QUARTERLY PROGRESS REPORT

[August 01, 2021 – October 31, 2021]

PROJECT TITLE: Non-Thermal Plasma Degradation of Per- and Polyfluoroalkyl Substances (PFASs) from Landfill Leachate

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PROJECT WEBSITE: https://web1.eng.famu.fsu.edu/~ytang/PFAS in leachate.html

Work Accomplished during this Reporting Period:

The project has four tasks. We have completed $\sim 80\%$ of Task 1, $\sim 95\%$ of Task 2, $\sim 30\%$ of Task 3, and $\sim 100\%$ of Task 4. The work that we completed in this reporting period is described below:

<u>Task 1: evaluate the removal of five representative PFAS in addition to PFOA at leachate-</u> <u>relevant PFAS concentrations (µg/L) by the gas-liquid flowing film plasma reactor</u>

We treated two real-world landfill leachates sampled from two different municipal landfills in Florida. The reactor operation conditions were the same as that for Task 1 in the previous reporting period. We are measuring the PFAS concentrations. Results will be reported in the final report.

We also treated deionized water containing one of the following six representative PFAS at ~50 ppm, including Perfluorohexanesulfonic acid (PFHxS, C6), Perfluoroheptanoic acid (PFHpA, C7), Perfluorooctanoic acid (PFOA, C8), and Perfluorononanoic acid (PFNA, C9), GenX, and Fomblin. The results are shown in Figure 1. Fomblin was the only PFAS that did not show mineralization to fluoride. It is a polymer.

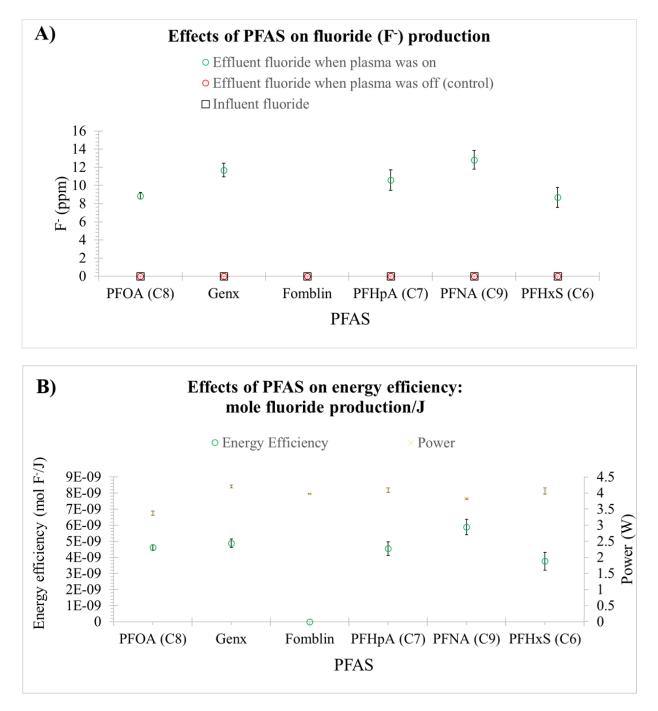


Figure 1. A) fluoride production and B) energy efficiency in plasma treatment of deionized water containing one of six PFAS at ~50 ppm.

Task 2: evaluate the effects of leachate components (e.g., inorganic substances, complex organic substances, simple organic substances, pH, and surfactants) on the removal of one representative PFAS: PFOA.

In the first and second quarters, we determined the effects of salinity, acetate and surfactants on fluoride production when water containing PFOA was treated by the plasma reactor. In this reporting period, we evaluated the effects of pH and humic acids as complex organic substance on fluoride production and energy efficiency. In these experiments, the flow rate was 2 mL/minute, and the power supply settings were 16 kV (input voltage), 40 ns (pulse width), and 5 kHz. We used a high PFOA concentration of ~50 ppm so that we could measure the fluoride production in the reactor effluent.

As shown in Figure 2A, higher concentrations of humic acids slightly decreased fluoride production. Similarly, the energy efficiency decreased with the increase of humic acids concentration (Figure 2B)).

The effect of pH is shown in Figure 3. We changed pH from 4 to 10 to evaluate the influence of pH on the fluoride production and energy efficiency. The following pH buffers were used to make the pH stable: acetate/acetic acid buffer for pH 4, borate for pH 10, and Na₂HPO₄/ NaH₂PO₄ for pH 6, 7, and 8. As shown in Figure 3A, the highest fluoride production corresponded to pH 7. The fluoride production decreased in lower and higher pH.

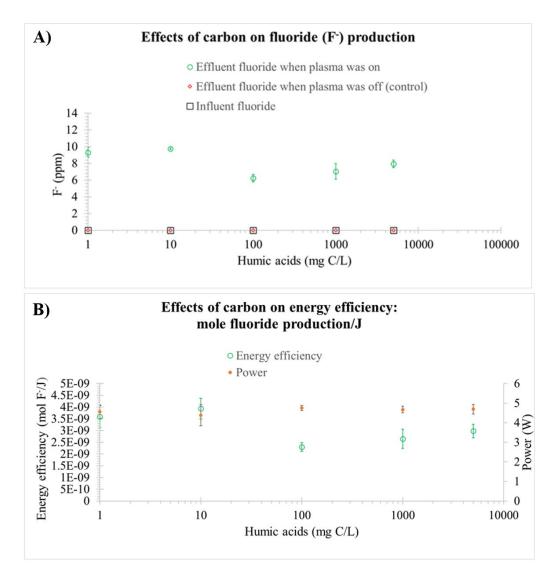


Figure 2. The effects of complex organic substance, represented by humic acids, on A) fluoride production and B) energy efficiency. Note: The 1 on the x-axis is actually 0 ppm of carbon. 0 ppm cannot be plotted in the logarithmic X axis.

