PFAS pollution in our water: the quest for novel treatment techniques

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Abstract

The industry widely uses perfluorinated alkylated substances (PFASs) for industrial and commercial applications. However, pollution and unregulated disposals have led to a widespread presence of these persistent and harmful contaminants in our environment. The European and U.S. governments are mandating the removal of these compounds from surface and waste waters, but the current treatment techniques to lower the concentrations of PFASs for large water bodies are expensive and inefficient. Within this research, we propose a hydrophobic, all-silica zeolite Beta material that is a highly selective and high-capacity adsorbent for PFASs, even in the presence of organic competitors. Advanced characterization data demonstrate a very negative adsorption enthalpy and favourable steric factors drives the absorption process.

Problem Statement

Perfluorinated alkylated substances (PFASs) are a class of persistent organic pollutants which, in recent years, have been gaining much attention. Extensively used over the past 40 years, they are only now fully recognized as top priority pollutants, due to their widespread occurrence in (drinking) water, food products, animals and even humans.[1] Exposure to PFASs is associated with a series of health risks, including liver and kidney cancer, and affects fetus and child growth.[2] Increased awareness of the dangers of PFASs has led to governmental regulation worldwide, ranging from restrictions on production and consumption to the implementation of threshold concentrations for PFASs in tap, surface and waste water. Most of the new regulation focuses on perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS), the two most used and spilt PFASs. The restrictions on PFOA and PFOS have pushed industrial players to use other fluorinated surfactants as drop-in replacements.[3] Most of these fluorinated alternatives are not (yet) restricted, meaning that levels of persistent and bioaccumulative fluorinated chemicals continue to build up in natural waters. Furthermore, historical emissions of PFOA and PFOS still cause locally elevated concentrations. In this light, the recent introduction of environmental quality standards imposes the urgent need for a clean-up strategy and new removal technologies.

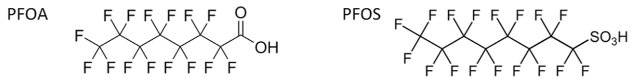

Fig. 1 – Chemical structure of perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS)

Background

PFASs contain a wide variety of molecules, varying in length, structure and functionalities, but they are all defined by having a completely fluorinated (stretch of) carbon chain. Compared to other (synthetic) organic compounds, PFASs have many unique and remarkable properties. Most of these are due to the particular character of the carbon-fluorine bond, one of the strongest bonds in organic chemistry. Perfluorinated carbon chains are extremely hydrophobic; they strongly repel every droplet of water. Very remarkably, though, they are also oleophobic. Whereas most molecules are either hydrophobic or oleophobic (repelling either fat-like or aqueous components), PFAS chains repel both hydrophobic and hydrophilic compounds. A very well-known example of this is the anti-sticking pan, coated with the linear perfluorinated polymer polytetrafluoroethylene, better known as PTFE or Teflon®. Animal fats, vegetable oils and watery solutions all do not stick to these pans. Additionally, PFASs are highly inert against high temperatures, electrical currents and other chemicals. They cannot be broken down by UV-light or microbiota, making them nearly indestructible. They have very low surface tensions, making them extremely suitable for a variety of applications, ranging from lubricants to firefighting foams.[4] All these features are very desirable for both household and industrial applications, but it is the combination of all these features in just one class of organic chemicals that is unique. This feature makes the fluorochemical industry a thriving and lucrative business that will not go away in the near or distant future.[5]

An important subgroup of PFASs are the surfactants in which the perfluorinated chain (or tail) is linked to a hydrophilic head, often a carboxylic or sulfonic acid group. These perfluorinated acids still have all the features mentioned above, but they are water-soluble due to their polar functionality. Compared to e.g. PTFE, their shorter chain length and water-solubility make them easier to apply as a coating or to dissolve in solutions or suspensions. Because of their surfactant character (i.e. their tendency to spread on interfaces and surfaces) and hydrophobicity, they are very well suited for specific cleaning applications or use in lubricants, stain- and water-repellent coatings for e.g. textiles, fat-repellent or food wraps.

