ENVIRONMENTAL AND WASTE MANAGEMENT: ADVANCEMENTS THROUGH THE ENVIRONMENTAL MANAGEMENT SCIENCE PROGRAM

Organized by

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Symposia Papers Presented Before the Division of Environmental Chemistry
American Chemical Society
Anaheim, CA March 28 – April 1, 2004

TRANSPORT, TARGETING AND APPLICATIONS OF METALLIC FUNCTIONAL NANOPARTICLES FOR DEGRADATION OF DNAPL CHLORINATED ORGANIC SOLVENTS

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INTRODUCTION AND OBJECTIVES

Dense non-aqueous phase liquids (DNAPLs) in the subsurface remain an important and costly environmental liability at numerous DOE facilities. DNAPL serves as a continuous long-term source of groundwater contamination. This project integrates several basic science fields to advance a particle-based strategy for *in situ* DNAPL degradation by providing targeted delivery of reactive particles directly to the DNAPL.

The project goal is to engineer reactive nanoparticles that can decompose and potentially isolate DNAPL pollutants in the subsurface. Delivering reactive particles directly to the surface of the DNAPL-water interface will decompose the pollutant into benign materials, reduce the migration of pollutant during treatment and reduce the time needed to remove residual pollution by other means, such as natural attenuation.

The primary research objectives are to:

- Determine how size, composition and history of novel metallic nanoparticle-based reactants affect their ability to degrade TCE.
- Design, synthesize and characterize inorganic-organic hybrid particles that can transport in the subsurface and partition to/in DNAPL.
- Demonstrate the transportability and targeting ability of particles in saturated porous media and determine how physical, chemical and hydrologic regimes existing in the subsurface affect nanoparticle migration.
- Test a second method of targeting particle delivery to DNAPLs where modified particles are delivered as suspensions in a benign organic medium.
- Develop a predictive numerical model for the transport and degradation of DNAPLs in bench-scale and meso-scale experiments.

EFFECTS OF PARTICLE MORPHOLOGY AND COMPOSITION OF Fe^0-BASED NANOPARTICLES ON THEIR REACTIVITY WITH TCE

Two types of iron nanoparticles (20-100 nm) were investigated: Reactive Nanoscale Iron Particles (RNIP, supplied by Toda American, Inc.) and Boron-doped Fe^0 particles (Fe^0/B) synthesized in our laboratory using the aqueous sodium borohydrate reduction method[1]. Both particle types are highly reactive and rapidly transform trichloroethylene (TCE) to nontoxic compounds. Fe^0/B particles have a 30-fold higher reaction rate ($15Lg^{-1}d^{-1}$) than RNIP particles ($0.5Lg^{-1}d^{-1}$) under similar reaction conditions. The primary reaction products for Fe^0/B particles are ethane (79%), butane (12%) and hexane (9%), while for RNIP ethane (78%) and ethene (22%), at an initial TCE concentration of 4.4mg/L. At a high initial TCE concentration (170mg/L) acetylene becomes a significant reaction intermediate (>50%) using RNIP particles. The product distribution using Fe^0/B particles did not change at higher initial TCE concentrations. These results suggest that different reaction mechanisms are occurring for each particle type. Fe^0/B particles are also more efficient (80%) than RNIP particles (40%) even though they use a less efficient electron transfer pathway. Efficiency is defined here as the fraction of electrons available from Fe0 oxidation that are used to reduce TCE.

HRTEM was used to examine the thickness and the composition of the surface layer formed on the particles before and after reactions. HRTEM clearly indicates a core/shell morphology (Figure 1). It is likely that the inner core is Fe^0 and the outer shell some iron oxide phase, but the exact chemical nature of these phases has not yet been determined. Reactivity of RNIP particles terminated with some of the core material intact, suggesting that the surface layer inhibits complete reaction of the particles. On the contrary, the core/shell appearance on the Fe^0/B particles did not exist after reaction with TCE in water for 20 days. Based on the products distribution and the Fe^0 consumed, both types of particles have a high selectivity (~10^4) for TCE over H_2O in a relatively high TCE concentration (>140mg/L).