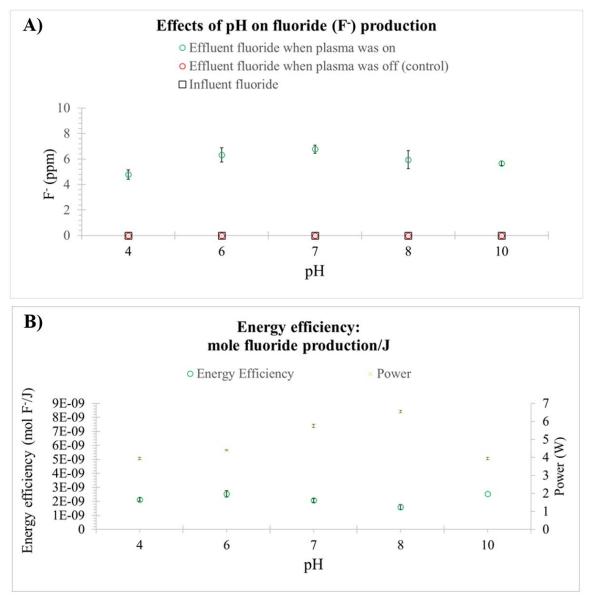


Figure 3. The effects of pH on A) fluoride production and B) energy efficiency

Task 3: determine the degradation intermediates found in the liquid and gas phases from <u>PFOA</u>

The degradation of PFASs leads to the generation of liquid and gas-phases byproducts. The concentration of gas-phase byproducts like cyclic perfluoroalkanes was low and below the detection limit of the chromatography-mass spectrometry (GC-MS). We are using a Model 7100 pre-concentrator (Entech Instrument Inc., USA) to lower the detection limit of the PFAS degradation products in the gas phase.

Task 4: determine the toxicity of the degradation intermediates of PFOA by an EPA recommended method

We conducted two sets of experiments with Microtox bioassay to assess the acute toxicity. In the first set, we assessed the toxicity of deionized water containing one of the six representative PFAS summarized in Table 1 at ~500 ppm. None of them showed acute toxicity.

Name	Abbreviation	Concentration (mg/L)
Perfluorooctanoic acid	PFOA	500
Perfluorooctanesulfonic acid	PFOS	500
PerfPerfluorononanoic acid	PFNA	500
Undecafluoro-2-mthyl-3-	GenX	500
oxahexanoic acid		
Perfluoroheptanoic acid	PFHpA	500
Perfluorooctanesulfonamide	PFOSA	100 (due to solubility
		limitation, 100 was used
		for this test)

Table 1. Six representative PFASs used in the acute toxicity assessment experiments

In the second set, we compared the influent (untreated samples), the effluent measured immediately after plasma treatment, and the effluent many days after the plasma treatment to remove the highly reactive species such as hydrogen peroxide due to plasma. As shown in Figure 4, our results showed that the toxicity of the samples increased immediately after the plasma treatment due to the highly reactive species, and eventually decreased.

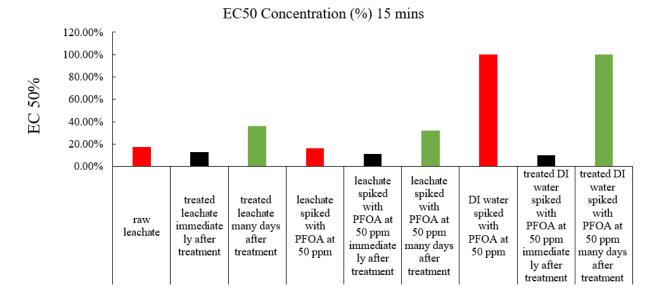


Figure 4. The acute toxicity of the influent, the effluent measured immediately after treatment, and the effluent many days after treatment. Note: EC50 = the effective concentration of a toxic sample causing light to be reduced by 50%; a higher EC50 means lower toxicity.

Metrics:

- 1. List research publications resulting from THIS Hinkley Center project. *None in this reporting period.*
- 2. List research presentations resulting from (or about) THIS Hinkley Center project. *None in this reporting period.*
- 3. List who has referenced or cited your publications from this project. *None in this reporting period.*

4. How have the research results from THIS Hinkley Center project been leveraged to secure additional research funding? What additional sources of funding are you seeking or have you sought?

None in this reporting period.

5. What new collaborations were initiated based on THIS Hinkley Center project? *None in this reporting period.*

6. How have the results from THIS Hinkley Center funded project been used (not will be used) by the FDEP or other stakeholders?

None in this reporting period.

Pictures:



The pre-concentrator and gas chromatography - mass spectrometry (GC - MS) system in the lab for gas-phase PFAS identification and quantification