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Nanoscale zero-valent iron (nZVI): Aspects of the core-shell structure and reactions with inorganic species in water

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ABSTRACT

Aspects of the core-shell model of nanoscale zero-valent iron (nZVI) and their environmental implications were examined in this work. The structure and elemental distribution of nZVI were characterized by X-ray energy-dispersive spectroscopy (XEDS) with nanometer-scale spatial resolution in an aberration-corrected scanning transmission electron microscope (STEM). The analysis provides unequivocal evidence of a layered structure of nZVI consisting of a metallic iron core encapsulated by a thin amorphous oxide shell. Three aqueous environmental contaminants, namely Hg(II), Zn(II) and hydrogen sulfide, were studied to probe the reactive properties and the surface chemistry of nZVI. High-resolution X-ray photoelectron spectroscopy (HR-XPS) analysis of the reacted particles indicated that Hg(II) was sequestrated via chemical reduction to elemental mercury. On the other hand, Zn(II) removal was achieved via sorption to the iron oxide shell followed by zinc hydroxide precipitation. Hydrogen sulfide was immobilized on the nZVI surface as disulfide (S_2^{2-}) and monosulfide (S^{2-}) species. Their relative abundance in the final products suggests that the retention of hydrogen sulfide occurs via reactions with the oxide shell to form iron sulfide (FeS) and subsequent conversion to iron disulfide (FeS_2). The results presented herein highlight the multiple reactive pathways permissible with nZVI owing to its two functional constituents. The core-shell structure imparts nZVI with manifold functional properties previously unexamined and grants the material with potentially new applications.

1. Introduction

Engineered nanomaterials have found increasing applications in environmental technologies, including water and wastewater treatment, air, water and soil remediation, and hazardous waste treatment, owing to their superior reactivity towards a variety of recalcitrant contaminants and their enhanced capacities for contaminant abatement (Karn et al., 2009; Li et al., 2006; Tratnyek and Johnson, 2006). Amongst this promising class of remediation agents, nanoscale zero-valent iron (nZVI) perhaps has received the most attention and has been shown to effectively degrade a wide spectrum of water contaminants, such as halogenated hydrocarbons, nitroaromatic compounds, azo dyes, perchlorate, nitrate, hexavalent chromium and various heavy metal ions (Kanel et al., 2005; Li and Zhang, 2006, 2007; Lowry and Johnson, 2004; Ponder et al., 2000, 2001; Tee et al., 2005).

Microscopic and spectroscopic studies have suggested that nZVI in the aqueous environment consists mainly of zero-valent iron and a surface layer of iron oxide (Martin et al., 2008; Nurmi et al., 2005; Sun et al., 2006). The oxide layer is thought to comprise of mixed Fe(II)/Fe(III) oxides near the interface with Fe^0 and mostly Fe(III) oxide near the oxide/water interface (Signorini et al., 2003; Wang et al., 2009). This core-shell structure has important implications

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for the chemical properties of nZVI. The defective and disordered nature of the oxide shell renders it potentially more reactive than a simple passive oxide layer formed on bulk iron materials (Wang et al., 2009). The relative composition of the oxide and the metal in nZVI is also markedly different from that of bulk ZVI. These considerations make the core-shell structure a highly important aspect to consider when studying the reactivity of nZVI for various remediation processes. The presence of two nano-constituents in the core-shell structure may impart combinational properties for contaminant removal: the metallic iron acts as the electron source and exerts a reducing character, while the oxide shell facilitates sorption of contaminants via electrostatic interactions and surface complexation, and at the same time, permits electron passage from the metal core. Fig. 1 proposes conceptually a structural model of nZVI and its reactions with several contaminants that are examined in this work.

