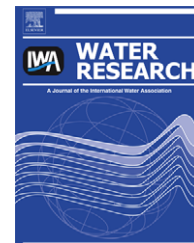


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Immobilization of mercury in sediment using stabilized iron sulfide nanoparticles

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ABSTRACT

Mercury (Hg) immobilization using stabilized iron sulfide (FeS) nanoparticles was investigated through a series of batch and column experiments. The nanoparticles were prepared using a low-cost, food-grade cellulose (sodium carboxymethyl cellulose, CMC) as the stabilizer. The hydrodynamic diameter of fresh FeS–CMC nanoparticles was measured to be 38.5 ± 5.4 nm. Batch tests showed that the nanoparticles can effectively immobilize Hg in a clay loam sediment. The Hg distribution coefficient for the nanoparticles was determined to be 8930 ± 1480 L/g, which is >4 orders of magnitude greater than for the sediment. When the Hg-laden sediment was treated at an FeS-to-Hg molar ratio of 26.5, the Hg concentration leached into water was reduced by 97% and the TCLP (toxicity characteristic leaching procedure) leachability of Hg was reduced by 99%. Column tests showed that water-leachable mercury from the sediment containing 3120 mg/L Hg was reduced by 67% and the TCLP leachability by $>77\%$ when the sediment was treated with 67 pore volumes (PVs) of a 0.5 g/L FeS nanoparticle suspension. Column tests proved that the stabilized nanoparticles were highly mobile in the sediment and full breakthrough of the nanoparticles occurred at ~ 18 PVs.

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1. Introduction

Mercury (Hg) is one of the most pervasive and bio-accumulative contaminants. In water and sediments, Hg undergoes a number of complex chemical and biological speciation and transformation processes, of which Hg methylation has been the primary environmental concern (Stein et al., 1996). Methylmercury (MeHg) is a potent neurotoxin and can accumulate along the aquatic food chain, where concentrations can reach one million times greater than in the water column (Stein et al., 1996). Consequently, even trace concentrations (ng/L) of Hg in the water column can lead to significant accumulation of MeHg in fish and waterfowl (Zillioux et al., 1993).

Traditionally, remediation of severely Hg-contaminated soils or sediments employs excavation and subsequent

disposal in a landfill (Barnett et al., 1997). However, this method is not only costly and environmentally disruptive, but the landfilled Hg is prone to leaching back into the environment (Barnett et al., 2001). Recently, phytoremediation with water hyacinths (Riddle et al., 2002) and biological processes (Wagner-Döbler et al., 2000) have been explored to remediate Hg-contaminated surface water and chemical wastewater, respectively. However, phytoremediation may result in high-Hg content water hyacinths which needs further disposal and biological processes require substrate and nutrients to support the growth of bacteria which are usually at low levels in groundwater.

Sulfur reducing bacteria (SBR) have been considered the primary methylators of Hg in aquatic sediments (Zillioux et al., 1993). Recent research indicated (Benoit et al., 2001;

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Drott et al., 2007) that methylation of mercury by SRB is directly related to concentration of neutral soluble mercury sulfide complexes (HgS^0 and $\text{Hg}(\text{SH})_2^0$). Therefore, mercury methylation can be reduced by controlling the formation of these soluble species. Mehrotra et al. (2003) observed that addition of Fe(II) reduced the concentration of these soluble Hg species, resulting in much reduced methylation.

Sulfide minerals are known to be effective adsorbents for Hg(II) (Behra et al., 2001; Brown et al., 1979; Hyland et al., 1990; Jean and Bancroft, 1986). In fact, sulfide minerals have been considered the primary sink for mercury in the environment (Barnett et al., 2001). Mercuric ion can be immobilized by iron sulfide (FeS) particles through adsorption or co-precipitation (Jeong et al., 2007; Morse and Luther, 1999). Iron sulfide has also been shown to exchange its Fe(II) with Hg(II) to form $\text{HgS}(\text{s})$ (Morse and Luther, 1999; Svensson et al., 2006), which is extremely stable ($K_{\text{sp}} = 2 \times 10^{-53}$) in the environment (Barnett et al., 2001). Recent spectroscopic studies (Skylberg et al., 2006; Wolfenden et al., 2005) revealed that Hg can strongly complex with reduced sulfur groups in soil/sediment organic matter, and the high affinity of Hg for S predominates even in highly oxic environments (Wolfenden et al., 2005).

Various methods have been reported for preparing FeS(s) nanoparticles, including dendrimer-stabilization (Shi et al., 2006), chemical vapor condensation (Ha et al., 2006), biopolymer-stabilization (Paknikar et al., 2005), SRB-assisted approach (Watson et al., 2000), high-energy mechanical milling (Chin et al., 2005), and micellar technique (Chadha et al., 1996).

