

Quarterly Progress Reports
January – December 2023
AESF Research Project #R-120

**Electrochemical Destruction of Perfluorooctanesulfonate
in Electroplating Wastewaters**

by
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Editor's Note: *This NASF-AESF Foundation research project report covers the year of project work for 2023) at the University of Illinois at Chicago. A printable PDF version of this report is available by clicking [HERE](#). A listing of previous reports to date is provided at the end of this report.*

Overview

The overall objective of this work is to utilize a cost-effective reactive electrochemical membrane (REM) for the removal of PFAS from synthetic electroplating wastewater. The REM is a patented technology that utilizes a conductive ceramic electrode material with micron-sized pores to electrochemically oxidize or reduce contaminants in a flow-through operation. Specific technical objectives associated with the proposed work include:

1. Development of REMs for destructive PFAS removal in synthetic electroplating wastewater.
2. Determination of the optimal operational mode.
3. Calculation of energy requirements for the REM-based system and compare to those determined for GAC adsorption and other technologies.

Achieving these objectives will provide the necessary data to determine if the REM system is competitive with other treatment options and thus will allow for the pursuit of further funding from industry and other funding agencies. Specific technical questions are stated below.

Question 1: Can adsorbent materials be added to REMs to produce next generation REMs with enhanced sorption capacities for PFAS?

Question 2: What is the best mode of operation for optimal REM performance for PFAS removal?

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Question 3: Will the REMs be a technically effective and cost-efficient remediation strategy for PFAS-containing electroplating wastewater?

12th Quarter (January-March 2023)

For the beginning of 2023, work resumed and a new student was hired on this project and has spent time learning the experimental setup and appropriate methods. In addition, a new catalytic reactor, which was developed on another project, will be tested in the next quarter for the degradation of PFAS in controlled samples and electroplating wastewater. Initial results for the oxidation of PFOA with this catalyst are shown below.

Figure 1 shows the concentration profile of PFOA at different potentials using three different catalysts: (1) a SnO₂ catalyst deposited by electrodeposition, followed by thermal oxidation (EDT) (*i.e.*, SnO₂-EDT/REM); (2) a Bi₂O₃ catalyst deposited by EDT (*i.e.*, Bi₂O₃-EDT/REM); and (3) two Bi₂O₃-SnO₂ catalyst (BTO) deposited by EDT (*i.e.*, BTO-EDT/REM). At 4.2 V_{SHE}, 42.4 ± 15.3%, 41.4 ± 2.6%, 59.0 ± 4.1% and >90% removal of PFOA was observed using SnO₂-EDT/REM, Bi₂O₃-EDT/REM, BTO-EDT/REM-2, and BTO-EDT/REM-1, respectively. Overall, the results showed higher removal of PFOA for SnO₂-EDT/REM compared to Bi₂O₃-EDT/REM. However, we observed that SnO₂ was leaching into the permeate solution at potentials ≥ 3.7 V_{SHE}. From the concentration profiles for BTO-EDT/REMs, it can be observed that presence of Bi₂O₃ improves removal of PFOA. We hypothesize that Bi₂O₃ stabilizes SnO₂.

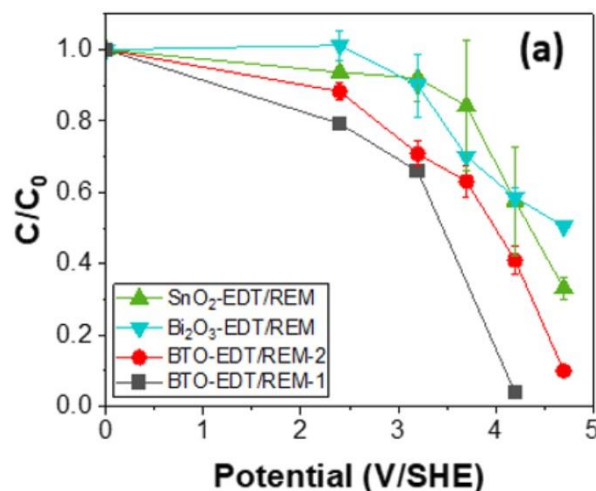


Figure 1: C/C₀ profile of PFOA (C₀ = 100 μM) as a function of potential.

