Electrochemical Approaches to Treatment of PFAS in Plating Wastewater

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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 tenth quarter of work (July-September 2023). A printable PDF version of this report is available by clicking **HERE**.*

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.

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In our last report, we described the performance and effect of surface fluorinated Ti_4O_7 anodes on PFAS degradation in batch reactor operation mode. We discovered that surface fluorination of Ti_4O_7 anodes slightly inhibited PFAS degradation, while significantly suppressed the formation of chlorate and perchlorate formation during EO treatment of PFOA, PFOS and 6:2 FTS, three representative PFASs. In this report, we will discuss the effect of surface fluorinated Ti_4O_7 anodes on PFAS degradation in reactive electrochemical membrane (REM) operation mode.

Experiments

Experiments of EO treatment were performed in reactive electrochemical membrane (REM) operation mode. The porous Ti_4O_7 plate was used in REM reactor simultaneously as the anode and a membrane through which the feed solution was filtered in crossflow mode (Figure 1). Both the pristine and F-18.6 Ti_4O_7 anodes were tested for comparison, and two current densities, 10 mA·cm^{-2} and 40 mA·cm^{-2}, have been applied, corresponding respectively to 2.79 V and 4.05 V *vs* SHE anodic potentials. The feed solution contained PFOA, PFOS and 6:2 FTS (2.0 µM each), 100-mM Na_2SO_4, and 1-mM Cl$^-$.
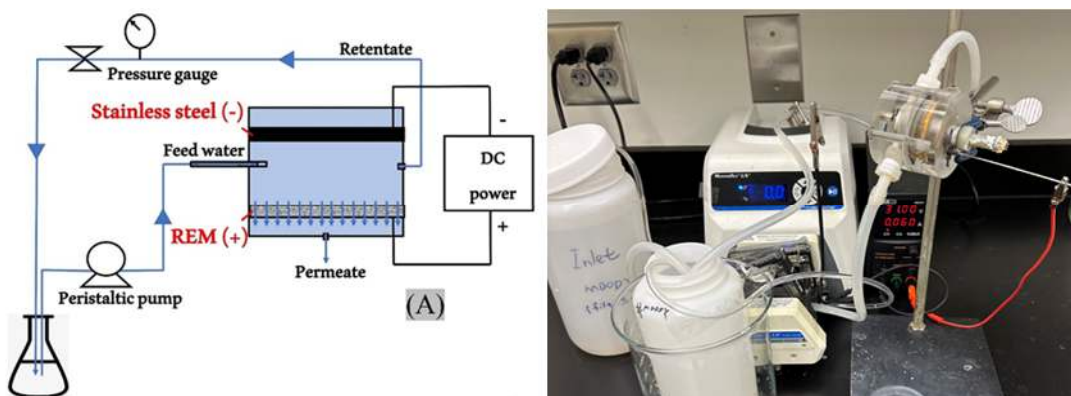

Figure 1. A schematic diagram of REM reactor with Ti_4O_7 anode in cross-flow filtration operation (A); a picture of actual operation system(B).

