Hello, this is Kevin O'Donovan, and I'd like to welcome you to the National Institute of Environmental Health Sciences Superfund Research Program monthly Research Brief podcast.

This month, we'll be looking at a double membrane remediation system to remove chlorinated organic contaminants from groundwater.

The Research Brief, Number 198, was released on June 1, 2011, and was written by SRP contractor Maureen Avakian in conjunction with SRP-supported researcher Dr. Dibakar Bhattacharyya.

The true extent of trichloroethylene (TCE) contamination of our groundwater is unknown. The Agency for Toxic Substances and Disease Registry's Toxicological Profile for TCE states that it is the most frequently reported organic contaminant in groundwater, estimating that 9% - 34% of U.S. drinking water sources have some level of TCE contamination. Remediation of groundwater contaminated with TCE and/or other chlorinated organics, such as PCBs and dioxins, remains a significant challenge. Cleanup approaches range from steam injection to monitored natural attenuation and are often money-, resource-, and time-intensive.

Advances in membrane technology led to the development of remediation techniques using synthetic membranes that function as permeable barriers for the physical separation of contaminants from water, based on size or differences in diffusion/sorption rates. With the intent of imitating naturally occurring membranes, scientists increased the effectiveness of synthetic membrane remediation tools by incorporating polymers, biological compounds, and functional groups on the pore surfaces of the membranes.

At the University of Kentucky SRP, a team of engineers and chemists developed a *double membrane* remediation system to remove chlorinated organic contaminants from groundwater. Working with their advisor, Dr. Dibakar Bhattacharyya, recent graduates Dr. Scott Lewis and Dr. Saurav Datta and current student Minghui Gui designed and conducted much of the research that led to the development of this system. The double membrane remediation system is based on the use of iron-based free radical reactions to drive the oxidative degradation of chlorinated contaminants to non-toxic end products. These membranes also allow fast transport of water and reactants through pores by pressure modulations.

The researchers "functionalized" the membranes by incorporating various polyelectrolytes (or polypeptides) in the membrane pores and using them to immobilize both enzymes and reactive iron species. The pores of the top membrane were functionalized using a polycation/polyanion layer-by-layer (LbL) assembly technique to electrostatically immobilize the enzyme glucose oxidase. Glucose oxidase is a well-known and robust enzyme commonly used in glucose sensing applications, such as glucose monitoring. The bottom membrane is a polyacrylic acid [PAA] network incorporated in microfiltration membrane, such as polyvinylidene fluoride (PVDF) pores, and contains bound iron species. The PAA network is a stimuli-responsive gel, creating controllable nanoporous structures in which pore openings can be controlled by modulating the stimulus such as pH or cation concentration.

To remove chlorinated organic contaminants, oxygen-saturated contaminated water and glucose are passed through the top layer. In this layer, glucose oxidase converts the glucose and oxygen to hydrogen peroxide and gluconic acid, but does not react with the contaminant. The hydrogen peroxide and gluconic acid are convectively transported to the bottom membrane, where hydrogen peroxide reacts with the iron species to form the free radicals that dechlorinate/detoxify chlorinated organic pollutants. While a single membrane could immobilize both the glucose oxidase and iron in both ionic and nanoparticle form, the researchers use two separate membranes to prevent the deactivation of glucose oxidase by the free radicals and to control each step independently.

These types of stacked membranes are very versatile and can be used for degradation of chloro-organics, such as trichlorophenol (TCP), TCE, etc. The investigators point out that the rate of TCP conversion could be varied by altering the amount of iron loading, the rate of hydrogen peroxide production, the membrane pore size (via pH change), the thickness of the membranes used, and/or residence time through pressure modulation. The researchers demonstrated highly effective dechlorinations with immobilized iron ions even in short residence times.

In order to demonstrate the applicability of this technology to the remediation of contaminated water, researchers exposed a membrane system containing immobilized iron oxide/ferrihydrite 50 - 60 nm nanoparticles to groundwater collected from the areas surrounding the US Department of Energy Paducah Gaseous Diffusion Plant Superfund Site. For the conditions tested, the degradation of TCE was ~ 70%; however, this could be easily increased by adjusting the quantities of reactants used or increasing total reaction time.

Additional advantages of this double membrane design include:

- The rate of hydrogen peroxide synthesis in the top membrane can be modulated by controlling the concentration of glucose entering the system and/or the residence time. This optimizes efficiency and reduces waste.
- The pH-responsive behavior of the bottom membrane permits controlled opening and closing of the membrane pores. Potential benefits include bringing immobilized iron ions or nanoparticles closer to the solution moving through the membrane, varying the residence time, and removing of entrapped precipitates.
- The researchers’ fabrication method reduces energy use and costs because it is conducted at room temperature, unlike many methods to synthesize ferrihydrite/iron oxide within a porous membrane that require elevated temperatures.
- The versatile membrane platform allows iron immobilization in both ionic and nanoparticle forms. The iron-containing membrane allows near neutral pH operation and eliminates iron loss.

University of Kentucky researchers synthesized reactive nanostructured stacked membrane systems with tunable pore size and achieved oxidative degradation of toxic organic compounds using glucose to generate hydrogen peroxide. They extended their work from membrane immobilized iron in ionic form to ferrihydrite/iron oxide nanoparticles, and showed their effectiveness for the degradation of a toxic organic contaminant in groundwater from a

Superfund site. The effectiveness of these reactive, nanostructured multimembrane systems presents an opportunity for conducting other complex reaction sequences quickly and efficiently.

Although these nanostructured materials were developed for environmental applications, the researchers believe that the practical and methodological advances are applicable to other applications, including disinfection and/or virus inactivation.

If you'd like to learn more about this research, visit the Superfund Research Program website at www.niehs.nih.gov/srp. From there, click on "Who We Fund" and follow the links to the University of Kentucky research summary. If you have any questions or comments about this month's podcast or if you have ideas for future podcasts, contact Maureen Avakian at avakian@niehs.nih.gov.

Join us next month as we examine Dr. Rolf Halden's investigation of developmental and immunological effects that might be associated with either chlordane or permethrin exposure.