13th Quarter (April-June 2023)

Considerable time was spent on developing a method for PFAS detection in our laboratory. A new catalyst was tested for 6:2-fluorotelomersulfonic acid (6:2 FTS) oxidation and showed significantly higher removal than Ti₄O₇ alone.

Figure 2 shows that concentration profile of 6:2 FTS at different potentials using the Bi₂O₃-SnO₂ catalyst (BTO) deposited on Ti₄O₇ (*i.e.*, BTO/Ti₄O₇). At all potentials tested, the hydraulic residence time was ~ 11 sec and the reported removal was obtained in a single pass through the porous electrode. At 3.6 V_{SHE}, the removal rate was >three-fold higher for the BTO/Ti₄O₇ compared to Ti₄O₇ alone.

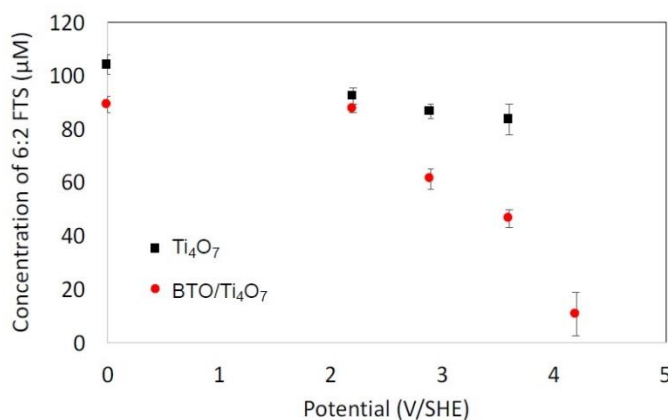


Figure 2 - Concentration profile of 6:2 FTS (C₀ = 100 μM) as a function of potential.

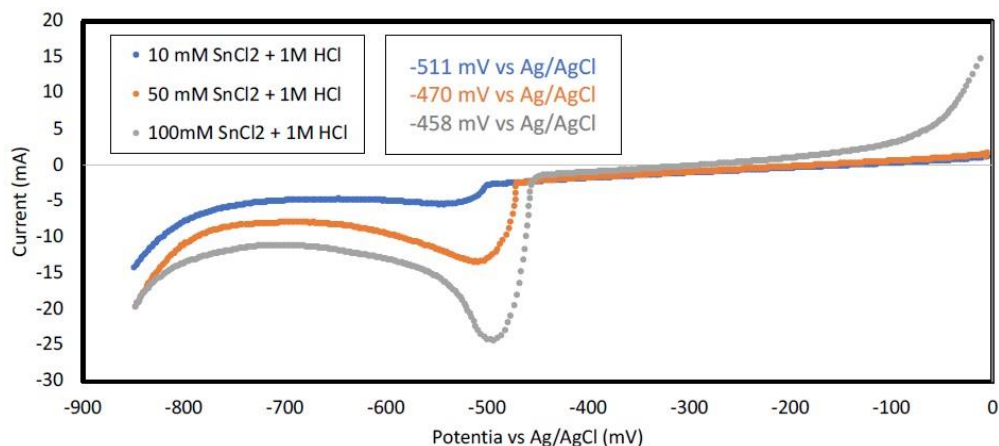
Furthermore, at 4.2 V_{SHE}, >90% removal of 6:2 FTS was observed using BTO/Ti₄O₇. However, we still are experiencing leaching of SnO₂ into the permeate solution at potentials ≥ 3.6 V_{SHE}. Work is underway to determine catalyst deposition methods to enhance the stability of the catalyst to achieve long term performance.

14th Quarter (July-September 2023)

Work this quarter was focused on optimizing the properties of the new catalyst for 6:2 FTS oxidation. By tuning the parameters of the catalyst synthesis step, higher removal of 6:2 FTS was achieved.

