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## Taking out the Perchlorate: A New, Chemical-Free Bioremediation Technique

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Perchlorate, a common contaminant of drinking water that can pose serious health risks (especially to pregnant women and newborns) is the primary ingredient of solid rocket fuels. Perchlorate molecules, shown in the models, are made up one chlorine atom (green) and four atoms of oxygen (red).

Bioremediation is Mother Nature's way of cleaning up after herself. This process, in which microbes restore a contaminated environment to its original condition, has also been used by humans for thousands of years. Even today, however, human-engineered bioremediation can be a slippery balancing act, where the addition of just the right amount of organic or inorganic chemicals stimulates a given microbe population to consume just the right amount of contaminant. Adding too much or too little can result in problems.

For at least one common contaminant of drinking water and groundwater, the curtain may be coming down at last on this delicate chemical balancing act. Berkeley researchers have developed a chemical-free bioremediation technique for removing perchlorate from water.

"We've demonstrated that microorganisms can utilize electrons donated from the cathode" the negatively charged electrode—"of an

electrochemical cell in lieu of chemical electron donors," says microbiologist John Coates, the leader of this research. "When the electron acceptor is a contaminant, bioelectrical stimulation of microbial reduction of that contaminant can be used as a bioremediative strategy." Coates holds joint appointments with Berkeley Lab's Earth Sciences Division and UC Berkeley's Department of Plant and Microbial Biology.

Perchlorates are salts, mostly human-made, which are extensively used in rocket fuels and other manufactured products including explosives, fireworks, matches, and airbags. Because they interfere with iodine uptake to the thyroid gland, perchlorates in drinking water or groundwater have been deemed a health risk. The greatest threat is posed to pregnant women and newborns, because iodine deficiency impacts the production of thyroid hormones that are critical to the normal growth and development of the central nervous system.

In 1997 Coates, who was then with Southern Illinois University, along with colleague Laurie Achenbach, began a search for microbes that could be used to remove perchlorates from soils, sediments, or water. Within three years they were able to identify about 40 different candidates, all members of the phylum Proteobacteria, which not only reduce perchlorates but do so in an anaerobic environment. That is, once the oxygen in their immediate environment has been depleted, these proteobacteria readily start consuming perchlorate as part of their metabolic process. Field tests have shown that when chemical conditions are right, strains of Dechloromonas and Azospira effectively remove all perchlorates by reducing them to innocuous chlorides.

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The trick, of course, is nailing down the right conditions. For remediation of drinking water or groundwater, this means setting up a bioreactor through which the water passes and adding just enough of a chemical electron donor, either organic or inorganic, to sustain microbial activity without causing any collateral damage. How tough is this? Consider that the conventional method of removing perchlorates from water calls for the use of organic compounds such as acetate, ethanol, or vegetable oil.

"This is bad," Coates says, because due to the organic carbon, "Such additives also stimulate growth of the microbes, which requires subsequent removal of these organisms and may lead to downstream issues with biofouling and the production of trihalomethanes," another hazardous pollutant.

To avoid the stimulation of microbial cell growth, alternative remediation technologies have been proposed that would use inorganic electron donors such as hydrogen gas, elemental sulfur, hydrogen sulfide, or ferrous iron. All are effective electron donors, but all can create problems of their own.

"Hydrogen gas is difficult to handle and explosive in nature," says Coates. "Hydrogen sulfide is a malodorous toxic compound which can cause corrosion issues, and particulate ferric oxide produced from ferrous iron oxidation results in unpleasant taste and odor, clogged pumps and treatment systems, and corrosion of steel pipes and distribution lines."

With the technique develop by Coates and his research group, a chemical electron donor is replaced in a bioreactor with a cathode made of graphite. In contrast to biochemical remediation, Coates's bioelectrical approach maintains the prerequisite microorganisms at constant levels. This not only eliminates the need for chemicaladditive guesswork, it also eliminates the biomass disposal costs that are inevitable when biochemicals are put into play.



Dechloromonas is a strain of proteobacteria that can effectively perform bioremediation on perchlorates, even in an anaerobic environment.

(Image by John Bozzola and Steven Schmidt, Image Facility of Southern Illinois University, Carbondale)

"Our technique offers great potential for wellhead treatment of drinking water, ex situ treatment of contaminated groundwater and waste water streams, as well as in situ remediation of ground water and liquid contamination sites," Coates says. "The technology has been demonstrated to work with both high—parts per million—and low—parts per billion—perchlorate concentrations, as well as with natural ground waters containing mixed wastes of perchlorate and nitrate."

The bioelectrical reactor developed by Coates and his research group consists of a single-chamber electrochemical cell with influent and effluent ports. Inside the chamber are an anode (a positively charged electrode) and a cathode in the form of a bed of packed graphite particles. The cathode may be inoculated with an active culture of perchlorate-metabolizing organisms, or it may be naturally seeded with indigenous organisms from the contaminated stream. Once the microbes have been introduced, a small electrical load is applied.

"The microorganisms couple oxidation of the cathode to reduction of a suitable electron acceptor such as nitrate or perchlorate for the purpose of gaining energy," Coates says. "At volumetric loading rates as high as 60 milligrams per liter of reactor volume per day"—which is equivalent to current commercial technologies—"we can reduce perchlorate to below our detection limit of approximately one part per billion, which is below current federal and state recommended levels."

Advantages of switching to a bioelectrical remediation system include significantly reducing the downstream issues usually associated with chemical bioreactors, such as biofouling, corrosion, and the production of trihalomethanes as a result of disinfecting treated waters. In the future, the electrochemical chamber that

Coates and his group developed for their bioelectrical reactor could also serve as the cathodic chamber of a microbial fuel cell. The ability of microbes to perform the chemistry needed for bioremediation can also be applied to biofuel cells for the generation of electrical energy.

"We are currently investigating the microbial processes in energy generation in both the anodic and cathodic chambers of a microbial fuel cell," Coates said.

Collaborating with Coates on the bioelectrical technique for removing perchlorates from water and for generating electricity are members of his research group Cameron Thrash, Forest Kaser, Kelly Wrighton, and Juan Fernando Villaromero.



Microbiologist John Coates (left) led a team, which included Forest Kaser, that developed a chemicalfree bioremediation technique for removing perchlorate from water.

## Additional information

More about the research of John Coates and his group is at <u>http://pmb.berkeley.edu/~coates/</u>.