

Understanding the Chemical Decomposition of Per- and Polyfluoroalkyl Substances (PFAS) in Water Using a Simple Metal/Oxidant System

Executive Summary

- This REU project is about **per- and polyfluoroalkyl substances (PFAS)**, so-called **forever chemicals** in water, which are the recent focus of US federal regulation due to their toxicity and persistence.
- The student team worked with the PI's graduate students to learn PFAS decomposition using a more practical and sustainable chemical treatment method requiring no energy input (i.e., a **simple treatment system of persulfate (oxidant) + metal**).
- Particularly, the focus was to **find the reactivity of various metals**.
- The team also had chances to attend a series of the PI's lectures on experimental techniques and to visit UTA centers (e.g., the Shimadzu Centers).

Background (PFAS)

Have you heard about PFAS or used PFAS-containing products?



Figure 1. Representative PFAS-containing products used in our daily life (too many to list).¹

- Due to their unique properties, PFAS (~15,000) have been widely used (non-stick coating, stain-resistant fabric, food packaging) (**Fig. 1**).
- PFAS are **not decomposed** naturally due to the extraordinarily strong C-F bonds in PFAS (so, known as **forever chemicals**) (**Fig. 2**).²
- Removing PFAS in water is a challenging but significant task (**national priority**).
- Biological treatment does not work.
- Physical separation works but it creates highly concentrated streams (i.e., no decomposition).

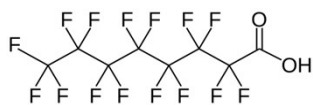


Figure 2. Structure of PFAS (as shown, PFOA). Due to complete substitution of C-H bonds with C-F bonds (the strongest bond), destruction of PFAS is challenging.

Problem Statement and Overall Goal

- Destructive technologies ensuring decomposition of PFAS are desired to avoid environmental liability issues.³
- However, most destructive treatment technologies inevitably require **energy-intensive extreme conditions** (e.g., microwave, UV, plasma, e-beam, heat).⁴
- As a result, **the overall goal of the research** is to develop more practical and sustainable chemical treatment technologies working under ambient reaction conditions to destroy PFAS in water, which is highly challenging.
- If successfully developed, such technologies will provide a stand-alone tool (**paradigm shift**) to decompose forever chemicals PFAS in water without introducing significant energy inputs and thus at lowered costs (**contribution**).

Overall Approach, Hypothesis, and Objectives

- The PI in his recent projects interestingly found the potential of sulfate radicals (SRs; $\text{SO}_4^{\cdot-}$) generated from a simple persulfate (**PS**; $\text{S}_2\text{O}_8^{2-}$; one of the commonly used oxidants) system activated by silver (**Ag**⁺; metal) to decompose PFAS under ambient conditions, including PFOA.⁵
- The observed decomposition of PFAS by the simple **PS/Ag⁺ system** at 20 °C (without external energy input) is **significant**.
- Hypothesis:** A chemical oxidant, PS would also be activated by various transition metals to generate different radical species.
- Objective:** The reactivity of other metals with PFAS should be examined to find **more efficient and affordable metals**.

Experimental Tasks

- Task 1. Conduct batch experiments with PS conjugated with various metals.**
 - Selecting potentially-working metals: **Ag, Cu, Au (Group 11), and Ce**.
 - Examining the 4 metals with PS in batch reactors to decompose PFOA.
 - Sampling at 8 and 48 hours.
- Task 2. Analyze PFAS samples to evaluate decomposition and defluorination.**
 - Applying the EPA Methods (533 and 537).
 - Pre-treating samples via solid phase extraction technique.
 - Running on liquid chromatography (LC)/mass spectrometry (MS).
 - Measuring fluoride ion concentration in water.