Recently, our group developed (patent pending) a technology for *in situ* immobilization of Hg(II) in soils and sediments (Zhao et al., 2006). To this end, we developed a "green" technique for preparing a new class of stabilized FeS nanoparticles using sodium carboxymethyl cellulose (CMC) as the stabilizer.

The overall goal of this study was to test the feasibility of this new remediation concept through a series of batch and column experiments. The specific objectives of this study were to: 1) prepare and characterize a class of stabilized and soil-dispersible FeS nanoparticles using a low-cost, food-grade CMC as the stabilizer; 2) test the effectiveness of the stabilized nanoparticles for removal of Hg(II) from water and for immobilization (defined as reduction in solubility and leachability) of Hg(II) in an estuarine sediment; and 3) examine the mobility of the stabilized FeS nanoparticles in the sediment.

2. Materials and methods

2.1. Chemicals

All chemicals used in this study were ACS-certified. All chemicals were obtained from Fisher Scientific (Fair lawn, NJ) except ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and CMC (M.W. = 90,000, D.S. = 0.7), which were obtained from Acros Organics (Morris Plains, NJ).

2.2. Preparation of stabilized FeS nanoparticles

Stabilized FeS nanoparticles were prepared in a 250 mL flask attached to a vacuum line. A CMC solution (1%, w/w) was

prepared by dissolving the CMC with deionized (DI) water and the solution was purged with purified N_2 (>99%) for half an hour to remove dissolved oxygen (DO). Solutions of 0.1 M FeSO_4 and Na_2S were also prepared with N_2 -purged DI water. The FeSO_4 solution was mixed with the CMC solution through a burette to yield a desired concentration of iron and the stabilizer. Based on our prior experience preparing stabilized zero-valent iron (ZVI) nanoparticles (He et al., 2007; He and Zhao, 2007), the CMC-to-iron ratio can be varied to yield nanoparticles of various size. In this work, 0.2% (w/w) of the CMC was used to stabilize 0.5 g/L FeS nanoparticles. The mixture was then purged with purified N_2 for half an hour to complete the formation of Fe^{2+} -CMC complexes. Then, the Na_2S solution was introduced into the Fe^{2+} -CMC solution at an Fe-to-S molar ratio of 1:1 to yield the FeS nanoparticles. The system was operated under inert conditions through continuous vacuuming. The flask was hand-shaken intermittently during the preparation. For comparison, non-stabilized iron sulfide particles were also prepared following the same procedure except no stabilizer was present. The particles were characterized or used within 1 h of preparation.

2.3. Characterization of FeS nanoparticles

Transmission electron microscopy (TEM) images were obtained using a Zeiss EM10 transmission electron microscope (Zeiss, Thornwood, NJ) operated at 60 kV accelerating voltage. The TEM images were analyzed using a specialty image processing software named ImageJ to analyze the particle size. Additionally, dynamic light scattering (DLS) tests were performed with a Nicomp 380 Submicron Particle Sizer (PSS, Santa Barbara, CA) at a measurement angle of 90° (internal He-Ne laser, wavelength 633 nm). The DLS data were processed and analyzed with a software package (CW380, Santa Barbara, CA) to yield number-weighted particle size distributions. Details of sample preparation and software operation have been reported elsewhere (He and Zhao, 2007).

2.4. Mercury-spiked sediment

A clay loam sediment was obtained from an aquacultural fishpond in Auburn AL, U.S.A. The sediment was air-dried. Then, the aggregates were broken by a mortar with pestle, sieved through a 2-mm screen, and then washed using DI water to remove all soluble compositions such as dissolved organic matter. The sediment contains 30% of sand, 33% of silt, and 37% of clay, which were determined following the pipette method (Gee and Or, 2002). The soil organic carbon (OC) was 2.5%, which was determined by first treating the sample with 4 N H_2SO_4 to dissolve free carbonates and then following the Dumas method with a LECO CN-2000 combustion unit (LECO Corp.) at 1050°C . The sediment was also digested per U.S. EPA method 3050B and analyzed for metals, which indicated 28 mg/g of Fe and non-detectable (<0.05 mg/kg) Hg. For this study, Hg(II) was pre-spiked to two sediment mixtures following the procedure by Piao (2002). Briefly, 100 g and 200 g of the sediment was mixed with 0.8 and 0.1 g of $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ in 5 and 10 mL, respectively, of DI water in sealed Teflon vials. The mixtures were hand-shaken intermittently and were aged for 1 month. At the end of 1

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