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 third quarter of work (July-September 2021).

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 Ti4O7 anode can be used to effectively destruct PFASs in plating wastewater.
3) The electrochemical treatment train comprised of EC and EO by Ti4O7 anode can remove and degrade PFASs in plating wastewater more efficiently than either process operated individually.

This report describes our continuing effort in Task 1 by analyzing the floc morphology characterization during EC treatment, as well as the experiments of Task 3.

As extremely recalcitrant chemicals, the destruction of PFASs for treatment purposes is challenging for the conventional treatment technologies or advanced oxidation processes (AOPs) based on the hydroxyl radical (•OH). EO exhibits stronger degradation ability than conventional AOPs due to the combination of the direct electron transfer (DET) reaction on the anode and the oxidation by •OH produced by anodic oxidation of water, which has been proven effective in destroying PFASs using “non-active” anodes, including boron-doped diamond (BDD), PbO2, SnO2-Sb and Magnéli phase titanium suboxides. In particular, Magnéli phase titanium suboxides, with the general formula of Ti₄O₂n₋₁ (4 < n < 10), have recently been explored as a promising electrode due to their wide electrochemical window for water oxidation, chemical inertness and low production cost. The degradation of organic contaminants occurs only near or at the anode surface, which is usually limited by mass transfer from bulk solution to the anode surface. Enhancement of the target concentration in the bulk solution is an effective way to improve the EO treatment efficiency, and it appears that the EC process may well serve such a purpose.
Experimental

An EC treatment was first carried out on a 250-mL solution of 10 PFASs (0.5 or 0.005 µM each) under 5 or 0.3 mA/cm². The floc recovered at the end of treatment was dissolved with 4.5M H₂SO₄ solution and then brought up to 10 mL by Milli-Q water. The collected foam was also added with drops of the acid until the foam disappeared, and then brought up to 10 mL by Milli-Q water. The acid solution resulting from PFAS-laden flocs was directly subjected to EO treatment described below. The acid solution from the foam dilution was supplemented with 20 mM Na₂SO₄ as supporting electrolytes and then subjected to EO treatment. EO experiments were conducted in a 25 mL electrolytic cell with a TiO₂ ceramic plate (1 × 2 cm) of 3-mm thickness as the anode, and a 304 stainless steel rod (5 mm diameter) as the cathode that was placed in parallel to the central axis of the anode at a 2 cm gap. For the treatment, a 10 mL solution was placed in the cell with continuous stirring using a magnetic stirrer (IKA-RCT, Germany), while a direct current was applied to the electrodes with different current densities. For the floc dissolved acidic solution, in pre-specified time intervals, triplicate 0.1-mL samples were withdrawn, diluted with water and adjusted to a final pH of approximately 6.0, then added with 40 µL of a mixed isotope labeled internal standard solution (100 ppb), followed by further cleanup using solid phase extraction (SPE). For the foam solution, 0.1-mL samples were withdrawn and mixed with 0.1-mL isotope labeled internal standards for subsequent analysis of PFASs concentrations as described below. All EC and EO experiments were carried out at room temperature (25±1 ºC).

Results and Discussion

Flocs were formed during the EC treatment, and their appearance varied with current density and reaction time. The flocs generated in selected tests were collected by membrane filtration as described in second report and then freeze-dried. The zinc hydroxide floc samples were characterized for the morphology by Scanning Electron Microscope (SEM) on a Hitachi’s-4800 FE-SEM system (Hitachi, Japan), and for the Brunauer–Emmett–Teller (BET) surface area using a surface area analyzer (TriStar II Plus, Georgia). As shown in Fig. 1, the hydroxide flocs generated at low current density (0.3 mA/cm²) showed a more crystalline flake-like structure. When a higher current density (5 mA/cm²) was applied, the flocs exhibited a more clustered amorphous or loose structure. The BET surface areas of dried flocs after degassing for 4 hours were determined at 50°C. The BET surface areas of the dried flocs generated at low current density (0.3 mA/cm²) and high current density (5 mA/cm²) were 101.18 and 13.36 m²/g, respectively. Despite the lower specific surface of the flocs produced at the higher current density, the total quantity of flocs formed at the high current density was however much larger, resulting in higher PFAS removal. The floc quantities generated at 5 mA/cm² was 16.67 times the quantities of floc generated using 0.3 mA/cm² at the same reaction time.

![Figure 1 - Field emission SEM analyses of hydroxide flocs generated in-situ in the EC process using low current density (0.3 mA/cm², 120 min) and high current density (5 mA/cm², 60 min), respectively.](image-url)
Figure 2 - PFAS concentration during EO treatment (current density = 10 mA/cm²) of three solutions prepared by EC: (A) Solution I: acid dissolved solution of the PFAS-laden flocs produced by EC at 0.3 mA/cm²; (B) Solution II: acid dissolved solution of PFAS-laden flocs produced by EC at 5 mA/cm²; (C) Solution III: foam solution produced during EC at 5 mA/cm².

For research purposes, the flocs and foams generated from the EC treatment at the high current density (5 mA/cm², 0.5 µM each of 10 PFASs) were collected respectively in Solution II and III that were then separately subjected to the subsequent EO treatment. In practice, the flocs and foams can be combined in one solution for EO treatment.

References


Past project reports


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.