Reductive sequestration of chromate by hierarchical FeS@Fe^0 particles

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ABSTRACT

Nanoscale Fe^0 (nFe^0) can detoxify Cr(VI)-bearing wastewater and groundwater, but rapid passivation is a negative factor for large-scale remediation applications. In this study, a magnetic FeS@Fe^0 hybrid material was fabricated by immobilization of iron sulfide (FeS) onto Fe^0 particles to improve the Cr(VI) removal capacity. The solid characterization confirmed that Fe^0 particles were encapsulated by amorphous iron monosulfide. The Cr(VI) uptake by FeS@Fe^0 hybrid particles was found to follow pseudo-second-order rate kinetics, and the Langmuir isotherm was most appropriate to describe Cr(VI) sorption. Meanwhile, the FeS@Fe^0 hybrid particles showed a much higher efficiency towards Cr(VI) sequestration compared to individual nFe^0. Moreover, the results of batch experiments with various adsorbent doses indicated that the reactivity of FeS@Fe^0 varies with different FeS-to-Fe^0 molar ratios. The reaction rate constants for Cr(VI) removal first increased with an increasing FeS-to-Fe^0 ratio from 0/1 to 1/9, and then decreased for the FeS-to-Fe^0 ratio increased further 1/5 or 1/3. For environmental parameters, there was a negative effect of increasing the solution pH and dissolved oxygen on Cr(VI) removal. Furthermore, a mechanistic analysis revealed that Cr(VI) reduction occurred predominantly at the solid-liquid interface, and that Fe(II) regenerated from FeS@Fe^0 corrosion may account for 52% of the Cr(VI) reduction, while electrons from Fe^0 and FeS account for the rest. After treatment, Cr(VI) was completely transformed and immobilized as solid Fe-Cr hydroxide precipitates, thus avoiding secondary contamination. The FeS@Fe^0 hybrid material has a better potential for treating Cr(VI)-bearing wastewater than nano Fe^0.

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1. Introduction

Chromium (Cr), a prevalent metal contaminant, can be detected globally in industrial wastewater, surface water, groundwater and soils (Kamaludeen et al., 2003). Normally, Cr exists in oxidation states of Cr(III) and Cr(VI), which display contrasting toxicity and mobility (Dhal et al., 2013). Cr(III) has low toxicity and is recognized as an essential trace element for human nutrition. Cr(III) is easy to hydrolyze in aqueous solution and thus has a very low solubility and is inclined to attach to mineral surfaces. In contrast, Cr(VI) species, such as CrO_4^{2-} and $Cr_2O_7^{2-}$, are soluble in aqueous media over a wide pH range. Cr(VI) is of serious concern due to its toxicity, and it is also a human carcinogen (Pettine et al., 1998; Cieślak-Golonka, 1996). Unfortunately, Cr-bearing wastewaters produced from a wide range of industries, such as electroplating, ore mining,

leather tanning, and pigment making, are dominated by anthropogenic Cr(VI) species (Dhal et al., 2013).

