QUARTERLY PROGRESS REPORT

November 1, 2020 to January 31, 2021

PROJECT TITLE: Break the Loop of PFAS Cycling in Landfills: Aqueous PFAS Destruction or Solid Thermal Incineration?

PRINCIPAL INVESTIGATOR(S): Gang Chen

AFFILIATION: Department of Civil and Environmental Engineering, FAMU-FSU College of Engineering

COMPLETION DATE: November 1, 2020 to January 31, 2021

PROJECT WEBSITE ADDRESS (URL):
http://eng-web1.eng.famu.fsu.edu/~gchen/index_files/Page7296.htm

EMAIL ADDRESS:
gchen@eng.famu.fsu.edu

PHONE NUMBER: 850-4106303

Project Summary

Per- and polyfluoroalkyl substances (PFAS) in the landfill leachate are presently of great health concern. Because of the effectiveness and easiness of operation, adsorption is the most commonly used method in removing these contaminants from the landfill leachate. However, after the adsorption, the saturated adsorbent with adsorbed PFAS is typically deposited back to the landfill, recycling PFAS back to the landfill. This research is designed to break the loop of PFAS cycling in landfills by investigating PFAS destruction in either the aqueous phase or the solid phase. In the aqueous phase, sonochemical degradation is to be explored. In the solid phase, adsorption of PFAS on engineered biochar and the subsequent incineration is to be examined.

Work Accomplished during This Reporting Period

1. Engineered Biochar Synthesis

Biochar was synthesized using the sludge collected form Thomas P. Smith Water Reclamation Facility (TPS) located in Tallahassee, Florida. The sludge was the granular pellet that was produced by the thermo-treatment of the sludge cake. $FeCl_3 \cdot 6H_2O$ was mixed with the feedstock for 12 h before pyrolysis. The feedstock was centered into the quartz tube and heated in the controllable S-line single-zone split tube furnace (Thermcraft Inc., Wiston-Salem, NC) at a temperature ramping rate of 10°C/min to the desired pyrolysis temperature of 400^{o}C for 60 min (Figure 1). The quartz tube was maintained absent of oxygen with continuous N_2 gas purge at a flow rate of 80 mL/min throughout the heating and cooling processes to prevent rapid oxidation and auto-ignition.