Results and discussion

The concentrations of PFOA, PFOS and 6:2 FTS in the permeate dropped immediately and maintained at low level when the electric current was applied (Figure 2). The PFAS removal was greater at the higher current density, while it was slightly lower on the F-18.6 anode than on the pristine one. At 40 mA·cm^{-2}, the removal of PFOA, PFOS and 6:2 FTS reached 70.5%, 88.3% and 58.9% on pristine Ti_4O_7 anode, and 68.6%, 86.7% and 56.3% on F-18.6 anode, respectively.
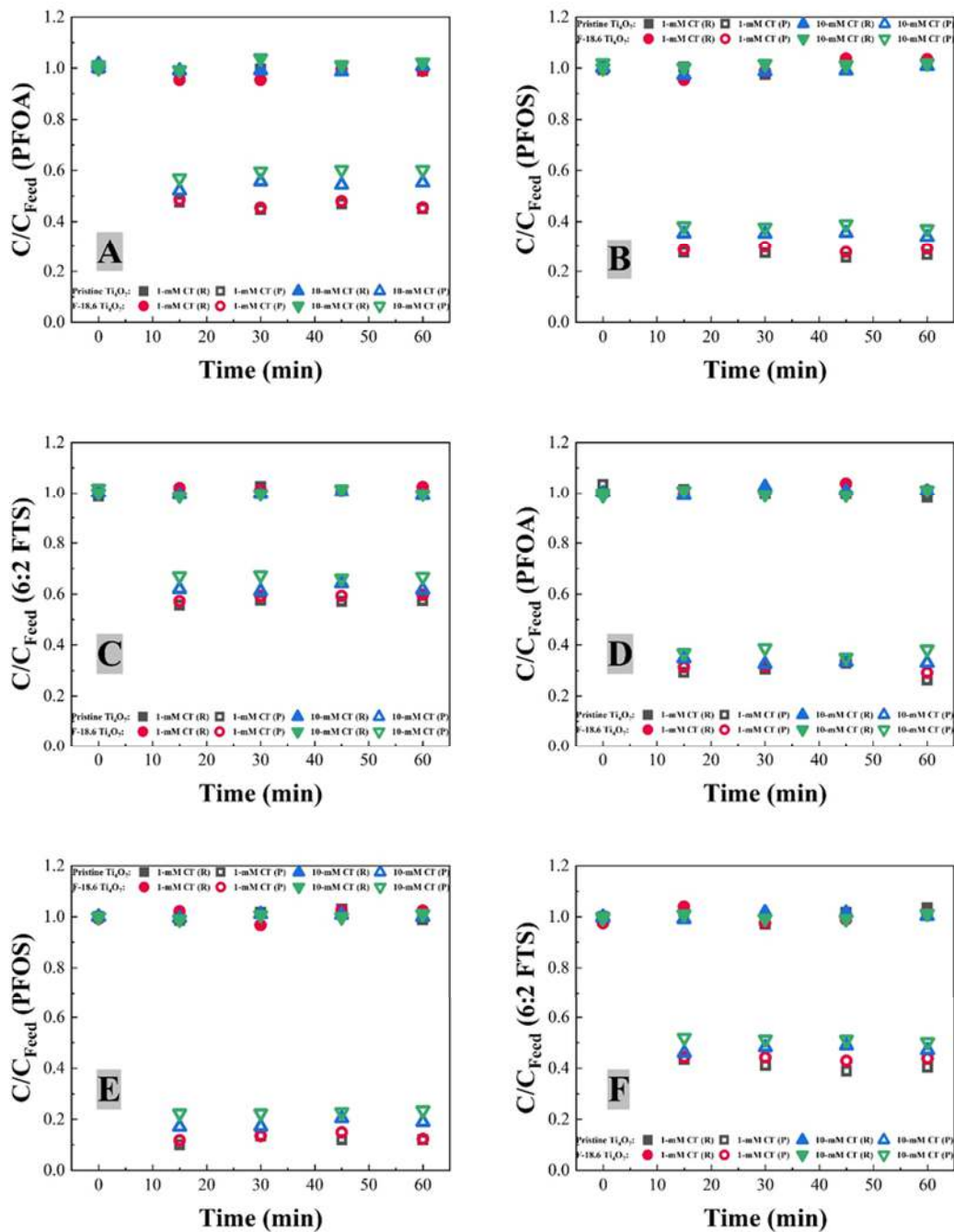
Figure 2. PFAS concentration in retentate and permeate flow during REM treatment on the pristine and F-18.6 Ti_4O_7 anode at 10 mA·cm^{-2}: PFOA (A), PFOS (B), 6:2 FTS (C) and at 40 mA·cm^{-2}: PFOA (D), PFOS (E), 6:2 FTS (F) with 1-mM or 10-mM Cl$^-$ in the feed solution. Initial PFAS concentration: 2.0 µM, supporting electrolyte: 100-mM Na_2SO_4