Nanoscale zerovalent iron (nFe^0) has attracted extensive interest for ex/in situ treatment of contaminants, such as chlorinated hydrocarbons and redox-sensitive heavy metals (Fu et al., 2014; Du et al., 2013; Huang et al., 2013). nFe^0 has the advantages of large surface area, inexpensive cost, high reducibility, feasible in-situ operation and easy magnetic separation (Fu et al., 2014; Guan et al., 2015). Compared to other adsorbents, nFe^0 can transform highly soluble Cr(VI) to insoluble Cr(III) via coupled oxidation of Fe^0 and Fe(II), with the subsequent formation of Cr(III)-Fe(III) precipitates (Manning et al., 2008; Ai et al., 2008; Hoch et al., 2008). After reacting, Cr-laden iron could be magnetically separated avoiding secondary pollution risks. However, Fe^0 corrosion in aquatic media may affect the Cr(III) detoxification process negatively. Release of ferrous ions and formation of an oxide shell occur simultaneously during Fe^0 corrosion (Yoon et al., 2011). A thick surface oxide layer would significantly depress further Fe^0 corrosion and lead to material passivation
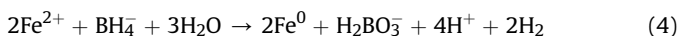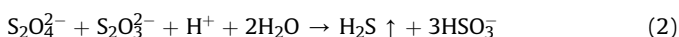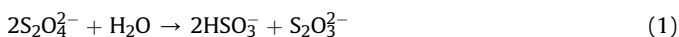
(Melitas et al., 2001; Huang and Zhang, 2005). Although Cr(VI) could be reduced directly by surface electrons and Fe(II) produced via Fe^0 corrosion, fast Fe^0 passivation will result in a low rate of Cr(VI) reduction. Some multicomponent materials have been investigated to improve nFe^0 reactivity via accelerating electron transfer from the Fe^0 core (Kim et al., 2011; Fan et al., 2013; Lv et al., 2011). Mu et al. prepared a series of core-shell $Fe@Fe_2O_3$ nanowires for anoxic Cr(VI) removal (Mu et al., 2014). They found that a moderate thickness of the Fe_2O_3 shell benefits iron corrosion and electron transfer from the Fe^0 core. Lv et al. reported a synergistically enhanced removal of Cr(VI) by nFe^0-Fe_3O_4 nanocomposites due to a more facile electron transfer from nFe^0 to the Fe_3O_4 surface (Lv et al., 2011, 2014). These previous findings indicate that hybrid materials with different components have advantages over single-component materials.

Iron monosulfide (FeS), a reactive mineral that is ubiquitous in anoxic soil and sediments, was used as an effective remediation agent for removal of heavy metals and chlorinated hydrocarbons (Gong et al., 2014; Bi and Hayes, 2014; Jeong and Hayes, 2007). However, FeS alone is easily air-oxidized, thereby losing a considerable portion of its reductive activity. Using a mixed combination of nFe^0 and FeS might be a feasible method of exerting a synergistic effect that is not available from individual components. Very recently, Kim et al. reported a type of S-doped nFe^0 (S-nFe^0) nanoparticle that was prepared by adding sodium borohydride and dithionite mixture to ferric solutions to obtain a type of S-incorporated nFe^0 (Kim et al., 2014). Then, Su et al. applied this type of S-Fe^0 nanoparticle for adsorptive removal of cadmium (Cd) (Su et al., 2015). They found that the doping amount of dithionite played a crucial role in the reactivity of the S-nFe^0 composite for Cd removal, and the S-nFe^0 composite with a proper Fe/S ratio exhibited a larger adsorption capacity than pristine nFe^0. Compared to pristine nFe^0, preparation of these S-nFe^0 nanoparticles would result in simultaneous generation of FeS and Fe^0 (Eqs. (1)–(4)) all over the body instead of pure Fe^0. However, according to their observations, vigorous H_2S was also generated from dithionite decomposition during S-nFe^0 synthesis as shown in Eqs. (1)–(2), which should be a potential environmental concern (Kim et al., 2011; Su et al., 2015). Instead, in-situ synthesis of FeS in the presence of nFe^0 could realize a surface sulfidation of Fe^0 and avoid the generation of hydrogen sulfide (Fan et al., 2013).

$$2S_2O_4^{2-} + H_2O \rightarrow 2HSO_3^- + S_2O_3^{2-} \tag{1}$$

$$S_2O_4^{2-} + S_2O_3^{2-} + H^+ + 2H_2O \rightarrow H_2S \uparrow + 3HSO_3^- \tag{2}$$

$$Fe^{2+} + H_2S \rightarrow FeS \downarrow + 2H^+ \tag{3}$$

$$2Fe^{2+} + BH_4^- + 3H_2O \rightarrow 2Fe^0 + H_2BO_3^- + 4H^+ + 2H_2 \tag{4}$$

In the present study, new FeS@Fe^0 hybrid particles were fabricated via a two-step method. First, nFe^0 was synthesized via chemical reduction by sodium borohydride. Then, FeS was successively synthesized in the presence of nFe^0 by stoichiometric precipitation of Fe^{2+} and Na_2S, forming an encapsulated structure named as FeS@Fe^0. In addition, the formation of the FeS@Fe^0 hybrid material may also proceed naturally in the subsurface under reducing conditions via interaction between nFe^0 with abundant S^{2-}. The performance of this material for Cr(VI) removal was tested by comparison with pure nFe^0, and the mechanisms are elucidated based on SEM, XRD, FTIR, XPS, and experimental results. The magnetic properties of the composite particles can facilitate the separation of Cr-laden material at the end of treatments.