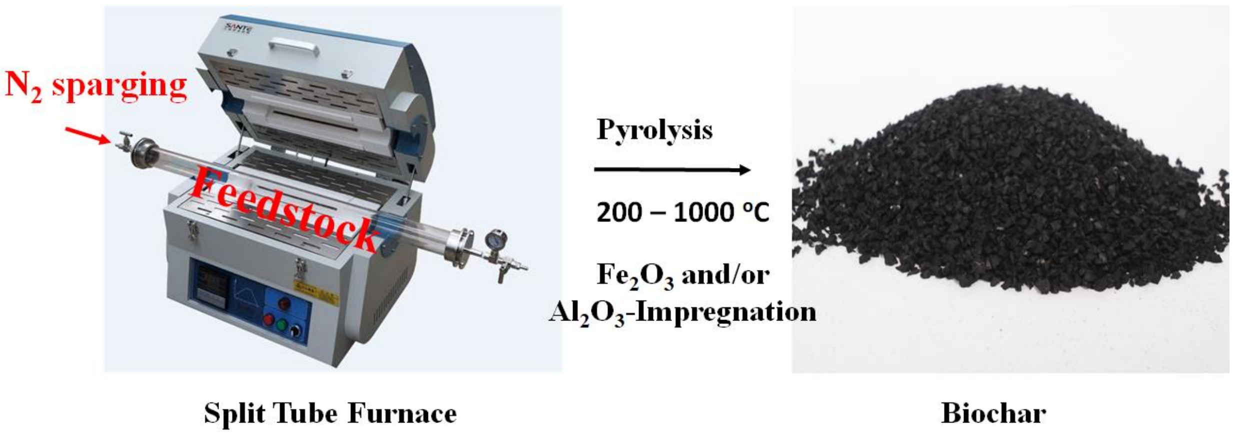

Figure 1. Biochar Synthesis Experimental Setup

2. Adsorption of PFOA and PFOS on Engineered Biochar

The produced biochar was rinsed and washed in 90°C-deionized water for 2 h to remove the impurities. Finally, the biochar was dried in an oven at 105°C for 48 h. Batch experiment was carried out at 180 rpm in an orbital shaker with 10 mL polypropylene copolymer (PPCO) Nalgene narrow-mouth bottles (due to its good resistance to perfluoroalkyl acids) containing 10 mL of PFOS or PFOA solution and 0.01 g engineered biochar at pH 5.0. After equilibrium was reached, the biochar was further characterized using Fourier transform infrared (FTIR) spectroscopy. The analysis was carried out on a PerkinElmer 100 spectrometer (Waltham, MA) using the non-contact reflectance imaging method for structure analysis of the engineered biochar with adsorbed PFOA or PFOS. The finely ground samples were analyzed with no further treatment. The FTIR spectra were collected in the mid-infrared region from 4000 cm^{-1} to 650 cm^{-1} with a spectral resolution of 4 cm^{-1} and total number of 16 scans. The influence of CO_2 and H_2O in the beam path was removed by the software prior to data processing. The following broad-bands were within the detection range: 3400 cm^{-1} – 3410 cm^{-1}, H-bonded O-H stretching vibrations of hydroxyl groups from alcohols, phenols, and organic acids; 2580 cm^{-1} – 2950 cm^{-1}, C-H stretching of alkyl structures; 1620 cm^{-1} – 1650 cm^{-1}, aromatic and olefinic C=C vibrations, C=O in amide (I), ketone and quinone groups; 1580 cm^{-1} – 1590 cm^{-1}, COO- asymmetric stretching; 1460 cm^{-1}, C-H deformation of CH_3 groups; 1270 cm^{-1} – 1280 cm^{-1}, O-H stretching of phenolic compounds; and ~ 815 cm^{-1}, aromatic C-H. As shown in Figure 2, PFOA and PFOS were adsorbed to the engineered biochar.

3. Sonochemical Degradation of PFAS

Sonochemical degradation of PFAS occurs through the application of ultrasound to an aqueous medium. Ultrasonic periodicity extent of 20–1000 kHz or a million-sound wave velocity (> 0.5 MHz) is required to degrade PFAS in the process of acoustic chemical disposal. Before the experiments, we characterized the wavelength of PFOS where the great peaks appeared (Figure 3).

