1st Quarterly Report
January - March 2021
AESF Research Project # #R-122

Electrochemical Approaches to Treatment of PFAS in Plating Wastewater

by
Prof. Qingguo (Jack) Huang*
College of Agricultural and Environmental Sciences
University of Georgia - Griffin Campus
Griffin, Georgia, USA

Editor's Note: *For 2021, NASF-AESF Foundation Research Board has selected a project on addressing the problem of PFAS and related chemicals in plating wastewater streams. This report covers the first quarter of work (January-March 2021).*

Introduction

This project was started in January 2021 with the goal of developing applicable electrochemical approaches to remove per- and polyfluoroalkyl substances (PFASs) present in plating wastewaters, including electrooxidation (EO) and electrocoagulation (EC). PFAS is a special group of contaminants that have drawn increasing public concern and regulatory scrutiny, as a result of their extreme environmental persistence and potential toxicity (Pistocchi and Loos, 2009; Guelfo and Adamson, 2018; Gomis, *et al.*, 2018; Conder, *et al.*, 2008). PFAS has been used for metal finishing and electroplating applications as mist suppressants and are thus often present in the plating wastewater at tens of μg/L levels (Bao, *et al.*, 2019; Du, *et al.*, 2016), orders of magnitude greater than the US Environmental Protection Agency's health advisory levels. Plating wastewaters contain high concentrations of ions and thus lend themselves particularly amenable to electrochemical treatment. EC generates metal hydroxide flocs that adsorb PFASs and separate them from water (Lin, *et al.*, 2015; Yang, *et al.*, 2016; Wang, *et al.*, 2016), while EO destroys PFASs in water by direct electron transfer and hydroxyl free radical attacks in concert (Lin, *et al.*, 2018; Soriano, *et al.*, 2019). They thus meet different treatment goals and are suitable for different situations. In particular, metal hydroxide flocs can be easily dissolved in controlled volumes of acid solutions, thus concentrating the PFAAs that can be subsequently destroyed by EO more efficiently. This EC-EO treatment train could be particularly useful for plating wastewater treatment.

This research includes three research tasks that are designed to investigate EC, EO and EC-EO treatment trains, respectively, with regard to PFAS removal in plating wastewaters. These tasks are designed to probe three hypotheses specified as follows:

1. EC generates amorphous metal hydroxide flocs that can effectively adsorb PFASs in plating wastewater, which, through an appropriate treatment, can release PFASs into a concentrated solution.
2. EO enabled by a Magnéli phase Ti_4O_7 anode can be used to effectively destroy PFASs in plating wastewater.
3. The electrochemical treatment train comprised of EC and EO by Ti_4O_7 anode can remove and degrade PFASs in plating wastewater more efficiently than either process operated individually.

This report describes part of the efforts contributing to the research planned in Task 1.

Experimental

The EC reactor was constructed with an acrylic cylindrical EC cell (8-cm diameter and 10-cm height). A zinc sheet (0.05 × 10 × 20 cm) was placed along the circumference of the cylindrical reactor to act as the sacrificial anode, while a 304 stainless steel rod of 3 mm diameter was placed in parallel to the axial center of the anode as the cathode (Fig. 1). In each treatment, 250 mL of solution contained either a total of ten PFASs, including perfluorononanoic acid (PFNA), perfluorooctanoic acid (PFOA), perfluoroheptanoic acid (PFHpA), perfluorohexanoic acid (PFHxA), perfluorooctanesulfonic acid (PFOS), perfluorohexanesulfonic acid (PFHxS), perfluorobutanesulfonic acid (PFBS), fluorotelomer sulfonic acid 8:2 (8:2 FtS), fluorotelomer sulfonic acid 6:2 (6:2 FtS), fluorotelomer sulfonic acid 4:2 (4:2 FtS), all at the same concentrations, or a single

