



NASF SURFACE TECHNOLOGY WHITE PAPERS
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AESF Research Project #R-122

Electrochemical Approaches to Treatment of PFAS in Plating Wastewater

by
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Editor's Note: *In 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 sixth quarter of work (April - June 2022).*

Introduction

This project 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). This project includes three research tasks that are designed to investigate EC, EO and EC-EO treatment train, respectively, designed to probe three hypotheses specified 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 destruct 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 our continuing effort on exploring EO enabled by a Magnéli phase Ti_4O_7 , with a focus on the perfluoroalkyl acids (PFAAs). Eight PFAAs, including perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorobutanesulfonic acid (PFBS), perfluorohexanesulfonic acid (PFHxS) and perfluorooctanesulfonic acid (PFOS), were investigated. Their degradation by EO with Ti_4O_7 anode was examined and compared across a range of anodic potentials, with reaction mechanisms explored.

Experimental

The procedure of the electrochemical oxidation experiments was described in our last report (5th quarterly report). The electrolytic cell (10 cm × 5 cm × 2.5 cm) contained 200 mL target solution, with one Ti_4O_7 plate (10 cm × 5 cm) placed in the middle as anode and two stainless steel plates of the same size on either side in parallel with a gap 2.5 cm as cathodes. A DC power supply unit (303 DM supplied by Electro Industries Inc) was used to supply electricity at constant current, and the solution was stirred by a magnetic stirrer at a constant speed throughout each experiment. The anodic potential was monitored using a CHI 660E electrochemical workstation (CH Instruments, Inc., Austin, TX) with Ag/AgCl reference electrode placed 0.5 cm from

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the anode, and all potentials are reported against standard hydrogen electrode (SHE) with internal resistance compensation. The reaction solution was prepared with each PFAA at the initial concentration of 2.0 μM , with 100 mM Na_2SO_4 as supporting electrolytes, unless otherwise specified. The electric current was applied after 30 minutes of solution stirring in the reactor. Aliquots of samples, 400 μL each, were collected at prescribed time intervals, and the samples were taken after pausing the current for 90 seconds while maintaining stirring to ensure solution homogeneity. Each sample was diluted 1:1 with 0.10 μM M8PFOA and M8PFOS in MeOH and filtered through a nylon-based syringe filter. Samples were processed through a UPLC-MS/MS system (Waters I-class UPLC; Water Xevo TQD triple quadrupole mass spectrometer) in negative electrospray ionization mode using multiple reaction monitoring (MRM). The UPLC was operated with methanol (A) and water (B) (5 mM ammonium acetate in each) as the mobile phases at a flow rate of 0.3 mL/min using a gradient program.

Results and Discussion

The degradation of PFAA was evaluated with all PFAAs spiked under different current densities, and the surface area normalized reaction rate constants k_{SA} values are plotted in Fig. 1 in relation to the chain lengths and the head functional groups. For each PFAA, the k_{SA} increased with increasing current density. For the PFAAs having the same functional group (PFSAs vs. PFCAs), the increase in carbon chain length led to greater reactivity. This is in accord with other studies showing shorter chain PFAAs more recalcitrant to electrooxidation.^{1,2} For the PFAAs of the same carbon chain length, the ones with sulfonate head group tend to degrade faster than those with carboxylic group. supporting electrolyte. The error bar represents the standard deviation. The data are shown in two figures according to magnitudes for better observation.

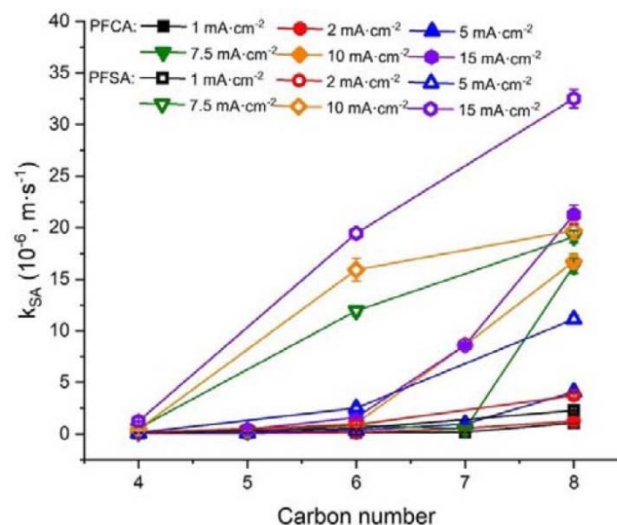


Figure 1 - The k_{SA} values of PFAAs of different carbon chain lengths and head functional groups, obtained in electrooxidation experiment with TSO anodes at different current densities. The test solutions contained all PFAAs with each at the initial solution of was 2.0 μM in 100-mM Na_2SO_4 as supporting electrolyte. Error bar represents standard deviation.

