Fighting PFAS with PFAS

Rafael Verduzco and Michael S. Wong

Charged and partially fluorinated hydrogels are demonstrated to be a promising new approach to selectively uptake PFAS contaminants in water.

As the old saying (or classic Metallica song) goes, “Fight fire with fire”. When the target is poly- and per-fluoroalkyl substances (PFAS), however, fire will not do the job. PFAS are toxic synthetic chemical contaminants widespread in the environment, including in drinking water and soil. PFAS contain partially fluorinated alkyl tails and can be amphiphilic and lipophobic and dissolve in water, making remediation particularly challenging. There is a need for technologies that can remove and remediate PFAS and perfluoralkyl acids (PFAA) in the environment to prevent further accumulation and reduce the impact on human health. In this issue of ACS Central Science, Kumarasamy et al. present an innovative strategy for removing PFAS from water with a hydrogel that contains perfluoropolyethers, literally fighting PFAS with PFAS.

PFAS are not a single compound but rather represent thousands of compounds that contain a perfluoroalkyl group CnF2n+1. Some PFAS can biotransform to produce PFAA, which are water-soluble, amphiphilic molecules that spread quickly through the environment. A number of PFAA and PFAA precursors have been restricted under regulatory frameworks, and several PFAA such as perfluorooctanoic acid and perfluoroctanesulfonic acid are being phased out. Some examples of PFAS, PFAA, and PFAA precursors are shown in Figure 1.

The physical and chemical characteristics of PFAA pose a number of challenges to uptake and remediation strategies. PFAA are amphiphilic, dissolve in water, and stick to surfaces and interfaces. The fluorinated alkyl tails are lipophobic, providing resistance to oils and grease. Adsorbents like granular activated carbon (GAC) take advantage of the surface activity of these materials but are less effective for short-chain contaminants and in the presence of other organic contaminants. Ion-exchange resins which contain fixed positive charges can attract and take up the negatively charged PFAA, but their effectiveness depends on the PFAA chemistry and alkyl chain length. Novel adsorbent materials that can provide higher capacities and faster adsorption kinetics for PFAA are being actively developed.

Kumarasamy et al. present an innovative strategy for the development of PFAA adsorbents. They produced hydrogels that mimic the molecular chemistry of PFAA, with the...
The hypothesis that dissolved PFAA would be attracted and retained by the hydrogel (see Figure 2). The hydrogels contained hydrophobic, hydrophilic, charged, and fluorinated functional groups. Positively charged hydrophilic organic groups both attracted the negatively charged PFAA and caused the polymer network to take up water. The fluorinated segments were designed to attract other fluorinated molecules while repelling nonfluorinated organic molecules. The overall network composition was modular, and the content of the charged groups could be systematically varied in order to screen different network compositions for effective PFAA uptake.

Through batch testing for uptake of both long- and short-chain PFAA, Kumarasamy and co-workers demonstrated that their hydrogel could effectively adsorb PFAA contaminants dissolved in water, even in the presence of dissolved organic contaminants. Hydrogels with positively charged quaternized ammonium cations outperformed hydrogels containing amines due to attractive electrostatic interactions between the positively charged hydrogel and PFAA contaminants. The charged hydrogels outperformed GAC, powdered activated carbon, and ion-exchange resins, which reflected, in part, the attraction of the PFAA contaminants to the fluorinated segments in the hydrogels. The hydrogels were effective even with short-chain PFAA such as GenX which are more water-soluble than their long-chain counterparts and more difficult to extract from water. The team further demonstrated that hydrogels were effective in the presence of other organic contaminants. Through batch tests using water collected from the Sweeney Water Treatment Plant in Wilmington, NC, they found that uptake of PFAA was not significantly affected by the presence of dissolved organic matter (1.3 mg/L) in the water. This reflected a more favorable interaction between the hydrogel and PFAA contaminants over these organic species, likely due to the presence of fluorinated segments in the hydrogel.