PFAS, and 20-mM Na_2SO_4 as a background electrolyte. The solution initial pH was adjusted to 3.8 using H_2SO_4 and NaOH and agitated constantly throughout the experiment using an air pump through valves equipped on the bottom of the reactor. All EC experiments were conducted in batch mode with direct current applied using a direct current (DC) power source (Electro Industries Inc., Monticello, Minnesota). A zinc anode was used for this study because our earlier study indicated a much greater perfluorooctanoic acid (PFOA) removal efficiency than other common metal anodes (iron, aluminum and magnesium) (Lin, et al., 2015) and that the residual zinc concentration was at relatively low, safe levels, and could be readily removed by precipitation.
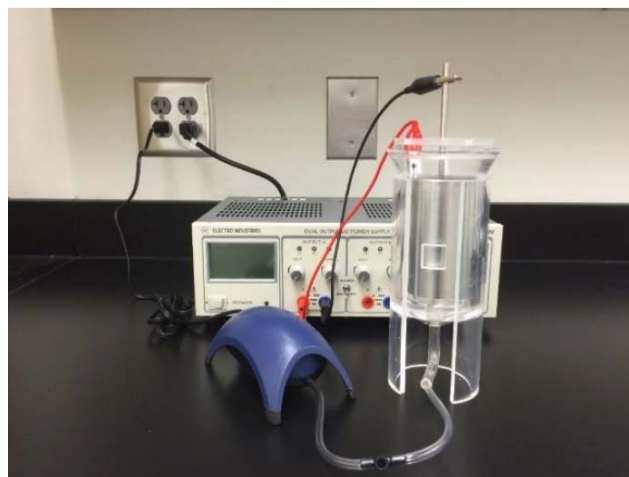

Figure 1 - Bench-scale EC reactor

The EC experiments were performed with the concentration of PFASs at different levels under different current densities. It was observed that a layer of foam was formed on the aqueous phase surface when the concentrations of PFASs were >0.1 µM and the current density was >1 mA/cm^2. For these conditions, the foam was collected by manually pipetting it out from the EC reactor throughout the treatment. For experiments examining the change of PFASs concentrations in the solution over time, triplicate 1-mL samples were withdrawn from the solution at pre-specified time intervals, and then centrifuged at 2000 RPM (268 × g) for 5 minutes (min) to separate the liquid and solid phases. For samples from experiments with the initial PFAS concentration >0.1 µM, 0.1 mL of the supernatant was taken and combined with 0.1 mL of the methanol-containing isotope labeled internal standards for subsequent PFASs analyses described below. For experiments with lower initial PFAS concentrations, the supernatant from centrifugation was concentrated using solid phase extraction (SPE) described below. For experiments examining the phase distribution of PFASs, triplicate aqueous samples were only taken at the end of the EC experiment. The remaining solution was then passed through a 0.22 µm acetate membrane (Sartorius, Germany), and the floc retained on the filter was transferred into a beaker and added 4.5M H_2SO_4 solution drop wise until floc dissolved, which was then brought up to 10 mL by Milli-Q water. Two milliliters of concentrated solution was withdrawn and adjusted to a final pH of approximately 6.0, and then processed using SPE described below. For the experiment with foam generation, the collected foam was mixed with 200-µL 4.5M H_2SO_4 solution, and then brought up to a total volume of 10 mL, from which 0.1 mL was taken and combined with 0.1-mL of mixed isotope labeled internal standard solution for subsequent PFASs analyses. The PFASs mass distribution in all phases after EC treatment was calculated using Equation 1:

$$Phase\ distribution\ =\ C_P V_P / C_O V_R \times 100\% \qquad\qquad (1)$$

where, C_P (mol/L) and V_P (L) are the PFAS concentration and the volume of different phases (aqueous, floc or foam), where the floc and foam phase volumes are those after acid dissolution (10 mL); C_O (mol/L) is the initial PFAS concentration, and V_R (L) is the reaction volume. The total PFASs mass recovery was the sum of the different phases' distribution.

The concentrations PFASs were quantified using a Waters AQCUITY I class ultra-performance liquid chromatography system coupled with a XEVO TQD triple quadrupole mass spectrometer (UPLC-MS/MS, Waters Corp., Milford, Massachusetts) in negative electrospray ionization mode (ESI-). The UPLC was equipped with an Acquity UPLC BEH C18 column (2.1 × 10 cm, 1.7 µm particle-size) operated at 40°C. A gradient composition of solvent A (5mM ammonium acetate in Milli-Q water) and solvent B (5mM ammonium acetate in methanol) was used as mobile phase at a 0.3 mL/min flow rate, with solvent A at 60% at time 0 decreasing to 20% at 4 min and then increasing to 60% at 5 min. The analysis was carried out in multiple reaction monitoring (MRM) mode, and quantification of PFAS concentration was achieved by the ratio between each PFAS and its isotope-labeled standard in reference to a five-point calibration curve. For samples subject to solid phase extraction (SPE) process, the sample was mixed with 40 µL of a mixed isotope labeled internal standard solution (100 ppb), and then subjected to SPE using HLB cartridges (Oasis HLB SPE cartridges, 3 cc, 60 mg, Waters, Milford, USA). Briefly, the cartridge was activated using 6 mL methanol and 6 mL Milli-Q water in sequence, followed by loading the sample at a flow rate of approximately 0.5 mL/min, and then rinsed with 10 mL Milli-Q water. The columns were blown dry under vacuum, and then eluted with 1.5 mL of methanol. The eluent was then blown dry and re-dissolved in 100 µL methanol for subsequent UPLC-MS/MS analysis.