Outcomes and Results

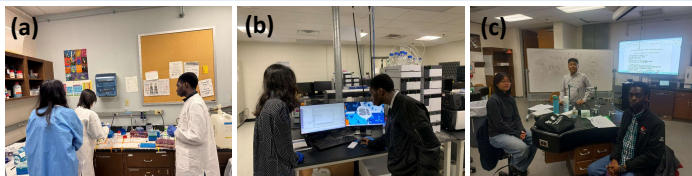


Figure 3. (a) Batch experiments for hands-on lab experience, (b) LC-MS/MS analysis of PFAS samples at the Shimadzu Center, and (c) lectures on experimental techniques and environmental instrumentation by the PI.

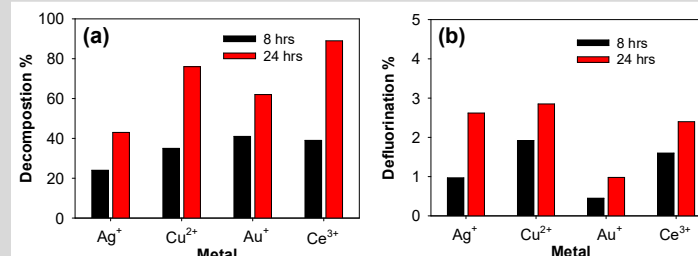


Figure 4. (a) Decomposition and (b) defluorination of PFOA by PS with various metals.

- PFOA decomposition (Ce>Cu>Au>Ag) and PFOA defluorination: (Cu>Ag>Ce>Au).
- Decomposition > defluorination (retarded defluorination).
- Cu: most affordable and Au: most expensive.

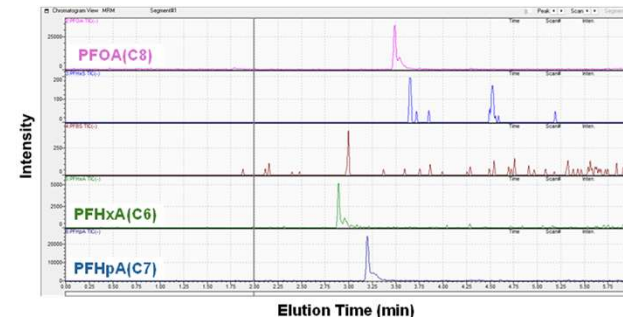


Figure 5. LC/MS chromatograms demonstrating formation of short-chain PFAS subspecies (e.g., PFHpA and PFHxA) during the decomposition of PFOA.

Conclusions and Recommendations

- The simple metal/oxidant system was proven to work for PFAS decomposition under ambient conditions (without external energy inputs).
- The various metals also worked, implying that cheaper, more efficient, and less toxic metals would be present.
- More metals and broader PFAS should be examined in future.
- This project provided the team with a unique opportunity to experience hands-on lab skills, modern instrumentation, collaborative work, and environmental stewardship.

References

- Depart. Ecology; Washington State (<https://ecology.wa.gov/Waste-Toxics/Reducing-toxic-chemicals/Addressing-priority-toxic-chemicals/PFAS>).
- American Chemical Society, "Forever Chemicals No More?", *Chemical and Engineering News*, 2019, Vol 97 pp28.
- Merino, N., Qu, Y., Deeb, R.A., Hawley, E.L., Hoffmann, M. R., and Mahendra, S., "Degrading and Removal Methods for PFAS", *Environmental Engineering Science*, 2016, vol 33 pp615-649.
- Trojanowicz, M., Bojanowska-Czajka, A., Bartosiewicz, I., and Kulisa, K., "Advanced Oxidation/Reduction Processes Treatment for Aqueous Perfluorooctanoate (PFOA) and Perfluorooctanesulfonate (PFOS)-a Review", *Chemical Engineering Journal*, 2018, vol 336 pp 170-199.
- Parenty, A., Gevaerd de Souza, N., Nguyen, H., Jeon, J., and Choi, H., "Decomposition of Carboxylic PFAS by Persulfate Activated by Silver under Ambient Conditions", *Journal of Environmental Engineering*, 2020, vol 146, pp 06020003.