Emissions of PFASs are mostly due to industrial production and usage: it appears that up to 60% of consumed PFASs for industrial use are emitted into the environment.[6] Contaminations can be direct from an industrial source or indirect (e.g. leaking percolate from a landfill). PFAS pollution is a global phenomenon since industrial sites that use or consume PFASs are spread all over the world.[7] On top of that, PFASs can be transported over long distances by either atmospheric transport of volatile precursors, or by the distribution of water-soluble PFASs via water streams and oceans. Traces of PFAS pollution have been found in both the Arctic and Antarctic, where no industrial emission sources are present.8 Nevertheless, PFAS concentrations are often the highest close to industrial production or consumption sites. PFOA and PFOS were only produced on a large scale at three production sites in the world: two in the US and one in Belgium (Port of Antwerp). It is no coincidence that some of the highest concentrations of PFASs ever reported (in both water streams and fauna) are found in Zwijndrecht and its surroundings.[9]

Up to 95% of the population in the Western world has traces of PFASs in their blood, with food products being the most important source of exposure.[10] Since most PFASs are water-soluble, every type of food that has a significant uptake of (ground)water can carry traces of PFAS compounds; e.g. grains, fruits, vegetables and potatoes. The increased awareness of PFAS spreading and the potential health risks thereof have evoked new legislation and regulations, both in the EU and the US. In 2013, the EU issued a directive on priority substances in the field of water policy, including restrictions on PFOA and PFOS in water streams. This European directive has been translated into Flemish legislation (VLAREM II), with newly imposed environmental quality standards (EQSs) for PFOS and its derivatives. No EQSs are in place yet for PFOA and its derivatives, but regulation and monitoring on PFASs are in full development, in Flanders but also in many other European regions and countries, so more restrictions on a variety of PFASs will be released soon. The imposed EQSs for PFOS and its derivatives are in place since 2018, yet the EU will strictly monitor them only from 2027.

Because conventional waste water treatment plants (WWTPs) are unable to remove PFASs from water, the implementation of EQSs in Belgium (as well as in many other countries) requires new and suitable techniques to remove PFASs in low concentrations from complex water matrices. More specifically, PFAS concentrations have to be reduced from a µg/L (or mg/L in the case of extreme contaminations) to less than 1 ng/L. Several techniques, like sonolysis and electrochemical or photochemical catalysis are currently explored for the degradation of PFASs in water, but they suffer from high energy demands and require several pre-treatment steps.[11] This makes them unsuitable for the treatment of large water volumes. In this regard, adsorption is arguably the best technique to treat large volumes while keeping energy costs modest. Even if a chemical degradation process would be considered as removal and treatment technique, adsorption would often be the go-to method as an essential preconcentration step. This factor makes the selection (and synthesis) of an adsorbent with adequate capacity and high selectivity for PFASs of utmost importance.

Solution

Since hydrophobicity has proven to be a favourable factor for PFAS adsorption, a hydrophobic all-silica zeolite was studied as PFAS adsorbent and compared to activated carbon, the current benchmark adsorbent for PFASs. Activated carbon has a relatively high adsorption capacity, and it is a widely applicable adsorbent for many types of (organic) compounds, but it, therefore, lacks selectivity. Based on various adsorption experiments (screening for capacity, affinity, selectivity and kinetics), all-silica zeolite Beta showed to be an outstanding adsorbent for PFAS adsorption. Zeolite Beta is a zeolite type with wide pores and straight channels, providing an open and accessible material. PFAS uptake was higher and quicker on this zeolite than on activated carbon. It was especially for PFAS selectivity that all-silica zeolite Beta shows genuinely outstanding results. PFAS uptake was undisturbed by competition of other organic compounds, even when these compounds were present in a 15-fold molar excess. In contrast, PFAS uptake on activated carbon was drastically reduced.

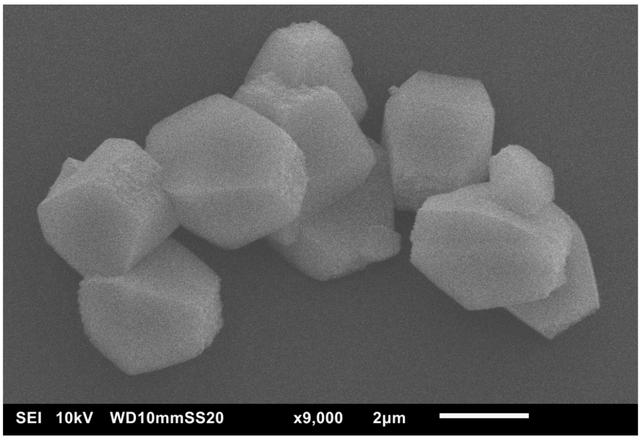

Fig. 2 – Microscopic SEM image of the crystals of all-silica zeolite Beta.

The question why all-silica zeolite Beta has such a high affinity and selectivity for PFASs was resolved by combining the results of advanced characterization techniques and computational modelling. Calorimetry measurements showed that PFOA adsorption on all-silica zeolite Beta is associated with a negative adsorption enthalpy, meaning that the adsorption reaction is very spontaneous and favourable. Computational simulations demonstrated that the adsorbed PFOA molecules interact in very stable head-head interactions, resulting from the formation of carboxylic acid dimers and driven by H-bonding. This result contributes significantly to the favourable adsorption process. These characterization experiments made it very clear that the adsorption of PFOA on all-silica zeolite Beta is very favourable in terms of enthalpy, while the perfluorinated chains are situated in the hydrophobic, straight channels of the zeolite. The helical conformation of the perfluorinated chains makes a very tight packing at maximal capacity sterically possible, explaining the exceptionally high affinity and selectivity of all-silica zeolite Beta for PFOA and similar perfluorinated compounds.