2. Materials and methods

2.1. Chemicals

Analytical grade chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. Cr(VI) stock solutions were synthesized by dissolving $K_2Cr_2O_7$. Solutions were prepared with deionized water, which was deoxygenated by bubbling N_2 gas through the solution for half an hour before use.

2.2. Preparation of nFe^0 and FeS@Fe^0 hybrid materials

FeS@Fe^0 hybrid particles were prepared via a two-step process (see Scheme S1 in Supplementary materials). First, nFe^0 was prepared by reduction with sodium borohydride. Briefly, 50 mL of $NaBH_4$ solution (0.8 mol/L) was added dropwise into 100 mL of $FeSO_4 \cdot 7H_2O$ (0.18 mol/L) solution under N_2 protection in a three-neck flask. Then, the black nFe^0 products were magnetically separated and rinsed three times with deoxygenated water to remove impurities. The overall process occurs according to Eq. (5).

$$Fe^{2+} + 2BH_4^- + 6H_2O \rightarrow Fe^0 \downarrow + 2B(OH)_3 + 7H_2 \uparrow \tag{5}$$
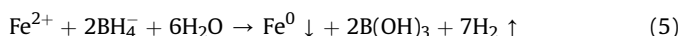
For synthesis of FeS@Fe^0 hybrid particles, the above nFe^0 particles were immediately re-dispersed in 150 mL of $FeSO_4$ solution (the total amount of $FeSO_4$ was 0.002 mol). Subsequently, 50 mL of 0.04 mol/L Na_2S (the stoichiometric ratio of Fe^{2+}_{mol}: S^{2-}_{mol} was equal to 1:1) was added dropwise into the flask to generate FeS@Fe^0 hybrid particles in situ as described by Eq. (6).

$$Fe^{2+} + S^{2-} \rightarrow FeS \downarrow \tag{6}$$

The hybrid particles were separated using an external magnet, thoroughly washed with ethanol and deoxygenated water, and finally vacuum-dried at 60 °C overnight. FeS@Fe^0 particles with different FeS contents were synthesized by changing the FeS_{mol}: Fe^0_{mol} ratio. In the present research, four types of FeS@Fe^0 hybrid particles (FeS_{mol}: Fe^0_{mol} = 1:3, 1:5, 1:9, 1:15, respectively) were tested for Cr(VI) detoxification.

2.3. Batch experiments of Cr(VI) removal

The influences of the initial pH, initial Cr(VI) concentration and different FeS/Fe^0 ratios were studied by batch removal experiments. All of the Cr(VI) removal experiments were conducted in three-neck flasks under a nitrogen atmosphere. Unless otherwise stated, 0.1 g of the FeS@Fe^0 hybrid particles with a Fe^0_{mol}:FeS_{mol} ratio of 9:1 was fed into the three-neck flasks with 200 mL of 20 mg/L Cr(VI) solution without pH adjustment (pH ≈ 5.8). The flasks were sealed with rubber screw caps and mechanically stirred during the experiments. The samples were collected by a 2-mL syringe at regular time intervals and analyzed immediately after being filtered through a 0.45 μm filter membrane. All experiments were conducted at least twice, and the results were averaged. To test the influence of the initial pH on removal behavior, the initial pH of the Cr(VI) solutions was adjusted by dilute H_2SO_4 and NaOH solutions. To evaluate the Cr(VI) removal efficiency, the data were analyzed by simulating pseudo first-order and pseudo second-order kinetics models. A typical Langmuir model and Freundlich model were used for adsorption isotherms simulation. Supporting information presents the details regarding the equations for these models.

Concentrations of aqueous Cr(VI) were measured using a UV−vis spectrometer by the 1,5-diphenylcarbazide colorimetric method at a wavelength 544 nm. The concentration of the total