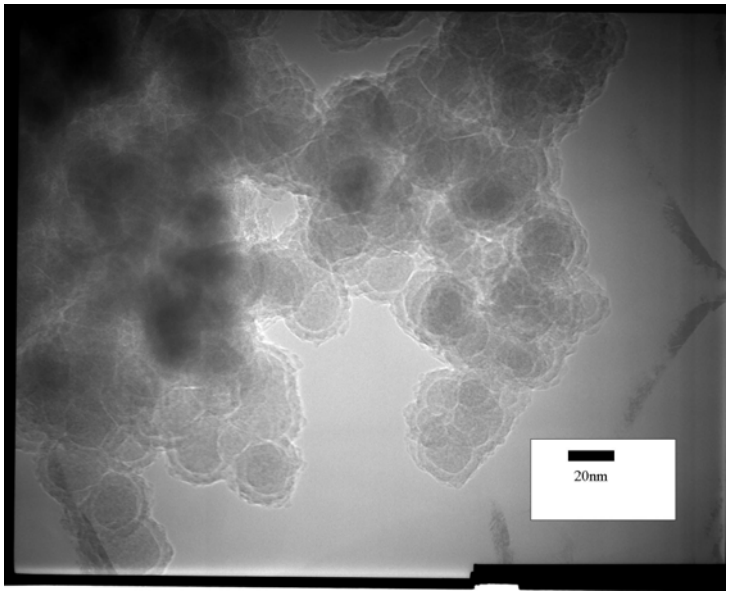

Figure 1. Fe^0/B particles before reaction. Particles have a ~5nm shell.

DESIGN AND SYNTHESIS OF WATER SOLUBLE INORGANIC-ORGANIC HYBRID PARTICLES

The nanoparticles with hydrophobic-hydrophilic shell were synthesized by Atom Transfer Radical Polymerization (ATRP), which is well-known as a robust technique for control/living radical polymerization[2-5]. ATRP allows the synthesis of well defined materials with prescribed block length and narrow polydispersity.

The hybrid nanoparticles consist of an inorganic core (SiO_2 or Fe^0) surrounded by a hydrophobic inner shell and a hydrophilic outer shell. The role of the hydrophobic block is to protect the core against contact with water, while the hydrophilic part was designed to enable the transport of the particles through groundwater layers. Our studies showed that a ratio 1/5 – 1/10 between hydrophobic and hydrophilic blocks is sufficient to assure protection to the inorganic core and also to provide water solubility of the hybrid nanoparticles. Studies performed on unattached block copolymers showed that polystyrene and poly(methyl methacrylate) (PMMA) are good candidates for the hydrophobic blocks. Sulfonated polystyrene (SPSt) was selected as the hydrophilic block due to its excellent water solubility. Other segments, such as methacrylate macromonomers with poly(ethylene oxide) side chains strongly adhered to silica due to the polyether blocks, obstructing the transport of the hybrid nanoparticles in the subsurface.

We used inorganic-organic particles (silica core-organic (polymer) shell as model nanoparticles for transport studies. The synthesis of silica-supported initiators, starting from 20 nm silica dispersed in methyl ethyl ketone, was described elsewhere[6].

Using the ATRP initiators covalently attached to the silica surface, we formed polystyrene shell with ~120 nm size *via* ATRP. The shell was further sulfonated using acetyl sulfate method[7]. The sulfonated nanoparticles (~90 nm) were completely soluble in water. As can be seen in Figure 2, the water soluble particles have a smaller size than the unsulfonated precursors, which can be explained by shrinkage of the hydrophobic part in water.

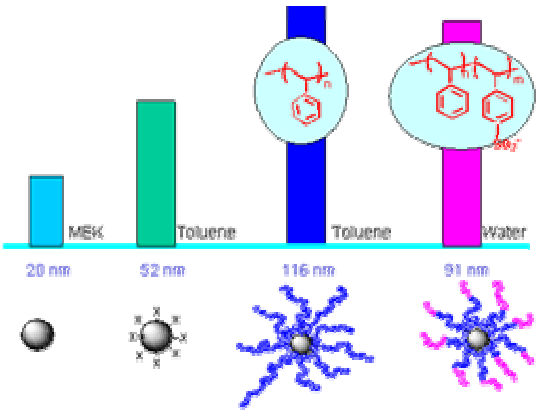

Figure 2. Particle-size measurements of bare silica, silica initiator, silica polystyrene and silica-sulfonated polystyrene nanoparticles. Measurements were performed using a Malvern Dynamic Light Scattering instrument.

We synthesized other hybrid particles by polymerizing methyl methacrylate using silica initiators and then by chain extension with styrene. Further, the silica-supported block copolymers underwent sulfonation, to allow the formation of water soluble nanoparticles even for block copolymers with higher molecular weights. Thus, silica-supported nanoparticles with molecular weight of the PMMA segment M_n=2800 g/mol and M_n=21,000 g/mol of PMMA-block-SPSt showed temperature size dependence as presented in Figure 3.