The concentrations of chlorate and perchlorate in the permeate flow during REM treatment was measured, and the results for the treatment at 10 mA·cm^{-2} with 1 mM Cl$^-$ in the feed solution are presented in Figure 3A and that with 10 mM Cl$^-$ in Figure 3B. Both chlorate and perchlorate were

detected when pristine anode was used. The concentrations of chlorate and perchlorate were 95.3 µM and 48.0 µM respectively with 10 mM Cl⁻ in the feed solution, 2.1-3.5 times greater than those with 1 mM Cl⁻. Interestingly, chlorate and perchlorate were below detection limits when F-18.6 anode was used at 10 mA·cm⁻² with either initial Cl⁻ concentration, indicating effective inhibition of chlorate and perchlorate formation in REM treatment at a practical current density. This is a remarkable observation having profound implication, as formation of chlorinated byproducts is a major hurdle to overcome for water/wastewater treatment technologies involving EO and other advance oxidation process[1,2].
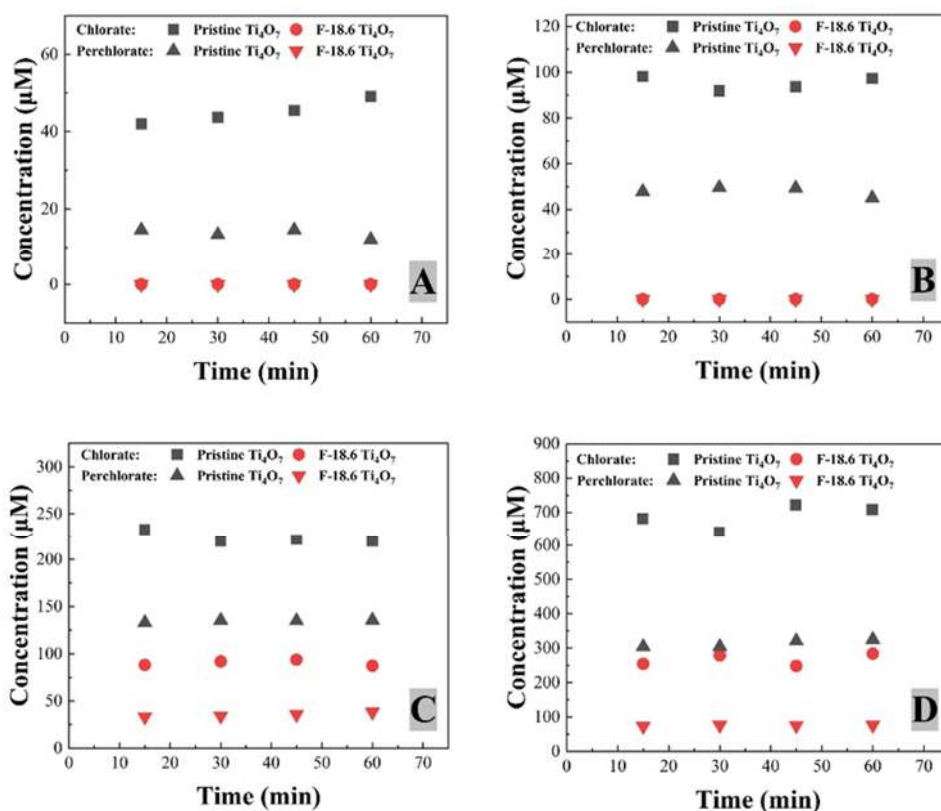

Figure 3. Chlorate and perchlorate generation in permeate flow during REM treatment on the pristine Ti_4O_7 and F-18.6 Ti_4O_7 anode at 10 mA·cm⁻²: 1-mM Cl⁻ (A), 10-mM Cl⁻ (B) and at 40 mA·cm⁻²: 1-mM Cl⁻ (C), 10-mM Cl⁻ (D) with 1-mM or 10-mM Cl⁻ in the reaction solution. Initial PFAS concentration: 2.0 µM, supporting electrolyte: 100-mM Na_2SO_4.

