoxygenated by bubbling N_2 for 0.5 h before use except for experiments under aerobic conditions.

2.2. Particle preparation and characterization

S-mZVI^{bm} particles were prepared following the reported method (Gu et al., 2017). Briefly, ZVI and sulfur powders (S/Fe molar ratio of 0, 0.1, and 0.2) were placed in stainless steel jars with zirconia balls and milled at 400 rpm under argon conditions in a planetary ball mill. After 20 h of milling, S-mZVI^{bm} particles were collected in a N_2 -filled glovebag and stored in a glovebox before use.

The specific surface area of S-mZVI^{bm} was measured by N_2 adsorption-desorption tests at 77 K using a Micromeritics ASAP2020 (USA). The oxidation states of elements on S-mZVI^{bm} surface before and after Cr(VI) removal were obtained by a Kratos AXIS Ultra DLD XPS and the details are provided in SI.

2.3. Batch experiments of Cr(VI) removal and particle efficiencies

Batch experiments of Cr(VI) removal were performed in a 250 mL, three-necked round-bottom flask with continuous mechanical stirring at 400 rpm. Typically, 200 mL Cr(VI) solution (10 mg/L) with initial pH of 6 was added to the flask followed by S-mZVI^{bm} or mZVI^{bm} (1 g/L). At selected time intervals, 1 mL of sample was withdrawn and filtered through a 0.22 μm nylon filter membrane (ANPEL Laboratory Technologies, Shanghai, China) for measurements of Cr(VI) and

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