

Tracking the 'evolution' of nanoparticles as they decontaminate groundwater

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(PhysOrg.com) -- Engineers use advanced imaging techniques to examine bimetallic materials that have remediated more than 50 toxic waste sites.

Iron [nanoparticles](#) 1,000 times thinner than a human hair have demonstrated an unprecedented ability to clean contaminated [groundwater](#) since they were invented 10 years ago at Lehigh.

The palladium-coated particles have remediated more than 50 toxic waste sites in the U.S. and other countries in one-tenth the time, and at a much greater economy of scale, than traditional “pump and treat” methods.

Now, thanks to Lehigh’s unrivaled electron microscopy and spectroscopy facilities, researchers have gained unmatched insights that could improve the efficiency and extend the applications of the powerful nanoparticles.

The researchers used scanning [transmission electron microscopy](#) (STEM) and X-ray energy dispersive spectroscopy (XEDS) to capture, for the first time, the evolution in the nanostructure of the bimetallic particles as they remove contaminants in water.

The advanced imaging instruments at Lehigh captured amazing details of the reactions within nanoparticles. As they react with pollutants such as trichloroethene (TCE), a toxic industrial solvent, the nanoparticles display huge structural changes. The particle core hollows out, the iron

diffuses outward, and the [palladium](#), a catalyst that makes up 1 percent of particle mass, migrates from the outer surface to the interior surface of the iron.

Writing earlier this month in [Environmental Science and Technology](#) (*ES&T*), the premier journal in its field, the Lehigh researchers reported that the nanoparticles' ability to remove toxins decreases as the particles "age" and undergo structural change with exposure to water.

Their results, they wrote, suggest that the nanoparticles' age and storage environment play a critical role in influencing their effectiveness as remediation agents.

Tiny but mighty

The *ES&T* article, titled "Structural Evolution of Pd-Doped Nanoscale Zero-Valent Iron (nZVI) in Aqueous Media and Implications for Particle Aging and Reactivity," was written by Weile Yan, a Ph.D. candidate in civil and environmental engineering, with Andrew Herzing '07 Ph.D., a materials research engineer with the National Institute of Standards and Technology; Xiao-Qin Li, who received a Ph.D. in civil and environmental engineering in 2008; Christopher Kiely, professor of materials science and engineering; and Wei-xian Zhang, professor of civil and environmental engineering.

The nanoparticles, which were invented by Zhang, average 50 nanometers in diameter (1 nm equals a billionth of a meter). Islands of palladium on the iron's outer surface measure 2 to 5 nm in diameter. The particles have removed pesticides, vinyl chloride, TCE and other contaminants in 10 states and in Europe and Asia. Treated sites include landfills, an electronics manufacturing plant, chemical plants and military facilities.

When injected into groundwater, the nanoparticles flow with the water and react with and detoxify contaminants. Their small size and greater proportional surface area give them more reactivity with toxins than larger quantities of the same catalyst.

This superior reactivity, says Harch Gill, president of Lehigh Nanotech LLC, a Bethlehem company that owns the commercial rights to the particles, enables the particles to remediate a toxic site in less than a year, compared to the 10 to 20 years required by pump-and-treat methods.

And according to the Association of University Technology Managers, which named Lehigh Nanotech one of the top 25 technology-collaboration stories in 2008, “it takes only six ounces of the tiny nanomaterials, versus a ton of larger compounds, to make sweeping changes in cleaning up contaminated environments.”

As a result, says Zhang, the nanoparticles are now one of the world’s most widely used nanomaterials.

A new focus

Yan, who has studied the nanoparticles since 2007, says the experimental results will help researchers develop better methods of handling and storing the particles, and of collecting and reusing the palladium after it has neutralized contaminants. Palladium, used in catalytic converters, electronic devices and fuel cells, is a rare and often expensive metal.

The results can also be used to improve the ability of iron-based nanoparticles to capture and remove heavy-metal toxins from contaminated sites, says Yan.

“This paper is just a starting point,” she says. “Using the same suite of

tools, we can study metal species and nZVI to learn how heavy metals are captured by nZVI, where they interact and where the final destination of the heavy metals is inside the nZVI.”

The group’s research, says Yan, was made possible by the fact that Lehigh has the largest electron microscopy lab in the U.S. The aberration-corrected STEM used by Yan’s team resolves images to 0.1 nm while identifying the chemical composition in this tiny “pixel” of a specimen. Combined with XEDS, it allowed the researchers to map the surface and interior of the iron nanoparticle, locate the islands of palladium, and track the infiltration of the palladium to the particle interior. The group also used X-ray photoelectron spectroscopy (XPS) to examine the changes in the chemical properties of the nanoparticles.

The instruments enabled the group to take a novel approach to its research, says Yan.

“The traditional way of doing environmental research is to examine the contaminants in water to make sure they are wiped out,” she said. “We are taking a different approach by looking inside the treatment agent to see what happens to it and how remediation actually takes place.”

Yan will give a presentation on the group’s research to the Environmental Chemical Division of the American Chemical Society at ACS’s annual conference in August in Boston.

More information: Journal paper:
pubs.acs.org/doi/abs/10.1021/es100051q

Provided by Lehigh University

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