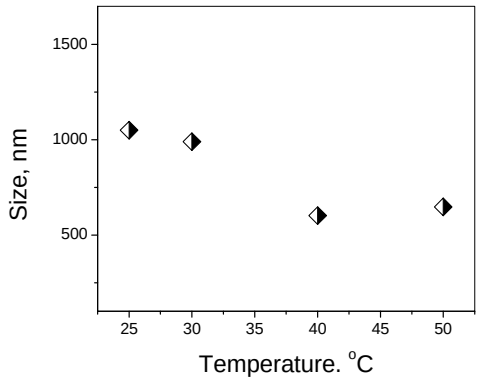

Figure 3. Dependence of particle size upon temperature for silica supported nanoparticles Si-$(PMMA)_{2800}$-block-$(SPSt)_{18200}$. The measurements were performed on water solution of nanoparticles (1 g/l)

Concerning the synthesis of Fe^0 nanomaterials, we developed a technique for building hydrophobic-hydrophilic hybrids which consist of a short anchoring poly(methacrylic acid) block, a hydrophobic PMMA protective shell and a hydrophilic SPSt outer block.(Fig. 4)

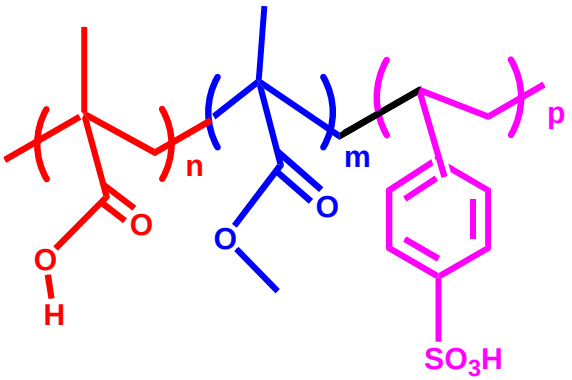

Figure 4. Hydrophobic-hydrophilic triblock copolymers containing a short anchoring group

The anchoring poly(methacrylic acid) block was obtained by hydrolysis of *t*-butyl groups from poly (*t*-butyl methacrylate), while the sulfonation reaction of polystyrene was performed following the same procedure as used for silica particles. The possibility of anchoring block copolymers on Fe^0 nanoparticles by means of poly(methacrylic acid) (PMAA) units was confirmed from our experiments. Thus, when using triblock copolymers $(PMAA)_{2300}$-$(PMMA)_{2000}$-$(SPSt)_{6300}$ we obtained water soluble Fe^0 nanoparticles whose size dependence upon temperature is presented in Figure 5.

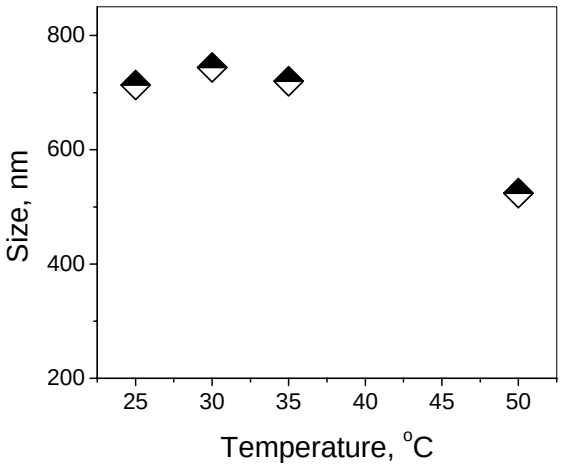

Figure 5. Temperature dependence of Fe^0 nanoparticles in water

Work is in progress to fully characterize these particles, to optimize the synthesis technique and to establish the optimum ratio between the anchoring part and hydrophobic and hydrophilic blocks.

DEVELOPMENT OF A PREDICTIVE NUMERICAL MODEL FOR THE TRANSPORT AND DEGRADATION OF DNAPLs IN SATURATED POROUS MEDIA

Brownian dynamic simulations were carried out to simulate stabilized (unmodified) nanoparticles. The particle was simulated using several number of beads distributed on a spherical surface. Those beads retained their spatial positions relative to each other by using constraining forces. Beads representing the polymer chain were then attached to the particle. The simulation was carried out using Brownian dynamic simulations without hydrodynamic interactions until equilibrium was achieved. Then, the simulation was conducted considering hydrodynamic interactions implemented using the Fixman method. The particle diffusion coefficient and hydrodynamic radius were then calculated. The initial study focused on the effects of simulation parameters such as bead radius, number of simulation beads and excluded volume on diffusion properties.

ACKNOWLEDGEMENTS

The authors thank Dr. Christopher Kim for performing the atomic resolution microscopy on the Fe^0 nanoparticles and the National Center for Electron Microscopy for the microscope time. The authors also thank the Department of Energy (DE-FG07-02ER63507) and the U.S. Environmental Protection Agency (RD-83089801) for their financial support.

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