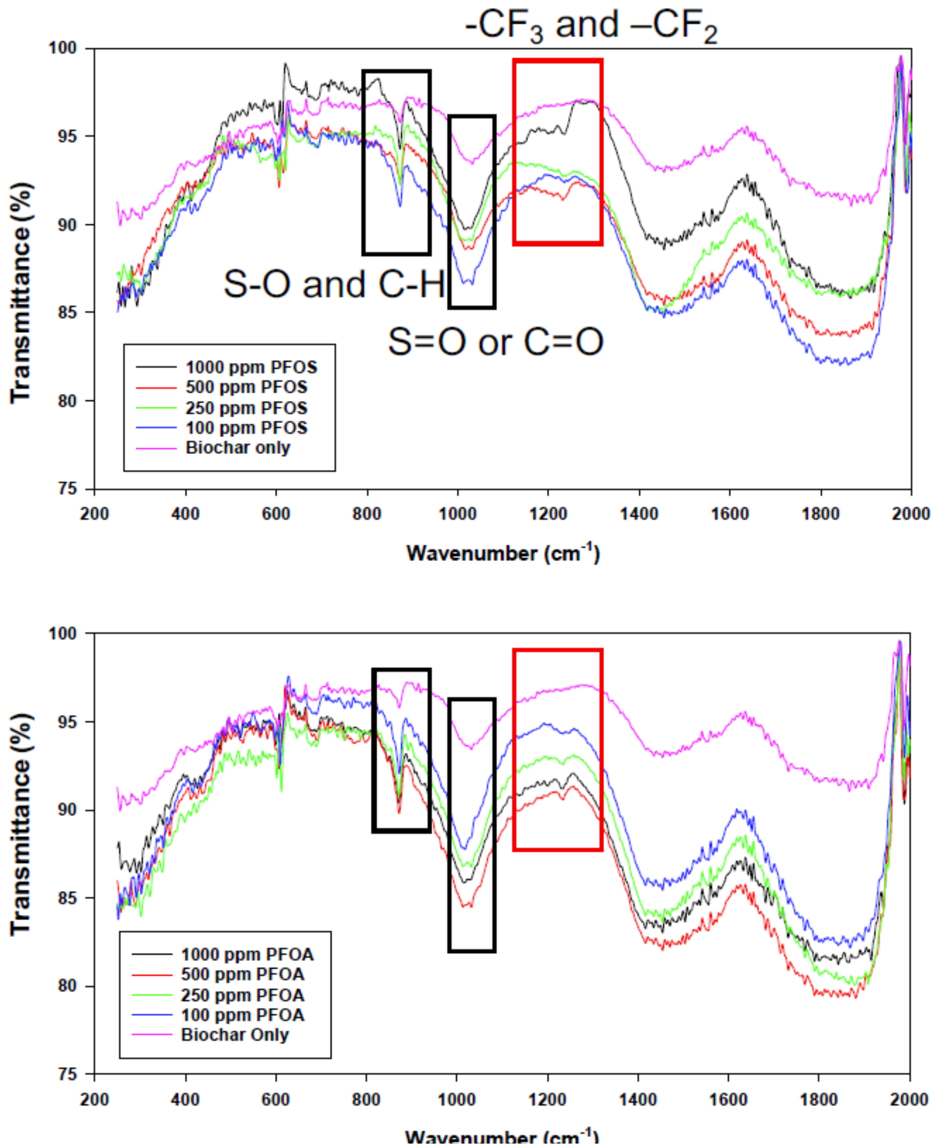

Figure 2. FTIR Analysis of PFOA and PFOS Adsorption on Engineered Biochar

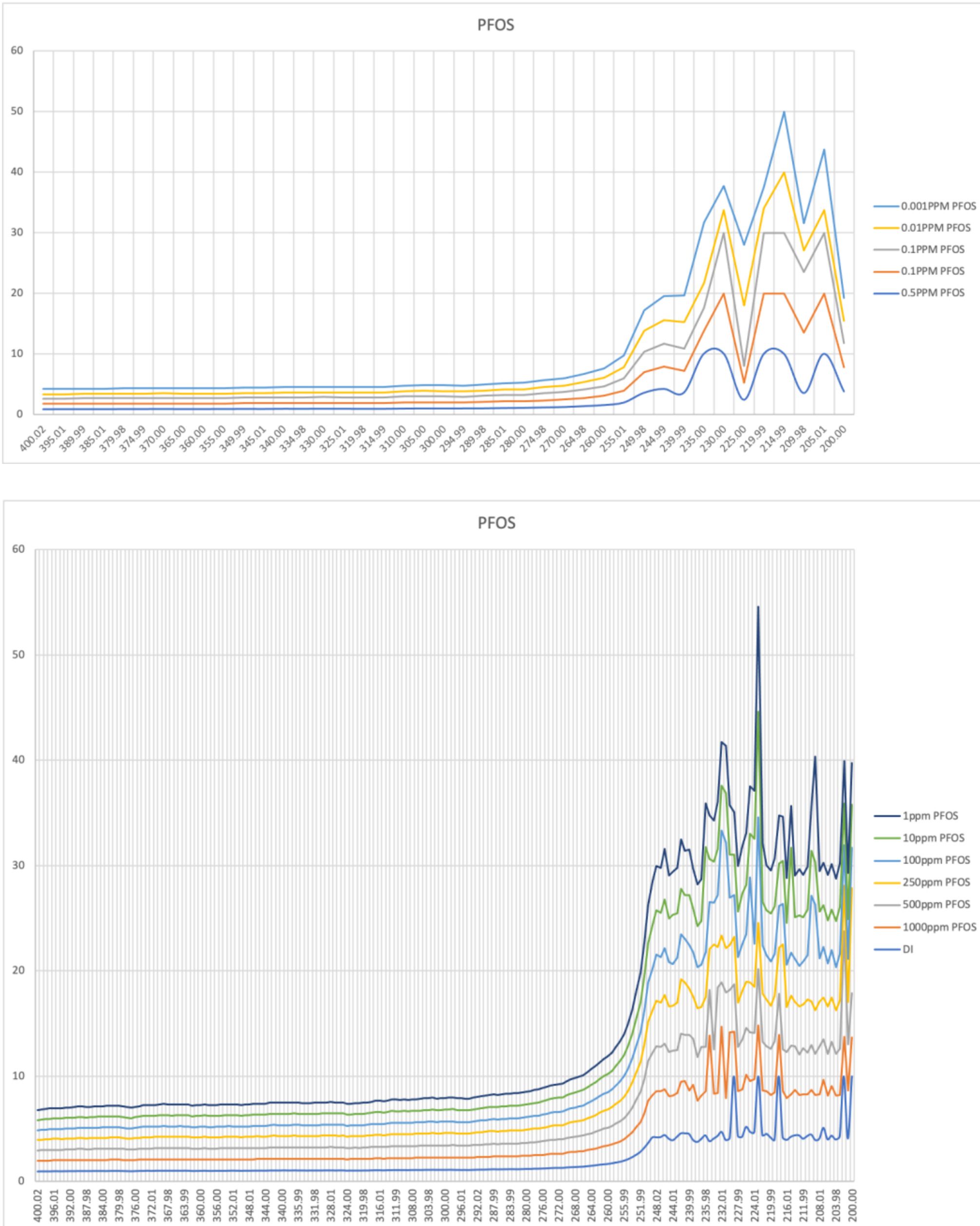

Figure 3. Wavelength of PFOS Adsorption

Work of Next Steps

1. PFOA and PFOS Adsorption Isotherm on Engineered Biochar

Batch experiment will be carried out at 180 rpm in an orbital shaker with 10 mL polypropylene copolymer (PPCO) Nalgene narrow-mouth bottles (due to its good resistance to perfluoroalkyl acids) containing 10 mL of PFOS or PFOA solution and 0.01 g engineered biochar and un-engineering biochar (as controls) at 25°C. For the adsorption kinetics, the initial solution pH will be maintained at 5.0, and the initial concentrations of PFOS and PFOA will be 5,000 ng/L. A series of bottles with identical initial conditions will be used. At different time intervals, one bottle will be taken out and the mixture will be centrifuged at 4,500 × g for 15 mins, after which the supernatant will be filtered by a 0.22 µm nylon membrane and PFOS/PFOA concentrations in the supernatant will be measured using LC/MS/MS. The thus determined time required to reach equilibrium will be used for the adsorption isotherm determination.

The adsorption isotherm experiments will be conducted in the solution at pH 5.0. A series of bottles with PFOS or PFOA at concentrations ranging from 0 – 5,000 ng/L containing 0.01 g engineered biochar and un-engineering biochar (as controls) will be shaken in the orbital shaker. The other conditions will be the same as above experiments. At the equilibrium time as determined above, the bottles will be centrifuged and PFOS/PFOA concentrations in the supernatant will be determined as described before. Adsorption equilibrium amount q_e will be calculated by:

