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AESF Research Project #R-122

Electrochemical Approaches to Treatment of PFAS in Plating Wastewater

by
Qingguo (Jack) Huang*, Yuqing Ji
College of Agricultural and Environmental Science
University of Georgia
Griffin, GA, 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 seventh quarter of work (July-September 2022). 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 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.

* Principal Investigator (PI) Contact Information:
Qingguo Huang, Ph.D,
Professor, Department of Crop and Soil Sciences,
University of Georgia,
1109 Experiment St.,
Griffin, GA 30215, USA.
Phone: (770) 229-3302
Fax: (770) 412-4734
E-mail: qhuang@uga.edu

Our previous report describes the results from experiments of EO with a Magnéli phase Ti_4O_7 anode on the degradation of eight perfluoroalkyl acids (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). Here in this report, we describe a work to further explore how the degradation of different PFAAs are related to their molecular structures.

Experimental

In this work, a suite of molecular descriptors was calculated based on quantum mechanical computation. Then, the relationships between the rate constants of PFAA degradation and the molecular descriptors were explored in this study. Measurement of the PFAA degradation rate constants was described in our last report, and the EO was conducted in solutions each containing an individual PFAA at the current density of $5 \text{ mA}\cdot\text{cm}^{-2}$. Quantum computation was performed using Gaussian 09 based on the density functional theory (DFT) at B3LYP/6-311G** level. The molecular geometry was optimized, and vibrational frequencies computed for each PFAA, based on which a suite of molecular descriptors were calculated, including the frontier electron densities (FEDs) of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), the energy level of HOMO (E_{HOMO}) and LUMO (E_{LUMO}) and their gap ($E_{\text{LUMO}}-E_{\text{HOMO}}$), and molecular polarizabilities.

Results and Discussion

The degradation rates of the eight PFAAs by EO were found very different in the study described in our last report. The relationships between the rate constants of PFAA degradation normalized to the effective electroactive surface area (EEAA) and the molecular descriptors were explored. It has been proposed that the combination of direct electron transfer and hydroxyl radical attack plays a major role in the electro-oxidative degradation of PFAA¹. Therefore, certain molecular and electrical distribution properties of the PFAAs relating to their reactivity with hydroxyl radicals and electron transfer have been examined.

Frontier molecular orbital energies often play an important role in determining reactivity of organic chemicals². Energy of the highest occupied molecular orbital (E_{HOMO}) and the lowest unoccupied molecular orbital (E_{LUMO}) represents the ability of a molecule to donate or gain an electron respectively, and the gap between them imply the stability of the molecule in terms of redox reactivity^{3,4}. In this study, greater $E_{\text{LUMO}}-E_{\text{HOMO}}$ gaps were seen for shorter chained PFAAs ranging from 0.244 hartrees for PFBA to 0.155 hartrees for PFOA. It thus makes sense that we have seen a negative correlation between the $E_{\text{LUMO}}-E_{\text{HOMO}}$ gap and the $\log k_{\text{SA}}$ (Figure 1A). Indeed, these values form a cohesive negative linear trend through each of the functional groups (PFSAs vs. PFCAs) when plotted $\log k_{\text{SA}}$ against the $E_{\text{LUMO}}-E_{\text{HOMO}}$ gap. The energy gap however does not capture the rate constant trend between the functional groups, although this is not surprising given the large difference that functional groups can make on molecular properties.

Another molecular descriptor of interest, molecular polarizability, indicates the electronic flexibility of each molecule, thus in connection to the tendency of oxidative reactivity as well as direct electron transfer on anode⁵. When plotted against the PFAA degradation rate constants, the molecular polarizability has a nice positive correlation across both functional groups, serving as a good indicator for the reactivity of PFAAs. This suggests that direct electron transfer may be the rate-limiting step in

PFAA degradation in TSO-based electrooxidation systems, although the hydroxyl radicals generated via water oxidation may also play a role in concert ¹.

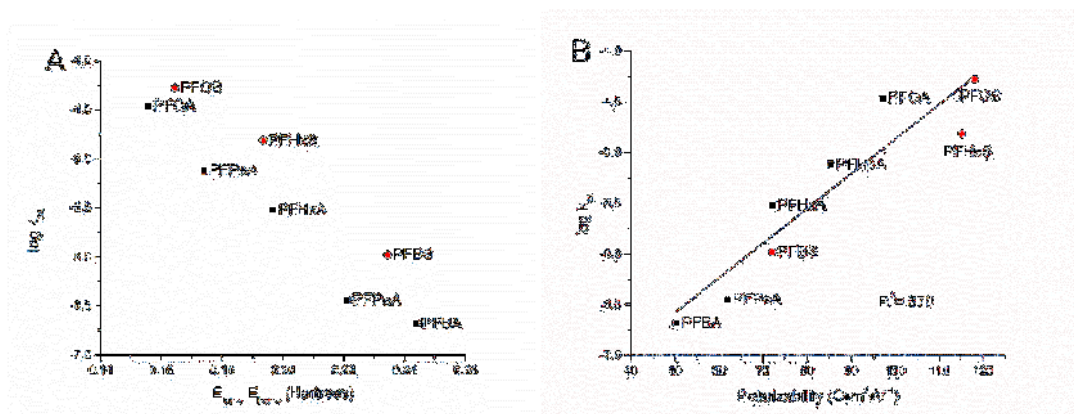


Figure 1. Relationship between the logarithm of the surface area normalized rate constants and $E_{LUMO} - E_{HOMO}$ gap (A) and molecular polarizability (B).

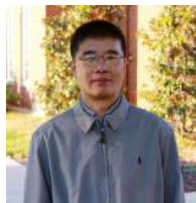
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Past project reports

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 (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), 5-8 (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), 5-9 (June 2022); 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>.

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