Before an industrial application is possible, four main aspects need further research and development; i) extending the scope of PFASs than can be removed, ii) regeneration of the adsorbent by PFAS degradation, iii) shaping of the adsorbent and optimization of the adsorption process and iv) upscaling of the all-silica zeolite Beta synthesis process.

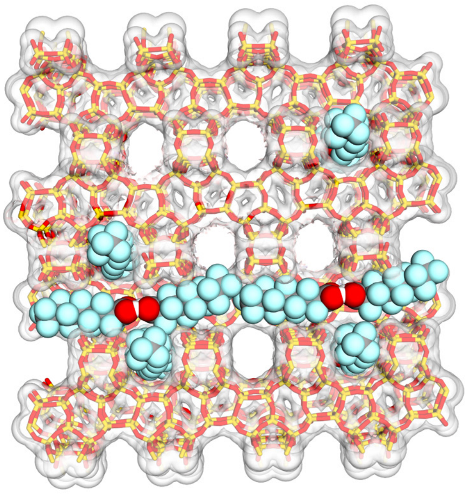

Fig. 3 – Graphical representation of all-silica zeolite Beta with adsorbed PFOA molecules.

Conclusion

Its outstanding adsorptive properties position all-silica zeolite Beta as the lead candidate for combating PFAS pollution via adsorption. Adsorbents with higher capacity exist, but they suffer from low selectivity and are hence ineffective in treating large volumes of surface or waste water with relatively low PFAS concentrations. In contrast, all-silica zeolite Beta is highly selective towards C8 PFASs against a complex background of dissolved organic matter. It has a strong potential to be effectively used for in situ treatment of waste and surface waters, and it can be the crux in a novel treatment for aqueous PFAS remediation. Such a novel technique is essential to comply with the recently introduced environmental quality standards.

References

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1. Clarke, B. O. & Smith, S. R. Review of 'emerging' organic contaminants in biosolids and assessment of international research priorities for the agricultural use of biosolids. *Environ. Int. 37*, 226–247 (2011).
2. Gomis, M. I., Vestergren, R., Borg, D. & Cousins, I. T. Comparing the toxic potency in vivo of long-chain perfluoroalkyl acids and fluorinated alternatives. *Environ. Int. 113*, 1–9 (2018).
3. Wang, Z., Cousins, I. T., Scheringer, M. & Hungerbühler, K. Fluorinated alternatives to long-chain perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkane sulfonic acids (PFSAs) and their potential precursors. *Environ. Int. 60*, 242–248 (2013).
4. Posner, S. Perfluorinated Compounds: Occurrence and Uses in Products. in *Polyfluorinated Chemicals and Transformation Products* (eds. Knepper, T. P. & Lange, F. T.) 25–39 (Springer, 2012). doi:10.1007/978-3-642-21872-9_2.
5. Lindstrom, A. B., Strynar, M. J. & Libelo, E. L. Polyfluorinated Compounds: Past, Present, and Future. *Environ. Sci. Technol. 45*, 7954–7961 (2011).
6. Prevedouros, K., Cousins, I. T., Buck, R. C. & Korzeniowski, S. H. Sources, Fate and Transport of Perfluorocarboxylates. *Environ. Sci. Technol. 40*, 32–44 (2006).
7. Rahman, M. F., Peldszus, S. & Anderson, W. B. Behaviour and fate of perfluoroalkyl and polyfluoroalkyl substances (PFASs) in drinking water treatment: A review. *Water Res. 50*, 318–340 (2014).
8. Ahrens, L. Polyfluoroalkyl compounds in the aquatic environment: a review of their occurrence and fate. *J. Env. Monit 13*, 20–31 (2011).
9. D'Hollander, W. et al. Occurrence of perfluorinated alkylated substances in cereals, salt, sweets and fruit items collected in four European countries. *Chemosphere 129*, 179–185 (2015).
10. Cornelis, C. et al. First assessment of population exposure to perfluorinated compounds in Flanders, Belgium. *Chemosphere 86*, 308–314 (2012).
11. Kucharzyk, K. H., Darlington, R., Benotti, M., Deeb, R. & Hawley, E. Novel treatment technologies for PFAS compounds: A critical review. *J. Environ. Manage 204*, 757–764 (2017).