$$q_e = \frac{(C_0 - C_e)V}{m}$$

where C_e is the equilibrium concentration of the PFOS/PFOA in the solution. For the investigation of the pH effect, above experiments will be repeated at pH range of 2.0 – 10.0 with an increment of 1. PFOS and PFOA adsorption on biochar will be described by Langmuir isotherms:

$$S = \frac{q_{max} K C_e}{1 + K C_e}$$

where S is the adsorbed PFOS or PFOA on biochar surface, q_{max} is the maximum mass of PFOS or PFOA required to form a mono-layer coverage of the biochar surface, and K is the Langmuir adsorption constant, which increases with the increase of the binding energy of adsorption.

2. Sonochemical Degradation of PFAS

Sonochemical degradation of PFAS will be conducted in an aqueous electrolyte solution. Specifically, ultrasonication will be performed in a reactor at a frequency of 354 kHz using an ultrasonic transducer (Figure 4). The applied power density will be 250 W/L. The PFAS solution will be maintained at 10°C by water cooling and sparged with argon or nitrogen for 30 min prior to and during the course of the reaction. The initial concentrations of PFOS and PFOA will be spiked to 50 − 5,000 ng/L for PFOA and 10 − 4,500 ng/L for PFOS, the typical concentrations found in landfill leachate. The PFOA, PFOS and byproducts will be quantified by LC/MS/MS.