Results and discussion

The EC performance was first evaluated at 5 mA/cm^2 for 60 min in a solution of 10 PFASs (each concentration at 0.5 µM) with 20mM Na_2SO_4 as a supporting electrolyte. The PFAS removal efficiency is shown in Fig. 2(A). After 60 min of EC treatment, the concentrations of all PFASs in the aqueous phase decreased but to varying degrees. The removal of PFOS, PFOA, PFNA and 8:2 FtS was greater than 99%, while that of PFHxS and 6:2 FtS was greater than 90%. The PFASs removal efficiency generally followed the chain length of the PFASs with better removal for the longer-chain PFASs. This difference of removal efficiency between long- and short-chain PFASs through the EC process was similar to what was observed in our previous study (Lin, *et al.*, 2015), because longer-chain PFASs have higher hydrophobicity and surface activity which was primarily responsible for the PFASs sorption (Kissa, 2001). It is also noted that the current efficiency (η) for zinc floc generation in this experiment was calculated to be 111.1%, a high value consistent with the previous report (Lin, *et al.*, 2015).
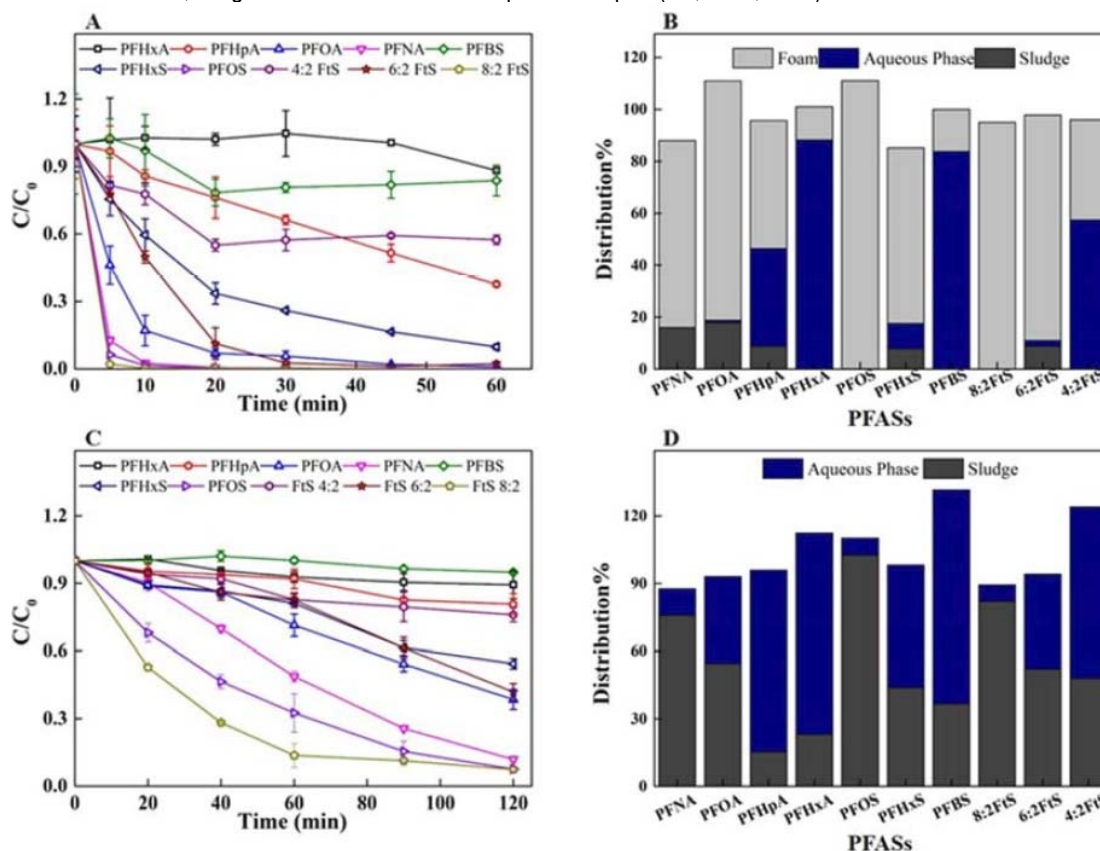

