

‘Forever chemicals’ no more? These technologies aim to destroy PFAS in water

Researchers are developing a battery of new treatments to better target and ultimately obliterate fluorinated contaminants in water supplies

by *Kerri Jansen*

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Credit: C&EN/Molview

At the Sweeney Water Treatment Plant in North Carolina, engineers are finalizing designs for a new system aimed at removing a mix of persistent industrial chemicals from their drinking water. These molecules are troublemakers—wily foes that have evaded capture by traditional water treatment methods. They’re known collectively as PFAS, the family of nonpolymer per- and polyfluoroalkyl substances nicknamed “forever chemicals.”

The plant has been paying special attention to PFAS. The facility supplies water to roughly 200,000 customers, drawing the bulk of that water from the lower part of the Cape Fear River, which researchers in 2016 found to be contaminated with PFAS **downstream** from a fluorochemical-producing Chemours plant.

The new facility will house four 12 m long beds of granular activated carbon, about 7 m wide and 3.7 m deep, to suck PFAS from the water. These beds are three times as deep as the plant’s existing ones, which it uses to house bacteria that help disinfect the water. Water will trickle through the new beds over the course of 10–20 min before it is considered clean. Every 400 days, the activated carbon, having soaked up a maximum level of contaminants, will need to be replaced—baked in a commercial incinerator to drive out the contaminants, then topped up with fresh carbon before being put back into service.

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Officials estimate construction of the new system will cost \$46 million, with yearly operating costs of \$2.9 million. Until that project is completed, sometime in 2022, the plant is relying on its existing carbon beds to remove PFAS as well as to disinfect its water. After the new system is operational, those beds will go back to their original purpose. In the meantime, the added burden of cleaning PFAS from the water means that the plant will need to replace the activated carbon more frequently. Some of the existing beds had lasted for as many as 10 years; now, they’ll be replaced every 12 months.

IN BRIEF

Nonpolymer per- and polyfluoroalkyl substances (PFAS), used to manufacture many nonstick and stain-repellent household products, have been detected in drinking water in

hundreds of locations around the US and beyond. Exposure to some of these chemicals has been linked to harmful health effects. Because the molecules contain tough carbon-fluorine bonds, once they leak into the environment, they are persistent. Commonly used adsorbent technologies at water treatment facilities trap the chemicals, but they are vulnerable to clogging, and they collect the PFAS, which then need to be disposed of. Now, chemists are not only designing new adsorbents that better target PFAS and don’t clog as often but also developing treatment methods to completely destroy the molecules rather than merely sequestering them.

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Such measures, though they may seem extreme, are what many water utilities find necessary to treat the collection of notoriously persistent PFAS. And at the moment, they are the best methods we've got.

PFAS have been detected in surface and groundwater in hundreds of locations in the US and around the world. Exposure to some of these chemicals is linked to harmful health effects in the liver, kidneys, blood, and immune system. The

compounds are used in many nonstick and stain-repellent household products and can get into the environment when manufacturing waste is improperly disposed of. Although the long-chain PFAS molecules—perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS)—are no longer manufactured in the US, **many smaller-chain PFAS are still in use**. PFAS also get into the environment through the application of **firefighting foams** at airports and military bases.

Each PFAS molecule has a hydrophilic “head” and a long, hydrophobic “tail” that contains carbon-fluorine bonds. The carbon-fluorine bond is one of the strongest single bonds in nature, giving the molecules their persistence in the environment and their “forever” moniker. PFOA and PFOS, which are the focus of most water treatment efforts, can, when broken down, form other, smaller-chain fluorinated molecules that persist in the environment and may still pose harm.

“They're just a completely different beast,” says

Clarkson University's Michelle Crimi about PFAS. She says removing PFAS is the hardest challenge she's faced in her 20 years of studying water remediation methods.

Today's water utilities have limited options for removing PFAS. Reverse osmosis, ion-exchange resins, and granular activated carbon trap PFAS, either in a concentrated liquid, in the case of reverse osmosis, or in a solid, as in the case of the resins and carbon. And those liquids and solids then need to be disposed of.

