PROJECT SYNOPSIS

TITLE: DEVELOPMENT AND APPLICATION OF AN INNOVATIVE NANOTECHNOLOGY FOR IN-INTU REMEDIATION OF Hg-CONTAMINATED ALABAMA SOILS AND SEDIMENTS

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Problem statement and research objectives

Mercury (Hg) is one of the most pervasive and bio-accumulative contaminants. The annual anthropogenic Hg emitted in the U.S. totals 158 metric tons, of which ~33.3% are deposited in the homeland. In addition, the global reservoir adds ~35 tons of Hg annually to the U.S. territory. When mercury enters water and sediments, it can undergo a number of complex chemical and biological speciation and transformation processes, of which Hg methylation has been the primary environmental concern. Methylated mercury (or methylmercury, MeHg) can accumulate along the aquatic food chain, reaching its apex in predatory fish, where concentrations may be up to one million times higher than in the water column.

Triggered by the toxicity and bioaccumulation concerns, the U.S. Environmental Protection Agency (EPA) has identified Hg as one if its twelve priority persistent bio-accumulative toxins (PBTs). As of 2003, EPA, FDA (Food and Drug Administration) and 45 states have issued ~3089 fish consumption advisories, of which ~80% are, at least in part, associated with Hg poison. Because of the heavy Hg hit, 100% of the Gulf coast line is covered by the advisories. In recent years, Hg at concentrations 10-20 times higher than the safe level of 0.5 ppb was widely detected in various popular fish such as largemouth bass in the estuaries near the Mobile Bay. In response, the State of Alabama has issued a number of Hg advisories, which essentially banned the consumption of fish in 17 south Alabama streams or bays.

This research aims to develop an environmentally benign, cost-effective process for effective immobilization/containment of mercury in water and soils and inhibition/elimination of Hg methylation from affected Alabama sources. A novel class of metal sulfide nanoparticles (FeS and MnS) will be prepared, characterized for in situ immobilization of Hg in water and estuarine sediments. The specific objectives are to:

(1) Develop a new class of stabilized, highly dispersive metal sulfide (MeS) nanoparticles, which uses select low-cost and environmentally friendly polysaccharides such as starch and cellulose as a stabilizer;
(2) Test the long-term feasibility of applying the new metal sulfide nanoparticles to in situ immobilization of Hg in estuarine sediments and for inhibition of Hg methylation; and
(3) Develop an innovative technology based on the new nanoparticles for in situ remediation of Hg contaminated marine sediments.

Research Methodology

The research was carried out by executing the following five tasks:

**Task 1: Synthesis of FeS nanoparticles.** Task 1 is designed to test the hypothesis that FeS nanoparticles of desired physical-chemical characteristics (size, dispersibility, mobility and Hg reactivity) can be prepared with the aid of low cost and environmentally friendly starch or cellulose as a capping agent. The FeS nanoparticles were prepared with the following 3 steps.

- **Step 1.** Prepare a dilute starch- or cellulose-Fe solution containing 0–0.5% (w/w) of a starch or cellulose and 0.1-1 M Fe$^{2+}$ and adjust pH to 8-9.

- **Step 2.** Vary the stabilizer-to-Fe molar ratio and/or types of the stabilizer for preparing particles of desired size and dispersibility.

- **Step 3.** Add stoichiometric amounts of Na$_2$S solution into the above solution and allow for reaction for 20 minutes under vacuum and at room temperature.

**Task 2: Physical characterization.** The particle size distribution and surface area of FeS nanoparticles were characterized by TEM (Zeiss EM10 transmission electron microscope, Zeiss, Thornwood, NJ, operated at 25 and 40 kV) and DLS (Nicomp 380 Submicron Particle Sizer, PSS, Santa Barbara, CA, operated at a measurement angle of 90° with Internal He-Ne laser, wavelength 633 nm).

**Task 3: Batch equilibrium.** Mercury removal by FeS nanoparticles in water solution was carried out with 25 ml Teflon vials. Removal of Hg$^{2+}$ in water (50 µg/L Hg$^{2+}$) was tested at various concentrations of FeS (0.5–60 mg/L) nanoparticles.

**Task 4: Soil mobility of nanoparticles.** Nanoparticle solutions of 0.2 g/L FeS were passed through a glass column filled with a sandy soil under gravity. The soil column has a bed volume of 2.5 ml, a soil porosity of 0.37 and a pore volume of 0.93 ml. Total iron in the effluent was measured using an Atomic Adsorption Spectroscopy (Varian 220FS).

**Task 5: Mercury immobilization.** A clay loam sediment was loaded with 318 mg/g Hg$^{2+}$. Then the Hg-loaded sediment was treated with various concentrations of FeS (solid:suspension = 1g:20ml). A Toxicity Characteristic Leaching Procedure (TCLP) was used to test the leachability of the FeS-treated or untreated Hg-loaded sediments. Hg in water or TCLP liquid was analyzed following EPA method 245.1 (Cold Vapor AAS).
Principal findings and significance

The major findings are summarized as follows:

(1) The freshly prepared FeS nanoparticles were characterized with TEM and DLS. While the non-stabilized FeS particles appear as bulky dendritic flocs, the CMC-stabilized FeS appear as discrete nanoscale particles with a mean diameter of 45±20 nm (standard deviation) and a surface area of 28.4 m²/g.

(2) The CMC-stabilized FeS nanoparticles can pass through a sandy soil column by gravity. Total iron measured in the effluent shows that stabilized FeS nanoparticles breakthrough occurred at 4.2 pore volumes. A comparison test indicated that non-stabilized FeS particles were completely intercepted at the top of the soil bed. The results imply that stabilized FeS nanoparticles can be used in an in-situ remediation/immobilization process by injecting the nanoparticle suspension in Hg-contaminated soil/sediment, solid waste or water/groundwater.

(3) The stabilized FeS nanoparticles remove efficiently mercury from water. The addition of ~10 mg/L starch-stabilized FeS can nearly completely remove/immobilize 48 µg/L Hg from water at neutral pH.

(4) The stabilized FeS nanoparticles can greatly reduce mercury leachability from Hg-contaminated soils. The experimental results indicate that treating Hg-laden sediment using 22.2 mg/L starch-capped FeS suspension can reduce the TCLP (Toxic Characteristic Leaching Procedure) leachability of Hg by over 95%. These observations strongly suggest that application of the FeS nanoparticles can substantially reduce the biological availability, hence methylation, of Hg in water and soils/sediments.