Preliminary Report (Last modified: 2/1/2021)

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Introduction

Polyfluoroalkyl and perfluoroalkyl substances (PFAS) are manufactured chemicals which degrade slowly in the environment. Humans are being exposed to PFAS, which is concerning because of the connection between PFAS exposure and immunocompromisation, altered metabolism, decreased fertility, and fetal growth.[1]

We will be focusing on perfluorooctane sulfonate (PFOS) and perfluorooctane carboxylate (PFOA), which are fully fluorinated carbon chains with a sulfonate head and a carboxylate head, respectively. We have chosen UVC-range photocatalytic degradation over boron nitride in order to destroy PFOA and PFOS due to the promising research being conducted at Rice University.[2]

Selected Destruction Technology: ***Novel UVC-range photocatalytic degradation over hexagonal BN***

Research into exact mechanism is ongoing but hypothesized to consist of an oxidative stepwise decarboxylation/defluorination reaction driven by photogenerated holes and other intermediate radical species.[2] Preliminary results indicate destruction of PFOA in solution to sub-detectable levels within 4 hours and ~52% defluorination rate within same period of time.[2] Deemed superior to conventional methods involving granular activated carbon (GAC) and incineration for multiple reasons:

- No need for separate removal step, as PFAS degrades directly in water[2]
- Less extreme reaction conditions (room temperature, ~3 pH vs. 1000+ ºC in incinerator)[2,3]
- More compact, cost-effective, and energy efficient reactor[2,3]

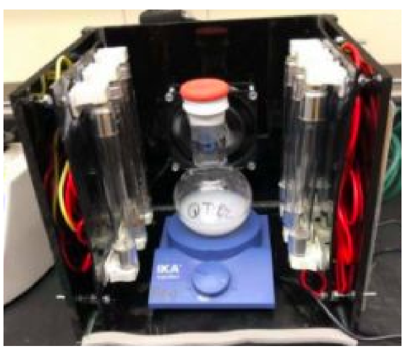

Figure 1. UV-BN photocatalytic reactor system set-up for a 15 mL solution.

Proposed Unit and Operating Parameters

UV-BN Photocatalytic Reactor System Set-Up:

- Custom-built, rectangular prism-shaped reactor (see Figure 1)
- Ambient lab conditions, sealed flask
- Six 4W 254-nm germicidal UV bulbs
- Magnetic stir plate with stir bar

Boron Nitride (BN) Preparations:

- 98% pure, analytical-grade, hexagonal BN powder
- Milled for 1 hour with 8 mm ZrO_2 balls in a milling jar.
- Ball milling causes BN defects, increases reaction efficiency[2]

PFOA Solution Preparations:

- 250 mL of deionized water with 10 ppm of PFOA (0.024 mM)
- Solution kept in sealed round bottom flask to simulate closed environment
- The initial pH of the solution is 6.5, decreases as reaction progresses[2]

Reaction:

- 250 mL of PFAS/DI water solution + 0.625 g of boron nitride catalyst run 13 hrs at max stirring
- 2.5 g/L concentration of BN has been proven effective in prior research[2]
- Reaction time calculated with half-life of 0.75 hours, assuming first-order kinetics[2]
- HPLC and ion chromatography will analyze the sample periodically
- Measures final PFOA concentration and released fluoride concentration, respectively.

Future Experiment Plans and Potential Changes:

- Larger batch size than 15 mL used in prior research,[2] more or stronger UV lamps, higher concentrations of BN, starting at lower pH, or different mixing mechanisms may be used.

Proposed Flow Diagram

Current process is represented by Figure 2, where a valve is used to control the flow into and out of the batch reactor, which represents our PFAS destruction technology (see Fig. 1 for technology set-up).

- Given previous calculations and assuming first-order reaction, 13 hours to achieve a PFAS concentration of < 70 ppt
- 5 gallon batch reactor
- 13 hours to achieve 5 gpd output
- Plan on testing methods of speeding up process and different configurations (i.e. batch in series, continuous flow)

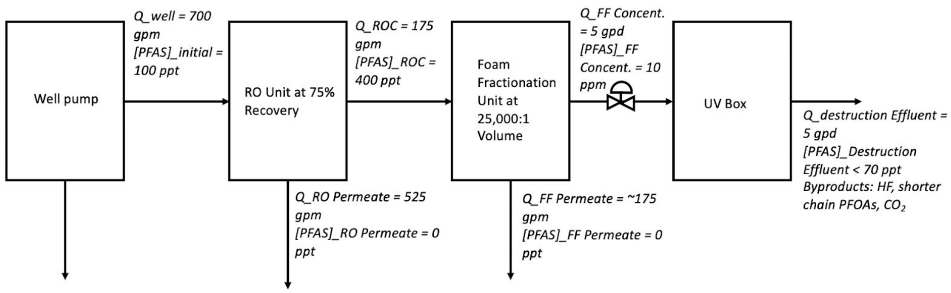

Figure 2. Process flow diagram for the current batch reactor process.

Proposed Power Requirements

The electrical energy per order (EE/O), or the electrical energy required to degrade a pollutant by 90% in 1 m^3 of water,[4] has been calculated for the 15 mL process in Duan et al.[2]:

- For EE/O_{CA}, or the electrical energy per order as acquired by chemical actinometry, the power value is 0.306 W. PFOA degrades 90% by 180 min, giving a final EE/O_{CA} of 45.9 kWh/m^3.
- For EE/$O_{UV\ Box}$, or the electrical energy per order associated with the output from the power source, the power is 41 W. With a degradation time of 180 min, EE/$O_{UV\ Box}$ is 6150 kWh/m^3.

For our 250 mL bench scale process, we will continue testing to determine the time needed for 90% PFOA degradation under the new parameters.

References

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2. Duan, L.; Wang, B.; Heck, K.; Guo, S.; Clark, C. A.; Arredondo, J.; Wang, M.; Senftle, T. P.; Westerhoff, P.; Wen, X.; Song, Y.; Wong, M. S. Efficient Photocatalytic PFOA Degradation over Boron Nitride. *Environ. Sci. Technol. Lett.* **2020**, *7* (8), 613–619. https://doi.org/10.1021/acs.estlett.0c00434.
3. Taylor, P. H.; Yamada, T.; Striebich, R. C.; Graham, J. L.; Giraud, R. J. Investigation of Waste Incineration of Fluorotelomer-Based Polymers as a Potential Source of PFOA in the Environment. *Chemosphere* **2014**, *110*, 17–22. https://doi.org/10.1016/j.chemosphere.2014.02.037.
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