This study demonstrates an effective approach to the development of polymer networks and hydrogels for PFAA uptake. The concept of tailoring the chemistry of the polymer network to match that of the contaminant is simple and effective and can potentially be applied to other PFAS contaminants. While the study focuses on the uptake of negatively charged PFAA, PFAS more generally can be neutral or contain positive or zwitterionic charges. A similar hydrogel could potentially be designed for capturing these contaminants by replacing the positively charged ammonium group with either neutral or negatively charged groups.

Further work is needed to fully evaluate the effectiveness of these hydrogels for PFAS and PFAA remediation. A full technoeconomic analysis taking into account material preparation, lifetime, waste, and waste disposal is needed to evaluate these hydrogels relative to other established materials such as GAC. These new materials pose a risk of their own as they can potentially release fluoroalkyl ether contaminants if the polymer networks degrade or decompose during the water treatment, and therefore, long-term stability tests under different environmental conditions are needed. Fluoroalkyl ethers are easier to degrade than PFAA, but they still present environmental challenges. Furthermore, a clear limitation of the proposed materials is that they absorb PFAS but do not degrade them. Activated carbons such as GAC can be thermally reactivated in a process that also destroys adsorbed PFAS contaminants, which can complement other treatment and remediation strategies like electrochemical treatment, reverse osmosis, and bioremediation. Finally, the performance of these hydrogels in high-salinity environments and/or in the presence of divalent anions should be evaluated. These dissolved salts can screen electrostatic interactions, reduce water uptake, and potentially reduce the effectiveness of the adsorbent.

Author Information

Rafael Verduzco — Department of Chemical and Biomolecular Engineering, Rice University, Houston, Texas 77005, United States, Houston, Texas 77005, United States; Email: rafaelv@rice.edu

Michael S. Wong — Department of Chemical and Biomolecular Engineering, Rice University, Houston, Texas 77005, United States, Houston, Texas 77005, United States; Email: michaelwong@rice.edu

Complete contact information is available at: https://pubs.acs.org/10.1021/acscentsci.0c00164
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REFERENCES

(1) Kumarasamy, E.; Manning, I.; Collins, L. B.; Coronell, O.; Leibfarth, F. Ionic Fluorogels for Remediation of Per- and Polyfluorinated Alkyl Substances from Water. ACS Cent. Sci. 2019, in press. DOI: 10.1021/acscentsci.9b01224.

(2) Wang, Z.; DeWitt, J. C.; Higgins, C. P.; Cousins, I. T. A Never-Ending Story of Per- and Polyfluoroalkyl Substances (PFASs)? Environ. Sci. Technol. 2017, 51, 2508–2518.

(3) A guide to the PFAS found in our environment. Chem. Eng. News. https://cen.acs.org/sections/pfas.html.

(4) Ross, I.; McDonough, J.; Miles, J.; Storch, P.; Kochunaryanan, P. T.; Kalve, E.; Hurst, J.; Dasgupta, S. S.; Burdick, J. A review of emerging technologies for remediation of PFASs. Remediat. J. 2018, 28, 101–126.

(5) Yu, J.; Lv, L.; Lan, P.; Zhang, S.; Pan, B.; Zhang, W. Effect of effluent organic matter on the adsorption of perfluorinated compounds onto activated carbon. J. Hazard. Mater. 2012, 225–226, 99–106.

(6) Zaggia, A.; Conte, L.; Falletti, L.; Fant, M.; Chiorboli, A. Use of strong anion exchange resins for the removal of perfluoroalkylated substances from contaminated drinking water in batch and continuous pilot plants. Water Res. 2016, 91, 137–146.

(7) Clark, C. A.; Heck, K. N.; Powell, C. D.; Wong, M. S. Highly Defective UiO-66 Materials for the Adsorptive Removal of Perfluorooctanesulfonate. ACS Sustainable Chem. Eng. 2019, 7, 6619–6628.

(8) Bentel, M. J.; Yu, Y.; Xu, L.; Kwon, H.; Li, Z.; Wong, B. M.; Men, Y.; Liu, J. Degradation of Perfluoroalkyl Ether Carboxylic Acids with Hydrated Electrons: Structure–Reactivity Relationships and Environmental Implications. Environ. Sci. Technol. 2020, 54, 2489.