Specific work focused on the deposition of a Bi₂O₃-SnO₂ catalyst (BTO) on Ti₄O₇ (*i.e.*, BTO/Ti₄O₇) using an electrodeposition method. The method utilized a pulse deposition method where a constant potential of -700 mV was held for a pulse time of between 10 to 50 msec, followed by a return to the open circuit potential for 1 sec. This process was repeated for up to 3564 cycles. This method was chosen to minimize the size of the catalyst particles that were deposited on Ti₄O₇. The selection of -700 mV for the constant potential was based on linear sweep voltammetry data shown in Figure 3. Peaks in Figure 3 show the potential at which Sn and Bi are deposited on the electrode surface.

(a)



(b)

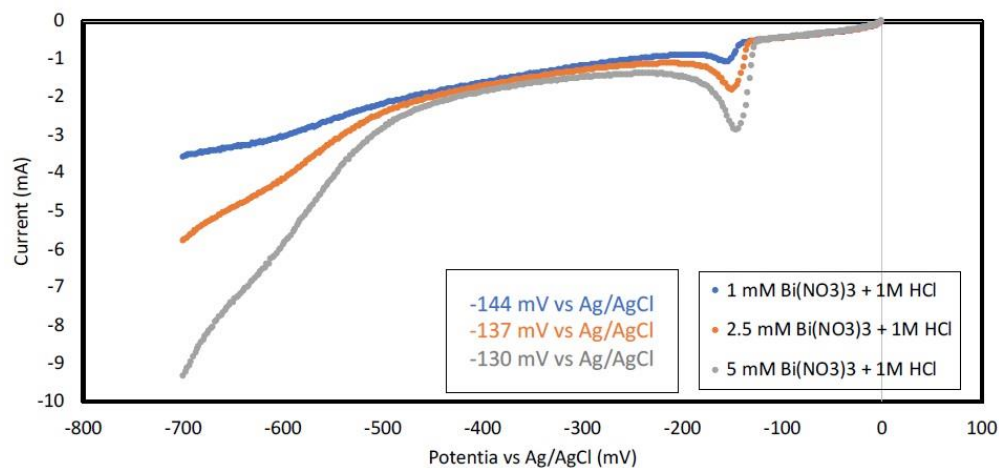


Figure 3 - Linear scan voltammetry for: (a) different concentrations of SnCl₂; (b) different concentrations of Bi(NO₃)₃. Peaks correspond to the electrodeposition of the metals.

The first set of catalysts were prepared by changing the pulse time and the number of cycles. Pulse times of 10, 20, and 30 msec were tested with corresponding cycle number of 3564, 1782, and 188, respectively. Therefore, all three methods utilized a total deposition time of 35.6 sec. The prepared samples were tested for 6:2 FTS removal in a flowthrough reactor with a hydraulic residence time was ~ 11 sec and as a function of potential (2.2. to 4.2 V_{SHE}). The reported removal was obtained in a single pass through the porous electrode. The results in Table 1 show that 6:2 FTS removal and defluorination both increase with increasing pulse time. The highest removal (75.4%) and defluorination (19%) was achieved for the 30 msec pulse time at 4.2 V_{SHE}.

Table 1 - 6:2 FTS removal and defluorination by BTO catalysts as a function of potential. Feed: 100 μM 6:2 FTS + 100 mM NaClO₄; flow rate = 240 LMH (11 sec residence time).

Pulse time/cycle #	Potential (V/SHE)	Removal (%)	Defluorination (%)
10 ms/3564	2.2	6±2	0
	2.9	5±1	18±8
	3.6	17±2	10±1
	4.2	57±4	16±1
20 ms/1782	2.2	9±21	9±6
	2.9	18±3	10±2
	3.6	55±2	9±1
	4.2	74±1	12±2
30 ms/1188	2.2	3±6	25±11
	2.9	16±17	8±1
	3.6	60±3	14±0.2
	4.2	75±4	19±1

The next set of catalysts was prepared by varying the pulse time (20, 40, 50 msec), and the number of cycles was held constant at 3564. This provided total deposition times of 71, 143, and 178 sec. The results in Table 2 show once again that 6:2 FTS removal and defluorination both increase with increasing pulse time. The highest removal (>85%, below the detection limit) and defluorination (41%) was achieved for the 50 msec pulse time at 4.2 V_{SHE}. Interestingly, the performance at both 3.6 and 4.2 V_{SHE} were similar for 6:2 FTS removal, with a slightly higher defluorination at 4.2 V_{SHE}.