It's from this list of options that water officials in North Carolina chose, running several tests in 2017 and 2018 and ultimately settling on the large carbon beds. The US Environmental Protection Agency's health advisory level for PFOA and PFOS, separately or in combination, currently sits at 70 parts per trillion, a number that may change as regulators grapple with setting enforceable limits for the chemicals. North Carolina officials aimed not just to beat that level but to remove as much PFAS from the water as possible. They expect the new treatment system will be capable of capturing 90% of PFAS from their water.

“There's no technology that's really going to remove 100%” of the PFAS, says Carel Vandermeijden, director of engineering at Cape Fear Public Utility Authority, which operates the Sweeney Water Treatment Plant. But no one knows exactly what the combined cumulative health effect is of all the PFAS, he says, “so our approach is to put in the best available technology.”

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But the best on the market still leaves room for improvement. Reverse osmosis, ion-exchange resins, and granular activated carbon, though capable of trapping PFAS, were not designed to specifically bind these newly scrutinized and little-understood pollutants. These technologies can also allow smaller PFAS molecules to slip through and are vulnerable to fouling from other substances in the water, causing them to lose efficiency. Plus, they create a concentrated waste stream.

So now, researchers are not only designing adsorbents that specifically take up PFAS but are also developing treatment methods to completely destroy the molecules rather than merely sequestering them. And they're doing this with an eye toward making as little long-term waste as possible.

The big three

Few technologies exist today for removing PFAS from drinking water. Here are the three most commonly considered by water treatment facilities.

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Credit: Evoqua Water Technologies

Granular activated carbon

- **Mechanism:** Long used to remove a variety of contaminants from water, granular activated carbon is typically the least-expensive PFAS treatment option. As water flows through packed beds of the material, PFAS molecules adsorb onto the surface of the porous carbon particles.
- **Caveats:** Other compounds can also adsorb to the carbon particles, reducing their capacity for PFAS. And smaller-chain PFAS molecules can evade capture by the particles.
- **Disposal:** Spent carbon can be landfilled or regenerated with high temperatures.



Ion-exchange resin

- **Mechanism:** Based on polymers, ion-exchange resins are similar to granular activated carbon. The positively charged resin particles attract and hold onto negatively charged PFAS molecules as they pass through.
- **Caveats:** Like granular activated carbon, conventional ion-exchange resins can become saturated, reducing their capacity for PFAS. Some newer varieties are designed to improve their efficiency.
- **Disposal:** Single-use resins are landfilled. Regenerable resins require the management of leftover liquid from the flush must then be managed, with

A BETTER MOUSETRAP

The first step in any water treatment is to figure out what exactly is in the water, says Detlef Knappe, an environmental engineer at North Carolina State University. That means understanding the contaminant itself, yes, but also the other components of the water. Water—especially river water and other surface water—contains compounds like naturally occurring carbon from soil and decaying plants that are much more prevalent than the contaminants and that also bind to adsorbent material. They can block PFAS from sticking to adsorbents and make materials such as granular activated carbon less efficient.

“It’s like we’re trying to pull needles out of a haystack, but the haystack also sticks to the filter,” Knappe says.

Most current data on PFAS removal, he notes, apply to groundwater, which is relatively clean compared with surface water, like that in the Cape Fear River. So his team is analyzing how other compounds in surface water affect different filtration media. The group is studying whether efficiency can be improved by tweaking the pore structure and surface chemistry of these materials.

This is a process that Francis Boodoo, director of applied technologies at the water treatment supply company Purolite, refers to as “making a better mousetrap”—developing treatments that do a better job trapping and holding on to contaminant chemicals. Purolite developed a single-use ion-exchange resin specialized for removing PFAS. Like many ion-exchange resins, it’s built on a chemical backbone of polystyrene and divinylbenzene, modified with a proprietary mix of functional groups

that give the copolymer a higher affinity for certain molecules. The goal, Boodoo says, was to bind a PFAS molecule's hydrophobic tail more strongly, along with binding to the hydrophilic head of the molecule, which standard ion-exchange resins can already do.

Boodoo reports that the company's resin can reduce PFOS and PFOA in treated water to levels below the detection limits of standard instruments for a period of about 2–3 years before needing to be replaced. The business is now working to develop a second generation of ion-exchange resins that targets a broader range of PFAS molecules. The resin is more expensive up front than activated carbon, but it requires a smaller footprint for installation, Boodoo says. Purolite has installed the PFAS-specialized resin in 10–15 municipalities around the world so far, Boodoo adds.

