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Reduction of Cr(VI) in simulated groundwater by FeS-coated iron magnetic nanoparticles

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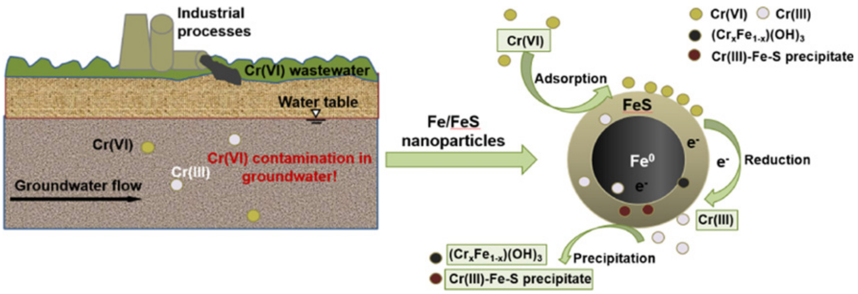
HIGHLIGHTS

- FeS coated on Fe^0 surface, effectively inhibited Fe^0 aggregation, and formed Fe/FeS
- Increasing S/Fe molar ratio from 0.138 to 0.207 enhanced Cr(VI) removal by 63%
- Fe/FeS inhibited the leaching of Fe, reducing the toxicity of the particles
- Fe/FeS removed aqueous Cr(VI) mainly by adsorption, reduction, and precipitation
- Fe/FeS effectively removed Cr(VI) through batch and column tests

GRAPHICAL ABSTRACT



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ABSTRACT

FeS-coated iron (Fe/FeS) magnetic nanoparticles were easily prepared, characterized, and applied for Cr(VI) removal in simulated groundwater. TEM, XRD, and BET characterization tests showed that FeS coating on the surface of Fe^0 inhibited the aggregation of Fe^0 and that Fe/FeS at a S/Fe molar ratio of 0.207 possessed a large surface area of 62.1 m^2/g. Increasing the S/Fe molar ratio from 0 to 0.138 decreased Cr(VI) removal by 42.8%, and a further increase to 0.207 enhanced Cr(VI) removal by 63% within 72 h. Moreover, Fe/FeS inhibited the leaching of Fe, reducing the toxicity of the particles. Mechanistic analysis indicated that Fe^0, Fe^{2+}, and S^{2-} were synergistically involved in the reduction of Cr(VI) to nontoxic Cr(III), which further precipitated as $(Cr_xFe_{1-x})(OH)_3$ and Cr(III)-Fe-S. The process of Cr(VI) sorption by Fe/FeS ($S/Fe = 0.207$) was fitted well with a pseudo-second-order kinetic model, and the isotherm data were simulated by Langmuir isotherm model with a maximum sorption capacity of 69.7 mg/g compared to 48.9 mg/g for Fe^0. Low pH and initial Cr(VI) concentration favored Cr(VI) removal. Continuous fixed bed column studies showed that simulated permeable reactive barriers (PRB) with Fe/FeS was considerably effective for in situ removal of Cr(VI) from groundwater. This study demonstrated the high potential of Fe/FeS for Cr(VI) immobilization in water, groundwater, and soil.

1. Introduction

Chromium (Cr) is widely used in industrial processes, including metal electroplating, metal finishing, steelworks manufacturing, leather

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tanning, and synthesis of pigments (Sarin et al., 2006; Yoon et al., 2011). It is one of the most toxic metals detected in groundwater, surface water, and soils. Cr exists in the environment primarily in two valence states: Cr(III) and Cr(VI) (Li et al., 2012). Cr(VI) species, such as $HCrO_4^-$ and $Cr_2O_7^{2-}$, are soluble in water and exert toxic effects on biological systems due to their strong oxidizing ability (Vainshtein et al., 2003). In contrast, Cr(III) is less hazardous and generally forms highly insoluble minerals. In fact it is an essential microelement for organisms at low concentrations (Sarkar et al., 2010; Villacis-Garcia et al., 2015). Techniques such as adsorption (Sarkar et al., 2010; Wang et al., 2015a), photocatalytic reduction (Wang et al., 2015b; Wang et al., 2015c), and membrane separation (Çengeloğlu et al., 2003) have been applied for Cr(VI) removal. However, these technologies exist some deficiencies, such as costly and production of other waste problems. Reduction of Cr(VI) to relatively nontoxic Cr(III) followed by chemical precipitation is a common method to mitigate Cr(VI) (Gupta et al., 2011; Lee et al., 2013; Wilkin et al., 2005).