So far, the majority of published work have focused on the reductive properties of nZVI, *e.g.*, reductive dehalogenation of organic compounds and reductive precipitation of hexavalent chromium (Lowry and Johnson, 2004; Ponder et al., 2001), There is no study that has examined the specific functions of the metal-core and the oxide-shell in different remediation systems. More informative knowledge of the core-shell structure and the surface chemistry of nZVI materials can accelerate the development of new applications, especially in the category of inorganic contaminants, whose treatment typically involves surface-mediated complexation and/or redox transformations (Stumm, 1992). Another aspect which has received less attention in the literature is the inevitable reaction of nZVI with water and its effect on the solution and surface chemistry. This point is of particular relevance to the treatment of ionic species including heavy metal ions, because their speciation and reactivity are profoundly dependent on the solution pH.

The objectives of this work are to obtain direct evidence of the core-shell structure with a state-of-the-art electron microscopic technique, and then to demonstrate the multi-faceted reactivity of nZVI towards different contaminants on the basis of its nanostructure. The study proceeds with an examination of the nZVI structure using an ultra-high resolution scanning transmission electron microscope (STEM) equipped with an X-ray energy-dispersive spectrometer (XEDS). The instrument employs a sub-nanometer probe afforded by a C_s-aberration corrector to perform XEDS spectrum imaging, enabling for the first time direct visualization and chemical mapping of the core-shell structure. Experimental studies involving three common aqueous contaminants, *viz.,* Hg(II), Zn(II), and hydrogen sulfide (H_2S), are then presented. These contaminants are markedly different from one another in terms of electrochemical or coordinative properties and are used as probe molecules to emphasize various reactive pathways permissible with nZVI treatment. For each contaminant studied, aspects related to reaction kinetics, sequestration efficiency, and the proposed reaction mechanism(s) based on spectroscopic and solution phase evidence are discussed. The distinct reaction pathways and the remarkable reactivity and capacity demonstrated by nZVI in these systems underline the notion that nZVI has manifold functions in addition to reductive-transformations, and has potential applications in treating a diverse group of environmental contaminants.

2. Methods and materials

2.1. Synthesis of iron nanoparticles

nZVI was prepared by reduction of ferric chloride ($FeCl_3$, ACS grade, Alfa Aesar) with sodium borohydride ($NaBH_4$, 98% purity, Finnish Chemicals) following procedures reported previously (Li and Zhang, 2006; Sun et al., 2006). Fresh nZVI particles were stored in 95% ethanol solution (Farmco-AAPER) at 4 °C prior to use. Our previous characterization work (Sun et al., 2006) shows that the median diameter of individual nanoparticles is approximately 60 nm, although in

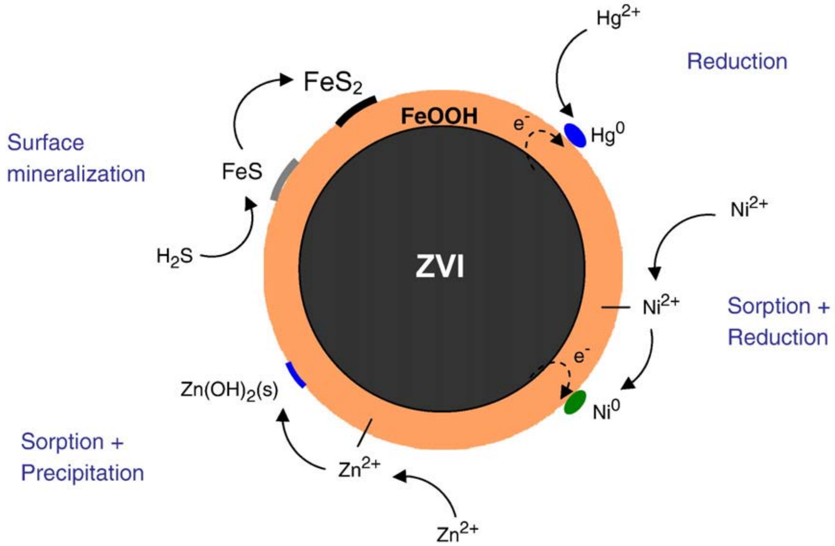

Fig. 1. The core-shell model of nZVI and schematic representations of the reaction mechanisms for the removal of Hg(II), Ni(II), Zn(II) and H_2S investigated in this study.