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Nanoencapsulation of hexavalent chromium with nanoscale zero-valent iron: High resolution chemical mapping of the passivation layer

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ABSTRACT

Solid phase reactions of Cr(VI) with Fe(0) were investigated with spherical-aberration-corrected scanning transmission electron microscopy (Cs-STEM) integrated with X-ray energy-dispersive spectroscopy (XEDS). Near-atomic resolution elemental mappings of Cr(VI)–Fe(0) reactions were acquired. Experimental results show that rate and extent of Cr(VI) encapsulation are strongly dependent on the initial concentration of Cr(VI) in solution. Low Cr loading in nZVI (<1.0 wt%) promotes the electrochemical oxidation and continuous corrosion of nZVI while high Cr loading (>1.0 wt%) can quickly shut down the Cr uptake. With the progress of iron oxidation and dissolution, elements of Cr and O counter-diffuse into the nanoparticles and accumulate in the core region at low levels of Cr(VI) (*e.g.*, <10 mg/L). Whereas the reacted nZVI is quickly coated with a newly-formed layer of 2–4 nm in the presence of concentrated Cr(VI) (*e.g.*, >100 mg/L). The passivation structure is stable over a wide range of pH except when pH is low enough to dissolve the passivation layer. X-ray photoelectron spectroscopy (XPS) depth profiling reconfirms that the composition of the newly-formed surface layer consists of Fe(III)–Cr(III) (oxy)hydroxides with Cr(VI) adsorbed on the outside surface. The insoluble and insulating Fe(III)–Cr(III) (oxy)hydroxide layer can completely cover the nZVI surface above the critical Cr loading and shield the electron transfer. Thus, the fast passivation of nZVI in high Cr(VI) solution is detrimental to the performance of nZVI for Cr(VI) treatment and remediation.

Introduction

Chromium has found numerous industrial applications, such as leather tanning, corrosion prevention, mineral extraction, ore refining and metal electroplating. Due to improper disposal and inefficient treatment, large amounts of chromium-containing wastewater and chromium residues have been released to the environment. As a result, detections of elevated levels of chromium in surface and ground waters, sediments and soils have been wide spread (Cao et al., 2010; Dhal et al., 2013; Gao and Xia, 2011; Saha et al., 2011; Wang et al., 2012; Yu et al., 2008).

Chromium compounds, especially Cr(VI) species, are highly toxic, nonbiodegradable, and bioaccumulative, subsequently they tend to persist in the environment and present a long-lasting threat to the environment and human health (Bagchi et al., 2002; Cervantes et al., 2001; Pellerin and Booker, 2000; Salnikow and Zhitkovich, 2007). Reduction of Cr(VI) to less soluble Cr(III) species can reduce toxicity, mobility, and availability to

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biota, thus providing a mechanism for chromium stabilization and remediation (Chen et al., 2007; Ellis et al., 2002; Shanker et al., 2005). For example, zero-valent iron [Fe(0)] has been demonstrated as an excellent reductant for Cr(VI) treatment (Blowes et al., 1997; Cundy et al., 2008; Fu et al., 2014, 2013; Ponder et al., 2000; Wilkin et al., 2005). The Cr(VI) removal by Fe(0) involves reduction of dissolved Cr(VI) to Cr(III) and the subsequent precipitation of insoluble $Cr(OH)_3$ and Fe(III)–Cr(III) (oxy)hydroxides (Cao and Zhang, 2006; Manning et al., 2007; Powell et al., 1995):

$$Fe^0 + CrO_4^{2-} + 4H_2O \rightarrow Cr(OH)_3 + Fe(OH)_3 + 2OH^- \quad (1)$$

$$xCr^{3+} + (1-x)Fe^{3+} + 3H_2O \rightarrow (Cr_xFe_{1-x})(OH)_3 + 3H^+ \quad (2)$$

$$xCr^{3+} + (1-x)Fe^{3+} + 2H_2O \rightarrow Cr_xFe_{1-x}OOH + 3H^+ \quad (3)$$

Among numerous forms and sizes of Fe(0), the performances of nanoscale zero-valent iron (nZVI) and its derivatives have received significant attentions (Adeleye et al., 2016; Ai et al., 2008; Bhunia et al., 2012; Li et al., 2008; Rajajayavel and Ghoshal, 2015; Shi et al., 2011; Su et al., 2014; WooáLee and BináKim, 2011; Xia et al., 2017; Xu and Zhao, 2007; Yirsaw et al., 2016). nZVI has shown higher reduction rate and much higher removal capacity due to its diminutive size, large specific surface area, and high surface activity. For example, studies observed that under similar conditions, the reduction capacity of nZVI was 50–100 times greater than that of micro-scale ZVI, and the reaction rate with the nZVI was at least 25–30 times faster (Alowitz and Scherer, 2002; Cao and Zhang, 2006; Li et al., 2008).