Various reducing materials such as zero valent iron (ZVI) (Melitas et al., 2001; Shi et al., 2011), divalent iron (Fe(II)) (Schlautman and Han, 2001), and iron sulfide (Kantar et al., 2015; Patterson and Fendorf, 1997) have been investigated for the reduction of Cr(VI) to Cr(III). ZVI is regarded as one of the most effective reductants due to its strong reactivity, low cost, and easy separation and disposal (Crane and Scott, 2012; Fu et al., 2014). However, there are still challenges with environmental application, such as high toxicity and aggregation of ZVI particles (Keller et al., 2012; Li et al., 2016). Moreover, ZVI is not thermodynamically stable in water and is subject to corrosion by water itself, producing gases such as hydrogen or dinitrogen (Gong et al., 2016).

Iron sulfide (FeS), a tetragonal ferrous monosulfide, has been widely applied for treatment of heavy metals, including Cd^{2+}, Zn^{2+}, Hg^{2+}, Cu^{2+}, and Mn^{2+} due to its unique surface chemical properties and molecular structure (Wharton et al., 2000). Typically, the metals are removed through sorption, ion exchange, and/or precipitation of highly insoluble metal sulfides (Gong et al., 2016). FeS is an important reductant providing a source of Fe(II) and S(-II) species, which can act as electron donors and facilitate Cr(VI) reduction (Demoisson et al., 2005; Mullet et al., 2004).

Combining iron sulfide with ZVI (Fe/FeS) may be a feasible method for preparing multicomponent nanoparticles, which can possess unique physical and chemical properties due to a synergistic effect induced by interaction between individual components. For instance, incorporation of FeS to ZVI can slow down the releasing rate of Fe^{2+} from the core ZVI (Saleh et al., 2008; Xiu et al., 2010), reducing the toxicity of ZVI; the presence of FeS can prevent the aggregation of ZVI (Li et al., 2016; Li et al., 2012) and greatly decrease the chance of Cr(III) reoxidation (Lan et al., 2005; Patterson and Fendorf, 1997). Recently, Kim et al. (2011) developed a simple synthesis process to prepare Fe/FeS particles and the particles were successfully applied for faster and more efficient removal of trichloroethylene (TCE) from water than pure Fe^0 nanoparticles. Su et al. (2015) reported that FeS/Fe at an S/Fe molar ratio of 0.28 had the maximum sorption capacity of 85 mg/g for Cd^{2+}, which was >100% higher than that for pure ZVI. Aging the particles for three weeks had no negative effect on Cd^{2+} removal and Cd-containing mixture remained stable for two months. Compared to ZVI particles, the Fe/FeS nanoparticles exhibit some advantages such as larger surface area, higher reactivity, stronger magnetic responsivity, longer reactive longevity, and possibly greater affinity towards many heavy metals, and thus, the nanoparticles have the potential to be used as ideal reactive materials for environmental remediation.

The overall goal of the present study was to investigate the removal efficiency and mechanisms of aqueous Cr(VI) via Fe/FeS magnetic nanoparticles. The nanoparticles were synthesized using simple one-pot method. The specific objectives were to (1) evaluate the influence of different S/Fe molar ratios on the physicochemical characteristics and Cr(VI) removal efficiency of Fe/FeS; (2) examine the effects of pH and initial Cr(VI) concentrations on the Cr(VI) removal by Fe/FeS; (3) explore the underlying removal mechanisms; and (4) test the performance of Fe/FeS acting as an reactive material in permeable reactive barriers (PRB) for Cr(VI) removal in groundwater through column tests.