Figure 2 - (A) Removal of 10 PFASs (high concentration) over time during EC process by zinc anode; (B) the mass distribution of 10 PFASs in different phases after EC treatment (C_O = 0.5µM, current density = 5.0 mA/cm^2, 20mM Na_2SO_4, EC reaction time = 120 min); (C) Removal of PFASs (low concentration) from aqueous phase over time in EC process; (D) The distribution of 10 PFASs after EC treatment. (C_O = 0.005 µM, current density = 0.3 mA/cm^2, 20mM Na_2SO_4, EC reaction time = 120 min).

Here, it was found that EC-derived foam was generated when current density greater than 1 mA/cm^2 was applied and when the PFAS concentration was high (individual concentration greater than 0.1 µM) during electrocoagulation. The PFASs fractionation into foam would impact the distribution of PFASs in different phases. The generation of foam apparently resulted from the gases formed on the electrodes (H_2 on the cathode and O_2 on the anode) in combination with the surfactant properties of PFASs, and it is also related to the concentration of the PFASs. Thus, longer chain PFASs were rapidly removed at the beginning time, and then the removal slowed down since less foam was generated with the reduction of PFASs in solution.

PFASs distribution among different phases (floc, aqueous, and foam) after EC treatment was examined as shown in Fig. 2(B). It appeared that a considerable fraction of the removed PFASs were distributed into the foam. The contribution of zinc hydroxide adsorption was relatively minor probably because of (1) competition from foam fractionation and (2) the relative high concentration of PFASs had saturated the sorption sites on the zinc hydroxide flocs. The preferential distribution of PFASs into the foam phase could have speeded up and enhanced PFASs removal from the aqueous phase, and the foam could be readily and rapidly recovered for subsequent EO treatment. The foam generation was not observed in the low current density EC experiment with low PFASs concentration (*e.g.*, 0.005 µM each PFAS).

The EC treatment using a very low current density of 0.3 mA/cm^2 was performed on a spiked solution comprising a mixture of 10 PFASs (0.005 µM each) and 20mM Na_2SO_4 as a supporting electrolyte. This solution was treated using EC for 120 min. The experimental results indicate that PFASs were removed from the aqueous phase to varying degrees by the EC process (Fig. 2(C)). After 120 min of reaction time, the removal efficiency generally corresponded to the chain lengths of the PFASs, and the long-chain PFASs were removed more than the short-chain PFASs (Fig. 2(C)). Greater than 90% removal was achieved for PFOS and 8:2 FtS after a 120-min reaction time. PFASs removal efficiency was below 24% when the carbon chain length was C6 or shorter. The PFASs removal at low current density was generally less than EC at a higher current density. The foam formation was not observed under this condition. The PFASs mass distribution in aqueous and floc phases for all 10 PFASs is presented in Fig. 2(D). The mass recoveries of all PFASs ranged from 87.6% PFNA to 131.6% PFBS, suggesting that removed PFASs were transferred to flocs generated in the EC process.

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Past project reports

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About the author
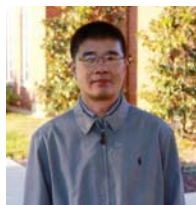
Qingguo (Jack) Huang is Professor in the Department of Crop and Soil Sciences, University of Georgia, Griffin Campus. He holds a B.S. in Environmental Science (1990) and a Ph.D. in Chemistry (1995) from Nanjing University, China as well as a Ph.D. in Environmental Engineering from the University of Michigan, Ann Arbor, Michigan. Dr. Huang's research interest focuses on catalysis involved in the environmental transformation of organic pollutants, and development of catalysis-based technology for pollution control and environmental remediation and management. His laboratory has been actively involved in several cutting-edge research topics:

- Enzyme-based technology for water/wastewater treatment and soil remediation
- Electrochemical and reactive electrochemical membrane processes in wastewater treatment
- Catalysis in biofuel production and agro-ecosystem management
- Environmental fate and destructive treatment methods of PFASs
- Environmental application and implication of nanomaterials

He has published over 150 peer-reviewed journal articles, five book chapters and four patents and three patents pending. He has taught three courses at the University Georgia: Introduction to Water Quality, Environmental Measurement, and Advanced Instrumental Analysis in Environmental Studies.