The concentrations of chlorate and perchlorate in the permeate flow during REM treatment at 40 mA·cm⁻² with 1 mM Cl⁻ and 10 mM Cl⁻ in feed solution are shown in Figure 3C and 3D, respectively. With 1-mM Cl⁻ in the feed solution, 223 µM chlorate and 134 µM perchlorate were formed for the REM with pristine Ti_4O_7 anode, while their formation dropped to 90.3 µM and 35.4 µM on F-18.6 anode. With 10-mM Cl⁻ in the feed solution, the formation of chlorate and perchlorate on pristine anode was 688 µM

and 314 μM, respectively, while those on the F-18.6 anode was significantly reduced to 266 μM and 75.4 μM. It should be noted that the background Cl^- is 12 – 46 $mg·L^{-1}$ in groundwater[3], close to 1 mM. Thus, REM tests were performed with 1-mM Cl^- in feed solution at 15 $mA·cm^{-2}$ (2.99 V), 20 $mA·cm^{-2}$ (3.28 V), 25 $mA·cm^{-2}$ (3.59 V), 30 $mA·cm^{-2}$ (3.77 V) and 35 $mA·cm^{-2}$ (3.98 V), in addition to 10 $mA·cm^{-2}$ (2.86 V) and 40 $mA·cm^{-2}$ (4.19 V) described above, and the concentrations of chlorate and perchlorate in the permeate flow are compared in Figure 4. The results in Figure 4 suggests that the formation of chlorate and perchlorate in REM can be avoided by using fluorinated Ti_4O_7 anode under a proper anodic potential range (< 3.0 V *vs* SHE).
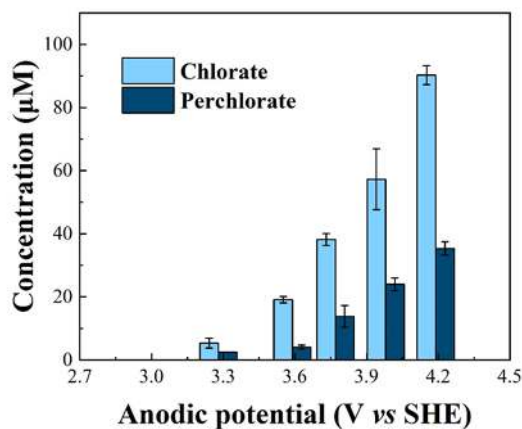

Figure 4. The concentrations of chlorate and perchlorate in the permeate during REM with F-18.6 anode at different anodic potential, including 2.86 V (10 $mA·cm^{-2}$), 2.99 V (15 $mA·cm^{-2}$), 3.28 V (20 $mA·cm^{-2}$), 3.59 V (25 $mA·cm^{-2}$), 3.77 V (30 $mA·cm^{-2}$), 3.98 V (35 $mA·cm^{-2}$) and 4.19 V (40 $mA·cm^{-2}$). Initial PFAS concentration: 2.0 μM, supporting electrolyte: 100-mM Na_2SO_4 + 1-mM NaCl.

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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), 11-14 (March2022); 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), 5-8 (June2022); 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), 5-9 (June2022); Full paper: http://short.pfonline.com/NASF22Sep2.
7. Quarter 6 (April-June 2022): Summary: *NASF Report* in *Products Finishing*; *NASF Surface Technology White Papers*, **87** (3), 1-4 (December 2022); Full paper: http://short.pfonline.com/NASF22Dec1.
8. Quarter 7 (July-September 2022): Summary: *NASF Report* in *Products Finishing*; *NASF Surface Technology White Papers*, **87** (6), 9-11 (March 2023); Full paper: http://short.pfonline.com/NASF23Mar2.
9. Quarter 8 (October-December 2022): Summary: NASF Report in Products Finishing; NASF Surface Technology White Papers, 87 (9), 19 (June 2023); Full paper: http://short.pfonline.com/NASF23Jun1.
10. Quarter 9 (January-March 2023): Summary: NASF Report in Products Finishing; NASF Surface Technology White Papers, 87 (12), 12-15 (September 2023); Full paper: http://short.pfonline.com/NASF23Sep2.

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