Research Brief 198: Chlorinated Contaminant Remediation – Dual Function Responsive Membranes

Release Date: 6/01/2011

Superfund Research Program

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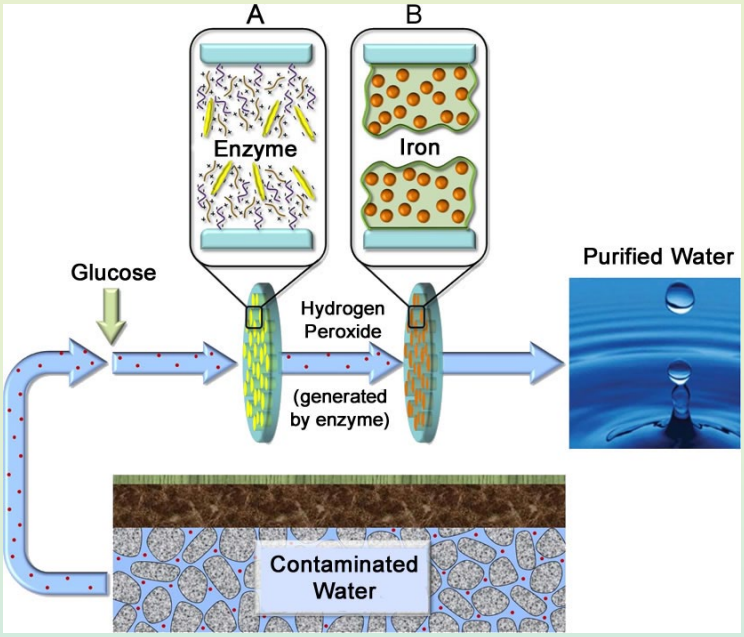
Background

The true extent of trichloroethylene (TCE) contamination of our groundwater is unknown. The Agency for Toxic Substances and Disease Registry (ATSDR) Toxicological Profile for TCE states that TCE 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 (PCBs, dioxins, etc.) 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.

Advances

At the University of Kentucky (UK) 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 doctoral students 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.



Modular double-functional membrane platform with immobilized enzyme and iron for clean water production.
A and B: expanded views of nanostructured membrane pores.

(Figure provided by D. Bhattacharyya)

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 (A in the figure) were functionalized using a polycation/polyanion layer-by-layer (LbL) assembly technique to electrostatically immobilize the enzyme glucose oxidase (GOx). GOx is a well-known and robust enzyme commonly used in glucose sensing applications (i.e. glucose monitoring). The bottom membrane (B in the figure) is a poly(acrylic acid) [PAA] network incorporated in microfiltration membrane, such as poly(vinylidene fluoride) (PVDF) pores and contains bound iron species (iron ions or ferrihydrite/iron oxide nanoparticles). The PAA network is a stimuli-responsive gel, creating controllable nanoporous structures in which pore openings can be controlled by modulating the stimulus (pH, cation concentration).

To remove chlorinated organic contaminants, oxygen-saturated contaminated water and glucose are passed through the top layer. In this layer, GOx converts the glucose and oxygen to hydrogen peroxide (H_2O_2) and gluconic acid, but does not react with the contaminant. The H_2O_2 and gluconic acid are convectively transported to the bottom membrane, where H_2O_2 reacts with the iron species to form the free radicals that dechlorinate/detoxify chlorinated organic pollutants. While a single membrane

could immobilize both the GOx and iron in both ionic and nanoaprticle form, the researchers use two separate membranes to prevent the deactivation of GOx 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 H_2O_2 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 H_2O_2 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 UK team's 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.

Significance

The UK researchers synthesized reactive nanostructured stacked membrane systems with tunable pore size and achieved oxidative degradation of toxic organic compounds using glucose to generate H_2O_2. 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.

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

Scott R. Lewis, Saurav Datta, Minghui Gui, Eric L. Coker, Frank E. Huggins, Sylvia Daunert, Leonidas Bachas, and Dibakar Bhattacharyya. Reactive nanostructured membranes for water purification. May 24, 2011. *Proceedings of the National Academy of Sciences*. 108(no. 21): 8577–8582
doi:10.1073/pnas.1101144108 (Open access article)

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