Will Dichtel, a chemist at Northwestern University and a founder of a water treatment technology company called CycloPure, is also developing improved adsorbents that are more specific to PFAS than today's treatment methods. His adsorbents are based on cyclodextrin—a ring of sugar molecules—that's been cross-linked with rigid aromatic groups containing multiple fluorines. These macrocycles create hydrophobic pockets that can specifically **trap PFOA**.

Because cyclodextrin is already on the market and is inexpensive, "we're optimistic about the cost," Dichtel says. It takes just one step to make his adsorbent material from cyclodextrin, he adds.

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Dichtel and colleagues recently demonstrated that the polymer networks can be attached to cellulose nanocrystals, forming particles that could be installed in treatment plants in a packed bed, similar to granular activated carbon (*ACS Appl. Mater. Interfaces* 2019, DOI: **10.1021/acsami.8b22100**). Early tests suggest the material is less prone to fouling than activated carbon, and the group has also developed a new variety of cyclodextrin polymer that can trap a wider range of negatively charged PFAS, Dichtel says.

Filtration methods remove PFAS from water without any chemical transformation of the molecules, leaving them intact. One option for dealing with this waste, which both Dichtel's group and Purolite are investigating, is regenerating their filter materials, potentially by flushing them with a chemical rinse. Some ion-exchange resins available today can be rinsed in this way, resulting in a small volume of highly concentrated liquid waste, which needs to be disposed of. Spent filter materials can also be landfilled, requiring long-term management of the compounds.

Physical adsorption technologies like carbon and these polymers may offer the fastest route to specialized PFAS treatment. And that appeals to many water utilities that are looking to get PFAS out of their water as soon as possible. These utilities have customers who aren't interested in waiting for more sophisticated technologies to mature. But scientists are still pursuing long-term strategies.

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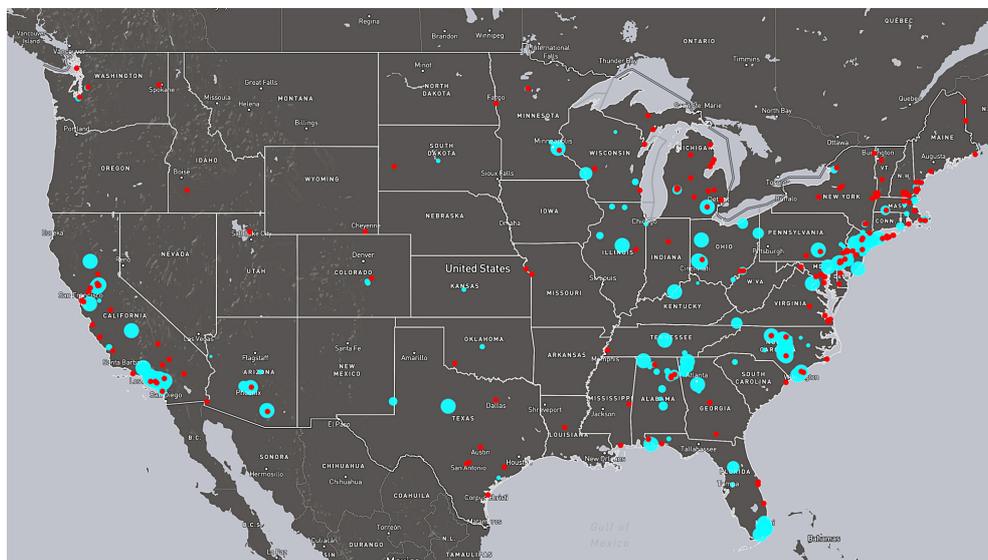
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Nationwide contamination

A map of PFAS water contamination in the US. Blue circles represent locations where PFAS have been detected in tap water as of 2016. The circles' diameter roughly corresponds to the size of the population served by a contaminated drinking-water system. Red dots represent contaminated industrial or military sites as of July 2018. Locations are approximate. View the full interactive map here.



Credit: Environmental Working Group/Social Science Environmental Health Research Institute/Northeastern University

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LET'S BREAK IT DOWN

At the moment, the only way to truly get rid of PFAS molecules is by incinerating the filter material they are stuck to at temperatures above 1,000 °C. In theory, this process uses enough energy that it can break the molecules into their component elements, a process called mineralization.