Most of previous studies have focused on the removal rate and efficiency of Cr(VI) by nZVI, also the environmental factors in aqueous solutions as such as pH, dissolved oxygen, Cr(VI)–Fe(0) ratio, and co-existing substances (Lai and Lo, 2008; Liu et al., 2008; Lo et al., 2006; Ye et al., 2017). Relatively much less has been published on the structural evolution and solid phase reaction mechanisms, which are fundamental to optimization of nZVI technology for chromium treatment and remediation. In particular, the deposition of $Cr(OH)_3$ and/or Fe(III)–Cr(III) (oxy) hydroxides on the outer surface of nZVI may have a great impact on the continuing reactions of Cr(VI) with the underlying metallic iron. The reduction of Cr(VI) by nZVI is to certain degree self-inhibiting as the insoluble and insulating Cr(III) deposition on nZVI surface can act as a physical and chemical barrier and block the electron transfer from Fe(0) to the solid–liquid interface, thus impede the further reduction of Cr(VI) (Hu et al., 2010; Melitas et al., 2001; Melitas and Farrell, 2002). In-depth study of the surface reaction processes, especially the intraparticle diffusion and transformation in the solid phase, has significant value in understanding the Cr(VI)–nZVI reaction mechanisms and activity change of nZVI.

Objectives of this study include: (1) to characterize the fine structure and composition of nZVI after reacting with Cr(VI); (2) to identify the nanoscale Fe–Cr passivation layer; (3) to assess the impact of surface passivation on Cr(VI) removal. Electrochemical tests were conducted to monitor the corrosion/passivation behavior of reacted nZVI. A state-of-the-art spherical-aberration-corrected scanning transmission electron microscopy (Cs-STEM) integrated with X-ray energy-dispersive spectroscopy (XEDS) was applied to map the reactions of Cr(VI), and to gain near atomic-scale details on the elemental distribution and translocations of Fe, O and Cr within a single nanoparticle. Recent advance in Cs-STEM enables the direct visualization of the pollutant-nZVI reactions with high spatial resolution and chemical sensitivity (Huang et al., 2017; Ling et al., 2015; Ling and Zhang, 2015, 2017). Furthermore, high-resolution X-ray photoelectron spectroscopy (HR-XPS) combined with Ar^+ sputtering for depth profiling was utilized to investigate the variations of elemental distribution and chemical states.

1. Materials and methods

1.1. Chemicals and materials

All reagents used (*e.g.*, $FeCl_3{\cdot}6H_2O$, $NaBH_4$, and $K_2Cr_2O_7$) were analytical-grade or better. The nickel foam (thickness: 1.2 mm, pore density: 110 PPI) was supplied by Kunshan Jiayisheng Electronics Co. Ltd. (Jiangsu, China). Fresh nZVI was prepared by the reduction of ferric chloride with sodium borohydride following the procedures published previously (Glavee et al., 1995; Li and Zhang, 2006; Wang and Zhang, 1997).

1.2. Batch experiments

Batch experiments were conducted in 50 mL serum bottles, with 1 g/L nZVI or micro-scale zero-valent iron (mZVI, 400 mesh) added to 35 mL of 10–1000 mg/L Cr(VI) solution. The batch bottles were sealed with screw caps and mixed on a shaker table (180 r/min) at ambient temperature. To eliminate the potential effect of dissolved oxygen (DO), the Cr(VI) solutions were purged with high-purity nitrogen (>99.9%) for 30 min prior to the introduction of iron. Solution pH was adjusted to desired values by adding dilute solution of NaOH or HCl at the start of experiments. After 24 hr, the samples were withdrawn and then filtrated with 0.22 μm PTFE syringe filters prior to analysis. The residual Cr concentrations in the filtrate were determined using inductively coupled plasma spectrometers (ICP-OES, Agilent 720ES and ICP-MS, Agilent 7700).

1.3. Electrochemical measurements

Electrochemical measurements were performed with a CHI660A electrochemical workstation (Shanghai Chenhua Co. Ltd., China). A traditional three-electrode cell was used. The reference electrode was a saturated calomel electrode (SCE) and the counter electrode was made of a platinum foil (1.0 cm × 1.5 cm). Iron nanoparticle arrays supported on nickel foam were prepared to act as the working electrode. Details about fabrication of the working electrode can be found in the Electronic Supplementary Material. The polarization tests in 10 mmol/L NaCl background electrolyte solution were measured by scanning the potential at 1 mV/s from −1.0 to 1.0 V.

1.4. STEM characterization

A FEI Titan™ G2 60-300 spherical-aberration-corrected scanning transmission electron microscopy (Cs-STEM) integrated with X-ray energy-dispersive spectroscopy (XEDS) was operated at 200 kV to perform the morphological, structural and elemental characterization on the Cr(VI) reactions in nZVI. Samples for

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