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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 second quarter of work (April-June 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 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 part of our continuing effort in Task 1, by evaluating the isotherm-like sorption behavior of the PFASs on EC-generated zinc hydroxide flocs.

The electrocoagulation (EC) process has shown potential to remove PFASs from water by some recent studies.[1,2,3] EC involves the dissolution of charged cations (*e.g.*, Zn^{2+}, Al^{3+}, Fe^{3+}) formed at the sacrificial anode with simultaneous formation of monomeric and polymeric hydroxyl complex species, which can strongly sorb certain pollutants and remove them from contaminated water.[4] Lin, *et al.*[1] evaluated PFAS removal using various sacrificial anodes, including aluminum, iron, zinc and magnesium, and found that PFASs can be quickly adsorbed on zinc hydroxide flocs, generated *in situ* during EC with zinc anode, mainly via hydrophobic interaction. Here in this report, we systematically examined the adsorption behavior of PFAS on the flocs generated during EC with a sacrificial zinc anode.

Experimental

The setup of the EC reactor and the procedure of EC experiments have been described in detail in our first report of this project. In order to further evaluate the adsorption behavior of PFASs on the flocs generated from the zinc anode during EC, a series of EC experiments were conducted using PFAS solution comprised of ten PFASs, including (1) perfluorononanoic acid (PFNA), (2) perfluorooctanoic acid (PFOA), (3) perfluoroheptanoic acid (PFHpA), (4) perfluorohexanoic acid (PFHxA), (5) perfluorooctanesulfonic acid (PFOS), (6) perfluorohexanesulfonic acid (PFHxS), (7) perfluorobutanesulfonic acid (PFBS), (8) fluorotelomer sulfonic acid 8:2 (8:2 FtS), (9) fluorotelomer sulfonic acid 6:2 (6:2 FtS) and (10) fluorotelomer sulfonic acid 4:2 (4:2 FtS). The Initial concentrations were at different levels ranging from 0.001 to 0.1 μm (*i.e.*, 0.001, 0.002, 0.005, 0.01, 0.02, 0.05 and 0.1 μm), and the reaction time was 120 min using a low current density of 0.3 mA/cm² to prevent foaming. The supernatant was collected from each test cell and analyzed for the ten PFASs. Floc was collected and weighed after freeze drying once reactions were terminated. The data were used to evaluate the sorption capacity of each PFASs constituents and the sorbate-sorbent interactions. The PFASs sorption data were best fitted using the Langmuir isotherm model, Equation 1.

$$Q_e = \frac{Q_m k_L C_e}{1 + k_L C_e} \tag{1}$$

where Q_e is the amount (µmol/g) of PFASs adsorbed at equilibrium; C_e is the equilibrium PFASs concentration (µM) in the solution; Q_m represents the adsorption capacity; and k_L is the adsorption affinity constant.