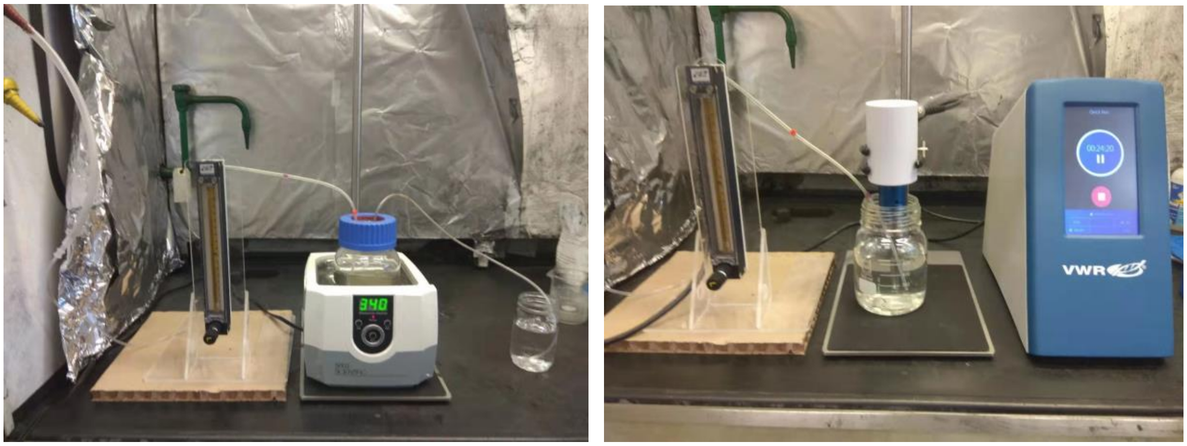

Figure 4. PFAS Sonochemical Degradation Experimental Setup

Information Dissemination Activities:

Metrics:

1. List graduate or postdoctoral researchers funded by this Hinkley Center project

Last name, first name	Rank	Department	Professor	Institution
Yudi Wu	Ph.D. Candidate	Civil and Environmental Engineering	Gang Chen	Florida State University
Lin Qi	Ph.D. Student	Civil and Environmental Engineering	Gang Chen	Florida State University

2. List undergraduate researchers working on this Hinkley Center project

Currently unavailable owing to the limited lab access to undergraduate students. One undergraduate student will be appointed once lab access limit is removed.

3. List research publications resulting from this Hinkley Center project

a. Yu, W., Qi, L. and Chen, G., 2021, PFOS and PFOA Adsorption to Engineered Biochar, Environmental Technology, in preparation.

4. List research presentations resulting from this Hinkley Center project

a. Yu, W., Qi, L. and Chen, G., 2021, PFOS and PFOA Adsorption to Engineered Biochar, Florida & Alabama Rural Water Associations Joint Conference.

b. Qi, L., Yu, W. and Chen, G., 2021, PFOS and PFOA Sonochemical Degradation, Florida & Alabama Rural Water Associations Joint Conference.

5. List who has referenced or cited your publications from this project?
Current research is in process. Our related published work on biochar has been cited from 45 times to 65 times:

a. Li, S. and Chen, G., 2018, Thermogravimetric, thermochemical, and infrared spectral characterization of feedstocks and biochar derived at different pyrolysis temperatures, Waste Management, 78, 198-207. Cited by 45

b. Li, S., Li, R., Barreto, V., Chen, G. and Hsieh, Y., 2018, Nitrogen retention of biochars derived from different feedstocks at variable pyrolysis temperatures, Journal of Analytical and Applied Pyrolysis, 133, 136-146. Cited by 62

c. Li, S., Harris, S., Anandhi, A. and Chen, G., 2019, Predicting biochar properties and functions based on feedstock and pyrolysis temperature: A review and data syntheses, Journal of Cleaner Production, 215, 890-902. Cited by 65

6. How have the research results from this Hinkley Center project been leveraged to secure additional research funding?
"Aqueous PFAS Destruction and Solid Thermal Incineration" has been submitted to the Environmental Engineering Program at National Science Foundation and is currently being reviewed.

7. What new collaborations were initiated based on this Hinkley Center project?
We have initiated collaboration with Florida Rural Water Association (FRWA), a nonprofit and non-regulatory professional association which was originally formed for the benefit of small water and wastewater systems throughout Florida. The primary purpose of this organization is to assist water and wastewater systems with every phase of the water and wastewater operations. This research is of the interest of the active members of this organization, who are associated with water and wastewater systems.

8. How have the results from this Hinkley Center funded project been used (not will be used) by the FDEP or other stakeholders? (1 paragraph maximum).
We keep close contact with managers of Leon County Landfill, Springhill Regional Landfill (Jackson County) and Perdido Landfill (Escambia County). In addition, we work closely with Thomas P. Smith Water Reclamation Facility located in Tallahassee, FL. We discuss the technical achievement of this project with the managers and request for suggestions to further our research. We also share the results with FDEP through TAG members. We also discuss the results with Florida Rural Water Association (FRWA), which services water and wastewater systems.

Tag Members: Sterling Carrol, Gary Williams, Chen Lin, Boya Wang and Simeng Li

TAG meetings: Information of this project is available through https://eng-web1.eng.famu.fsu.edu/~gchen/index_files/Page7296.htm. The first TAG meeting will be held on February 22, 2021 by Zoom Meeting. More information of the TAG meeting will be distributed in early February.