Several scientists C&EN spoke with, however, expressed concerns about the lack of data around incinerating PFAS. Do the molecules really break down completely? How do they change during the incineration process? Incompletely degraded molecules could simply form smaller PFAS molecules that are still potentially harmful, says York University atmospheric scientist Cora J. Young.

"Incineration of PFAS, if it's going to be done on a large scale, should be explored to make sure the PFAS is fully mineralized," she says, noting that incompletely degraded compounds released from an incinerator would be put directly into the atmosphere, where they might spread widely.

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With urgency growing around PFAS and without an ideal disposal method, researchers are exploring more controlled ways of destroying the sturdy molecules. Most scientists are focusing on treating highly contaminated water, such as landfill leachate, wastewater stockpiles, and groundwater near military sites where PFAS-containing firefighting foams were used heavily. Left untreated, the PFAS in those locations—with levels that can be hundreds of times as high as the levels found in tap water—could potentially spread to drinking-water sources. On the other hand, treating the PFAS in those locations via traditional activated carbon and single-use ion-exchange materials would use those adsorbents up too quickly to be practical.

To clean these PFAS-laden waters, some researchers are instead developing electrochemical, thermal, and ultrasonic treatment methods that could fully degrade PFAS molecules, working alone or in combination with other techniques.

"You have all of these people developing adsorbents, and they all might work well, but every single one of them is going to need a destructive technology behind that," says Cory Rusinek, an electrochemist at Fraunhofer USA Center for Coatings and Diamond Technologies, on the campus of Michigan State University. His group is among those developing electrochemical methods to destroy PFAS molecules.

Rusinek's technology involves a series of niobium electrodes coated with a diamond-boron film, which makes the electrodes resistant to oxidation. Applying high voltage and current to the system

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Credit: Derrick Turner/MSU

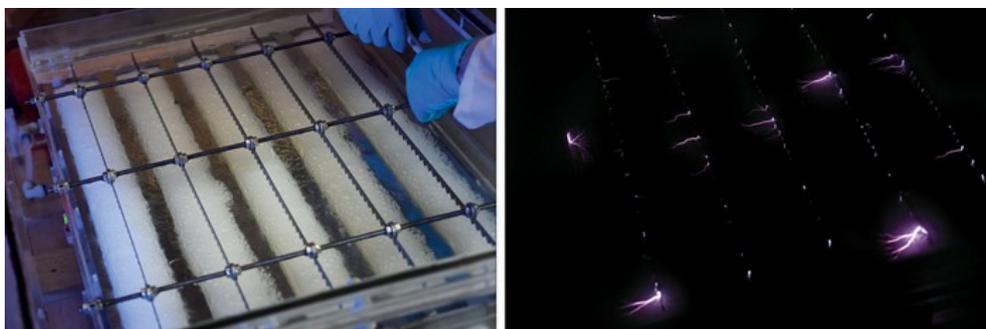
Cory Rusinek (right) and Michigan State University graduate student Mary Ensch use electrodes coated with a diamond-boron film to degrade PFAS in water.

causes oxidation of the PFAS molecules, leading to their defluorination. Although Rusinek and his team know the technique breaks down the molecules, they aren't yet clear on whether the PFAS molecules need to come into direct contact with the anode or merely come close. That's something the group is figuring out, along with the by-products the process may produce. Ideally, the system would drive PFAS compounds to mineralization, producing only fluoride ions, carbon dioxide, and water.

The attractiveness of the approach, Rusinek says, is that PFAS could be removed completely from a water sample.

Tests with a lab-scale system reduced high concentrations of PFAS—2 ppm—by three orders of magnitude in 4 h, Rusinek reports. The system draws too much energy to be cost effective in a large-scale municipal water treatment plant, but it could be effective for lower volumes of highly contaminated water, he says. His team is working to make the process faster and is developing a system for lower concentrations of the contaminants.

Plasma, on the other hand, can break down PFAS molecules much faster but may not degrade them completely. At Clarkson University, chemical engineer Selma Mededovic Thagard and her colleague Thomas M. Holsen are developing a water treatment system that uses electricity to generate highly reactive species from argon gas. These species can degrade long- and short-chain PFAS and other organic compounds in a matter of minutes.



Credit: Courtesy of Selma Mededovic Thagard

A plasma reactor (left) developed by researchers at Clarkson University zaps PFAS with plasma (right) to break down the molecules.