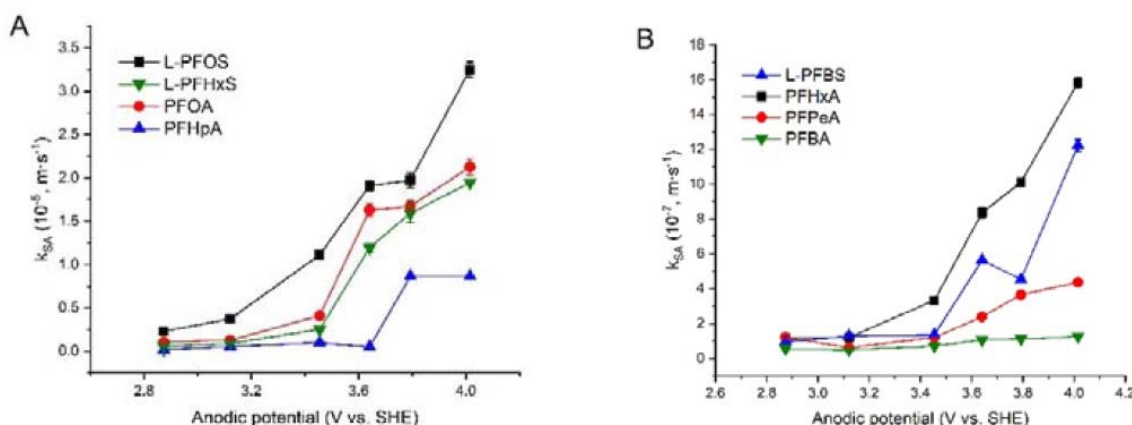


Figure 2 - The k_{SA} values of 8 PFAAs plotted against the anodic potential vs. SHE (standard hydrogen electrode) for electrooxidation. The test solutions contained all PFAAs with each at the initial solution of was 2.0 μM in 100-mM Na_2SO_4 as supporting electrolyte. The error bar represents the standard deviation. The data are shown in two figures according to magnitudes for better observation.

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Increased PFAA removal under higher current densities may be ascribed to the higher anodic potentials. The surface area normalized degradation rate constant for each PFAA obtained from the experiments are plotted against anodic potential in Fig. 2.

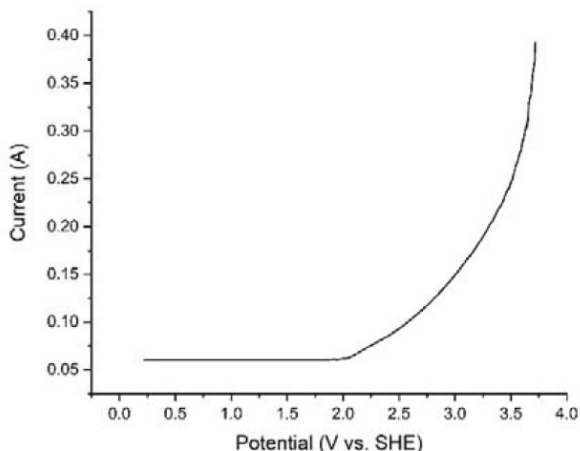


Figure 3 - Profiles of linear sweep voltammetry (LSV) at a scan rate of 50 mV/sec in 100-mM Na₂SO₄ solution with TSO anode.

behavior when the anodic potential was above about 2.83 V_{SHE} when water oxidation occurs, suggesting that the hydroxyl free radicals generated via water oxidation play a role in PFAA degradation. For the PFAAs having the same head acid group (PFSAs vs. PFCAs), the increase in carbon chain length led to greater reactivity. For the PFAAs of the same carbon chain length, the ones with sulfonate head group tend to degrade faster than those with carboxylic group.

It is again evident that the PFAAs with relatively longer carbon chains tend to have greater degradation rates across the tested anodic potential range than the shorter ones, as well as the PFSAs have higher rates than the PFCAs (Fig. 2). Regardless of the length of carbon chains, all PFAA degradation rates increased along with the anodic potential. The PFAAs started to exhibit degradation behavior when the anodic potential was above about 2.83 V_{SHE} (standard hydrogen electrode). This corresponds to the anodic potential where water oxidation started to occur according to linear sweep voltammetry (LSV) shown in Fig. 3, which corroborates that the hydroxyl free radicals generated via water oxidation play an essential role in PFAA degradation during electrooxidation on TSO anode.² It is noted that direct electron transfer (DET) and hydroxyl radical attack take place in a concerted manner that leads to PFAA degradation during electrochemical oxidation.³

To summarize, the PFAAs started to exhibit degradation

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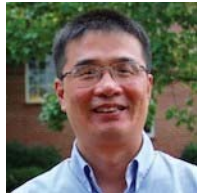
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Past project reports

1. Introduction to Project R-122: Summary: *NASF Report in Products Finishing, NASF Surface Technology White Papers*, 85 (6), 13 (March 2021); Full paper: <http://short.pfonline.com/NASF21Mar1>.
2. Quarter 1 (January-March 2021): Summary: *NASF Report in Products Finishing, NASF Surface Technology White Papers*, 85 (12), 13 (September 2021); Full paper: <http://short.pfonline.com/NASF21Sep1>.
3. Quarter 2 (April-June 2021): Summary: *NASF Report in Products Finishing, NASF Surface Technology White Papers*, 86 (3), 18 (December 2021); Full paper: <http://short.pfonline.com/NASF21Dec2>.
4. Quarter 3 (July-September 2021): Summary: *NASF Report in Products Finishing, NASF Surface Technology White Papers*, 86 (6), 16 (March 2022); Full paper: <http://short.pfonline.com/NASF22Mar2>.
5. Quarter 4 (October-December 2021): Summary: *NASF Report in Products Finishing, NASF Surface Technology White Papers*, 86 (9), 21 (June 2022); Full paper: <http://short.pfonline.com/NASF22Jun2>.
6. Quarter 5 (January-March 2022): Summary: *NASF Report in Products Finishing, NASF Surface Technology White Papers*, 86 (12), 22 (September 2022); Full paper: <http://short.pfonline.com/NASF22Sep2>.

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About the author



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- 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 160 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*.