2. Materials and methods

2.1. Chemicals

All chemicals used in this study were of analytical grade or better. Ferric chloride ($FeCl_3 \cdot 6H_2O$, 99%, analytical grade), sodium dithionite ($Na_2S_2O_4$, 95%, analytical grade), sodium borohydride ($NaBH_4$, 98%, analytical grade), NaOH (analytical grade), and HCl (analytical grade) were provided by Jiangtian Chemical (Tianjin, China). Potassium dichromate ($K_2Cr_2O_7$, 99.5%, guaranteed grade) was purchased from Guangfu Technology Development (Tianjin, China). All solutions were prepared with N_2-purged deionized (DI) water.

2.2. Preparation and characterization of Fe/FeS particles

Fe/FeS particles were prepared following a revised version of the approach by Kim et al. (2011). Briefly, $FeCl_3 \cdot 6H_2O$ (14.48 g) was dissolved in 900 mL of DI water, and an 100-mL solution containing 9.74 g $NaBH_4$ with various amounts of dithionite (0, 0.32, 0.64, and 0.96 g, respectively) (pH 10.1) was added dropwise to the $FeCl_3$ solution (pH 1.9). Particles with S/Fe molar ratios of 0 (or Fe^0), 0.070, 0.138, and 0.207 were obtained. Preliminary tests showed that particles were no longer magnetic at an S/Fe molar ratio > 0.207, therefore, particles with S/Fe molar ratios ≤ 0.207 were chosen for further investigations. The mixture (pH 9.0) was idle for 15 min after reduction. The resultant particles were collected using a permanent magnet, rinsed with DI water three times, and subsequently freeze-dried in a vacuum freeze dryer (FD5-3, SIM International Group, CA, USA). All the particles were sealed under N_2 protection prior to use.

Surface morphology was obtained by a T-20 transmission electron microscope (TEM, JEM-2100, JEOL, Japan). Specific surface area was examined with a BET adsorption method (ASAP2460, Micromeritics, Atlanta, GA, USA). Zeta potential was measured with a Zetasizer Nano ZS90 (Malvern Instruments, Malvern, UK). The crystalline compositions were investigated by X-ray diffractometer (XRD) (D/max-2500, Rigaku, Tokyo, Japan). X-ray photoelectron spectroscopy (XPS, PHI-5000, Ulvac-Phi, Japan) was used to determine the surface elemental compositions of the particles and XPS spectra were analyzed using CasaXPS software (version 2.3.18). Gaussian (Y%)-Lorentzian (X%) was defined in CasaXPS as GL(X) (Fairley, 2016) and the elements peaks (S2p, Fe2p, and Cr2p) fitted best with a GL (30) line shape in this study. The magnetic properties of the particles were measured with a magnetic measuring system (Squid-vsm, Quantum Design, USA).

2.3. Effects of S/Fe molar ratios on Cr(VI) removal by Fe/FeS

Batch experiments were performed in sealed 40-mL glass vials under anoxic conditions. Fe/FeS particles with different S/Fe molar ratios (0, 0.070, 0.138, and 0.207) (0.012 g) were added to the vials, followed by the addition of 40-mL 25 mg/L Cr(VI) solutions. pH of the mixture was maintained at 5.0 ± 0.3 with HCl (0.1 M) and NaOH (0.1 M). The vials were then mixed at 40 rpm on an end-over-end rotator at 25 ± 1 °C. At predetermined time intervals, duplicate vials were sacrificially sampled. Magnet was used to separate the particles from the solution within 5 min and 10 mL supernatant was collected for Cr(VI), total Cr (TCr), and Fe analysis. Control tests without the addition of the particles were performed to evaluate the loss of Cr(VI) under otherwise identical conditions. All the experiments were conducted in duplicate.