The team pumps argon gas into a large tank of contaminated water. As the gas rises through the water, it picks up the contaminants and concentrates them at the surface of the water in the tank. With a push of a button, the researchers generate plasma between a series of electrodes located above the water's surface and ones slightly below the water's surface. The argon ions and electrons generated by the plasma break down PFAS contaminants.

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“The C-F chain is sticking up in the plasma, and the hydrophilic part is just in the water,” Mededovic Thagard says. “So you have argon ions and electrons continuously hitting on that hydrophobic tail and just chopping it off,” removing carbons one by one until a fluoride ion is formed. Currently, the system can treat about 7.5 L/min, drawing about the same amount of energy as a microwave oven. But more research is needed on the by-products it produces, Mededovic Thagard says. Early tests treating PFOS and PFOA detected some remaining smaller-chain PFAS molecules in the water after treatment (*Environ. Sci. Technol.* 2019, DOI: [10.1021/acs.est.8b07031](https://doi.org/10.1021/acs.est.8b07031)). The group is working with the US Air Force to perform field tests of the system at contaminated sites this year.

Other researchers are pursuing methods that involve applying ultraviolet light to contaminated water, potentially with a photocatalyst or other sensitizing compound to encourage degradation of PFAS. The molecules can also be broken down with intense heat and pressure, an approach that Timothy Strathmann, an environmental engineer at the Colorado School of Mines, is pursuing. His team’s pressure-cooker technology heats concentrated contaminated water to around 350 °C while compressing it to about 150–200 times atmospheric pressure at sea level. The method destroys a broad array of PFAS molecules, he says, with few fluorinated by-products. His team is trying to understand how the molecules break down so the researchers can optimize their conditions.

For groundwater, Clarkson University’s Crimi considers leaving it in the ground the simplest treatment option. This saves the energy that would otherwise be expended to pump it out for treatment, clean it, and then put it back. Her team is developing a system that would be installed underground and that would emit sound waves to degrade PFAS molecules in the water.

At a frequency in the hundreds of kilohertz—higher than the frequencies that humans are capable of hearing—sound waves applied to an underground reservoir of groundwater would create lots of tiny bubbles. When the bubbles collapse, they produce localized energy, which blasts PFAS molecules apart and also breaks down water into free radicals. These radicals can degrade the contaminants further, Crimi says. Her team has tested a prototype and is looking for field-testing opportunities.

In some cases, these destruction technologies—sound waves, plasma, and the like—that are being developed for highly contaminated water might be paired with a filter material like granular activated carbon or an ion-exchange resin to eliminate the problem of long-term waste when treating larger volumes of less-contaminated water. For example, an ion-exchange resin could be regenerated with a solvent rinse, then the concentrated rinse solution treated with plasma or an electrochemical approach to destroy the PFAS.

Chris Higgins of the Colorado School of Mines, who studies emerging contaminants like PFAS, says he sees these “treatment trains” as key in the future of PFAS treatment. The availability of multiple efficient technologies to remove and destroy PFAS would enable water utilities to customize their treatment systems according to their unique water chemistry, contaminant levels, and technological needs.

“There’s not going to be a one-size-fits-all solution,” Higgins says.

Of course, as multiple scientists noted to C&EN, the ideal scenario to ensure clean water would have been to stop PFAS from ever entering the environment.

“The best solution is to not pollute in the first place,” Northwestern’s Dichtel says. “But here we are.”

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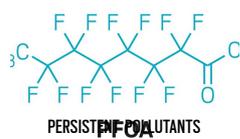
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COMMENTS

Cathy Swanson

(March 26, 2019 12:12 PM)

Single-use ion exchange resins can also be incinerated for destruction of PFAS molecules.

Reply »

Joe Cotruvo

(March 27, 2019 3:42 PM)

There is nothing new about the first article on deep bed GAC columns. Selective absorptive polymers might be interesting. Cyclodextrin seems interesting if cheap, and if it does not add organic carbon to the water. It does not mention high energy particles like betas, except in passing related to UV. They have been tested back at least 70 years. Beta's might be perfect for PFAS because the ground water where they are usually found normally have low organic carbon content so low MW TOC production might not be a problem as it is for surface waters and some groundwaters. One problem with high energy systems is that they are not selective so a lot of the energy can be dissipated in reactions with TOC.

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