Results and discussion

The sorption data of each PFAS obtained by data fitting are shown in Fig. 1(A,B,C) and Table 1. As seen, the adsorption capacity of the ten PFASs followed the order PFOS > PFNA > 8:2 FtS > PFOA > PFHxS > 6:2 FtS > Fluorotelomer sulfonic acid 4:2 (4:2 FtS) > Perfluoroheptanoic acid (PFHpA) > Perfluorohexanoic acid (PFHxA) > PFBS. It is in line with the order of the carbon chain length for each category, while, for a similar carbon chain length, is perfluoroalkanesulfonic acids (PFSAs, including PFOS, PFHxS, and PFBS) > fluorotelomer sulfonic acids (FTSAs, including 8:2 FtS, 6:2 FtS, and 4:2 FtS) > perfluoroalkyl carboxylic acids (PFCAs, including PFNA, PFOA, PFHpA and PFHxA). PFASs with longer carbon chain length tend to be more hydrophobic. This result confirmed that hydrophobic interaction plays a key role in the sorption capacity of PFASs on the zinc hydroxide flocs (Lin, *et al.* 2015), while charge interactions may also have an impact, as sulfonate head groups tend to have higher charge density than carboxylates in PFASs. According to the adsorption affinity constant (k_L) shown in Table 1 (a smaller value indicates greater sorption affinity), the sorption affinity of the ten PFASs followed the order PFHxS > PFOS > PFNA > PFOA > 6:2 FtS > PFHpA > 8:2 FtS > 4:2 FtS > PFHxA > PFBS. The order differs somewhat from that for the sorption capacity, with the larger molecules (PFNA, 8:2 FtS) shifted down in the order. It seems that the larger molecules may be disadvantaged in terms of sorption affinity, while charge interactions play an important role in the intensity of the sorption interactions.
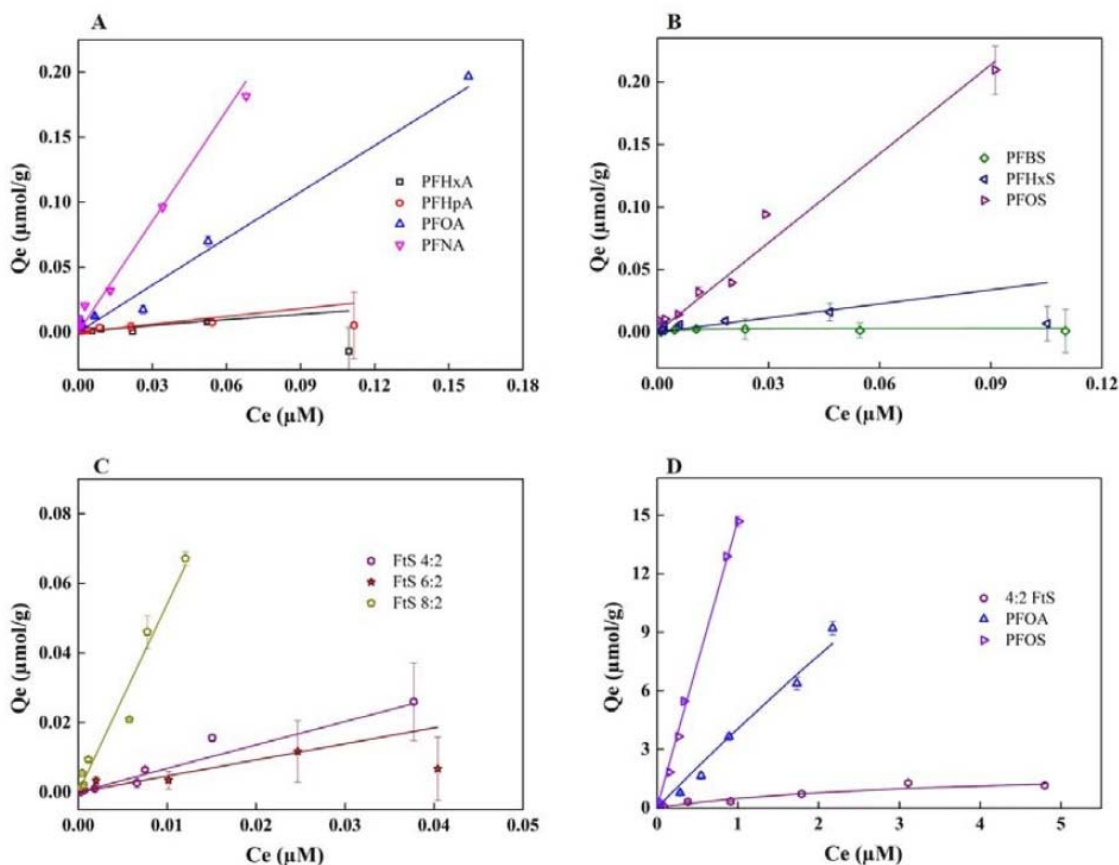

Figure 1 - (A, B, C) Langmuir sorption isotherm of the ten PFASs on the flocs (C_0 = 0.001 - 0.1 µM, current density = 0.3 mA/cm², 20 mM Na$_2$SO$_4$, EC time = 120 min); (D) Langmuir sorption isotherm of single 4:2 FtS, PFOA and PFOS on the flocs, respectively. (C_0 = 0.002 - 5 µM, current density = 0.3 mA/cm², 20 mM Na$_2$SO$_4$, EC time = 120 min).

Table 1 - Parameters obtained by fitting isotherm-like sorption data using Langmuir equation.

Solution	Compound	Q_m (µmol g^{-1})	k_L (L µmol^{-1})
10 PFASs solution	PFNA	40.78	0.07
	PFOA	15.11	0.08
	PFHpA	1.01	0.20
	PFHxA	0.10	1.8
	PFOS	55.36	0.04
	PFHxS	13.52	0.03
	PFBS	0.01	194.38
	8:2FtS	21.71	0.25
	6:2FtS	4.17	0.11
	4:2FtS	1.94	0.35
Individual PFASs solution	PFOS	498.07	0.03
	PFOA	97.33	0.04
	4:2 FtS	2.03	0.31

In order to identify if competitive sorption occurred in the ten PFASs solution, EC experiments were also performed to study the Langmuir sorption isotherms of three individual PFASs, including 4:2 FtS, PFOA, and PFOS, on the flocs using the same reaction conditions above. These three PFASs were chosen to represent PFSAs, FTSAs, and PFCAs, respectively. As shown in Fig. 1(D) and Table 1, the sorption capacity of PFOS and PFOA obtained in the individual solutions were much greater than those obtained in the mixture solutions, apparently indicative of competitive sorption effects in the solutions containing multiple PFASs. The sorption capacity of 4:2 FtS was, however, similar for the individual and mixture solutions. This is likely because 4:2 FtS has weaker affinity on flocs, for which competitive sorption effect may not be evident.

References

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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 .
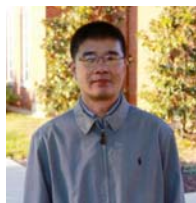
About the author

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.