National Institute of Environmental Health Sciences | **Superfund Basic Research Program**

RESEARCH BRIEF 123

Nanosized Metals for Organic Detoxification

Environmental contaminants are found under a variety of conditions with respect to media, the geochemical characteristics at hazardous waste sites, and whether they are the sole contaminant at a site or part of a mixture. As a result, we need to develop multiple strategies for the remediation of some common contaminants.

Trichloroethylene (TCE) is the most prevalent groundwater contaminant in the United States and is found at most hazardous waste sites. Researchers across the country are working to develop and optimize biological and chemical remediation strategies based on both oxidative and reductive processes. Dr. Dibakar Bhattacharyya, Dr. Leonidas Bachas, and Ph.D. students Jian Xu, David Meyer and Y. Tee at the University of Kentucky SBRP are designing and testing nanostructured metals to degrade TCE and PCBs. Because nanoscale metals have significantly more surface area per unit mass than bulk-scale metals and enhanced reactive sites, reaction rates with nanoscale metals can be several orders of magnitude higher than with bulk-scale metals. The presence of a second dopant metal (such as nickel or palladium) also provides a catalytic hydrodechlorination pathway. Dr. Bhattacharyya's goal is to create environmentally-applicable nanoparticles for both remediation of hazardous waste sites and prevention of pollution by improving industrial processes.

Dr. Bhattacharyya and his research group have developed fundamentally new techniques to synthesize bimetallic nanoparticles directly in polymeric membranes:

1. Use of conventional membrane polymers (such as, cellulose acetate [CA]) and phase-inversion method to form nanoparticles.
2. Polyelectrolyte coating of open structured microfiltration membranes to synthesize nanostructured metals.

The main advantage of these membrane-based techniques is that they enhance the researcher's ability to control the size distribution of the resulting nanoparticles. In a test with the goal of producing metallic nanoparticles in a target range of <50 nanometers (nm), Dr. Bhattacharyya and his research group successfully synthesized CA membrane-immobilized bimetallic particles with an average diameter of 24 nm.

Researchers in Dr. Bhattacharyya's laboratory conducted batch experiments to evaluate the effectiveness of TCE dechlorination by iron-nickel (Fe/Ni) nanoparticles (1-20% nickel by weight) immobilized in CA film. They hypothesized that, compared to iron-only particles, the inclusion of nickel would enhance the reaction rate and alter the reaction mechanism, eliminating toxic intermediate formation. For example, the hybrid CA films (Fe/Ni with 20% Ni) demonstrated over a 75% reduction in TCE levels in 4.2 hours, using only a fraction (1/10) of the metal loading used in the literature. Analysis of the aqueous phase for metal content showed that only minimal leaching of metal into the surrounding solution and reusability tests suggest that the synthesized films are capable of the destruction of TCE in large volumes of aqueous solutions.

Just as important as the rapid degradation rate is the fact that ethane was the only observable product of the TCE degradation. This is significant as some intermediates in the reductive dechlorination of TCE - especially vinyl chloride - are highly toxic.

In follow-on studies to refine the bimetallic nanoparticle synthesis process using polyelectrolyte-coated microfiltration membranes rather than cellulose acetate, Bhattacharyya's laboratory achieved greater than 95% dechlorination in less than 1 hour with ethane as the primary product of TCE degradation. A typical SEM image (below) shows quite narrow particle size distribution with an average particle size of about 30 nm.

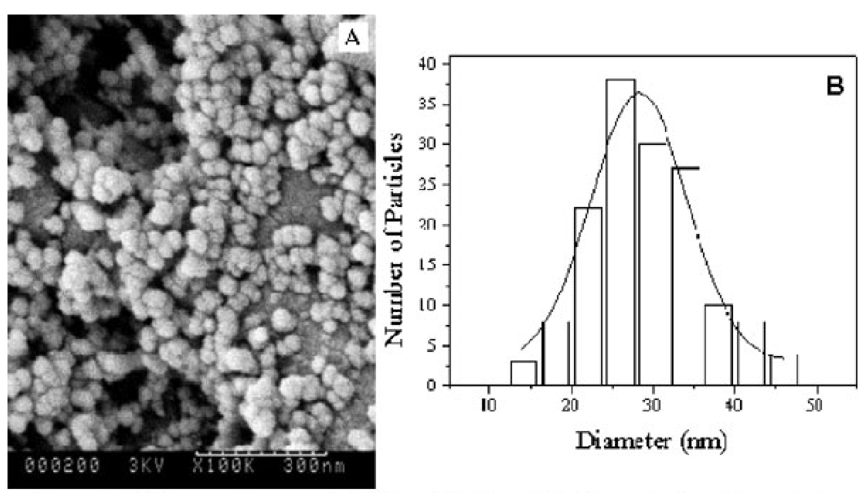

Figure 1. SEM image of nanoscale Fe/Ni particles immobilized in a polyelectrolyte-coated microfiltration membrane

In similar studies, they have synthesized palladium coated iron nanoparticles and determined that, in less than 2 hours, milligram quantities of the membrane-immobilized nanoparticles achieved nearly complete dehalogenation of two types of PCB compounds.

Dr. Bhattacharyya expects that this research with nanostructured metals immobilized in membrane phase will have significant positive impact on remediation of chlorinated organics. The nanostructured metals allow for compact and flexible dechlorination technology development, yielding high reaction rates at room temperature, significant reduction of metals usage, and potential for significant improvement in water quality.

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To learn more about this research, please refer to the following sources:

- Xu, Jianing, Alan Dozier, and Dibakar Bhattacharyya. 2005. Synthesis of Nanoscale bimetallic particles in polyelectrolyte membrane matrix for reductive transformation of halogenated organic compounds. *Journal of Nanoparticle Research*. 7(4-5):449-467.
- Meyer, D.E., K. Wood, Leonidas G. Bachas, and Dibakar Bhattacharyya. 2004. Degradation of chlorinated organics by membrane-immobilized nanosized metals. *Environmental Progress*. 23(3):232-242.