Table 2 - 6:2 FTS removal and defluorination by BTO catalysts as a function of potential. Feed: 100 μM 6:2 FTS + 100 mM NaClO_4 ; flow rate = 240 LMH (11 sec residence time).

Pulse time/cycle #	Potential (V/SHE)	Removal (%)	Defluorination (%)
20 ms/3564	2.2	8.5 \pm 8	0
	2.9	58 \pm 14	3 \pm 1
	3.6	80 \pm 4	13 \pm 2
	4.2	>85	18 \pm 4
40 ms/3564	2.2	0	8 \pm 7
	2.9	22 \pm 16	7 \pm 1
	3.6	76 \pm 4	20 \pm 3
	4.2	>85	32 \pm 5
50 ms/3564	2.2	9 \pm 8	4 \pm 3
	2.9	49 \pm 7	15 \pm 6
	3.6	82 \pm 1	30 \pm 2
	4.2	>85	41 \pm 2

To assess the long-term performance of the BTO catalyst, a 5-hour experiment was conducted for the 40 msec pulse time and 3564 cycle number at 3.6 V_{SHE} . The results in Table 3 show that both removal and defluorination decrease over time, which was attributed to catalyst leaching. Work is underway to determine methods to increase catalyst stability.

Table 3 - 6:2 FTS removal and defluorination by BTO catalysts as a function of time at 3.6 V_{SHE} . Feed: 100 μM 6:2 FTS + 100 mM NaClO_4 ; flow rate = 240 LMH (11 sec residence time).

Time	Removal (%)	Defluorination (%)
30 min	78	18
45 min	64	16
1 hr	49	15
1.5 hr	39	16
2 hr	27	17
3 hr	21	16
4 hr	29	11
5 hr	29	10

15th Quarter (October-December 2023)

In this quarter, we focused on deposition of Bi and Sn catalysts to the reactive electrochemical membranes (REMs) and electrochemical oxidation of 6:2-fluorotelomersulfonic acid (6:2-FTS) in a NaClO_4 background electrolyte. Oxidation experiments were performed with bismuth/tin oxide electrodeposited catalysts (BTO/EDT/REM) and BTO catalysts deposited by the incipient wetness method (BTO/IW/REM). An

additional BTO electrodeposited catalyst was treated at 550°C in argon gas (BTO/EDT/Ar/REM). Finally, catalyst stability was investigated during the electrochemical oxidation of 6:2-FTS using a BTO/EDT/REM for a duration of 8 hours at a consistent potential of 4.2 V_{SHE}. The oxidation experiments were conducted in the crossflow cathode-anode (CF-CA) flow mode. The oxidation experiment with BTO/IW/REM showed >85% 6:2-FTS removal and 41 ± 3% fluoride yield at 4.2 V_{SHE} for the NaClO₄ background. The longevity experiment at 4.2 V_{SHE} showed 6:2-FTS removal of 69.3 ± 4.5% and a 20.8 ± 2.5% fluoride yield after 2 hours. The ICP-MS analysis of the longevity experiment indicated significant leaching of Bi within the initial 2-hour period, which affected 6:2-FTS removal.

Results and discussion. Electrochemical oxidation experiments were carried out using a 100 μM 6:2-FTS feed solution in 100 mM NaClO₄. In the CF-CA flow mode, the concentration profiles of 6:2-FTS and fluoride yields from the conducted experiments with BTO/IW/REM were compared with those conducted using BTO/EDT/REM and BTO/EDT/Ar/REM, as illustrated in Figs. 4a and b, respectively. The oxidation experiment with BTO/IW/REM, BTO/EDT/REM, and BTO/EDT/Ar/REM showed 41 ± 3%, 36 ± 1.5% and 38 ± 5% fluoride yield at 4.2 V_{SHE}, respectively and >85% 6:2-FTS removal for all prepared REMs. The lower fluoride yield for BTO/EDT/REMs was attributed to the catalyst leaching. However, it is imperative to conduct a detailed analysis of catalyst leaching in the case of BTO/IW/REMs.

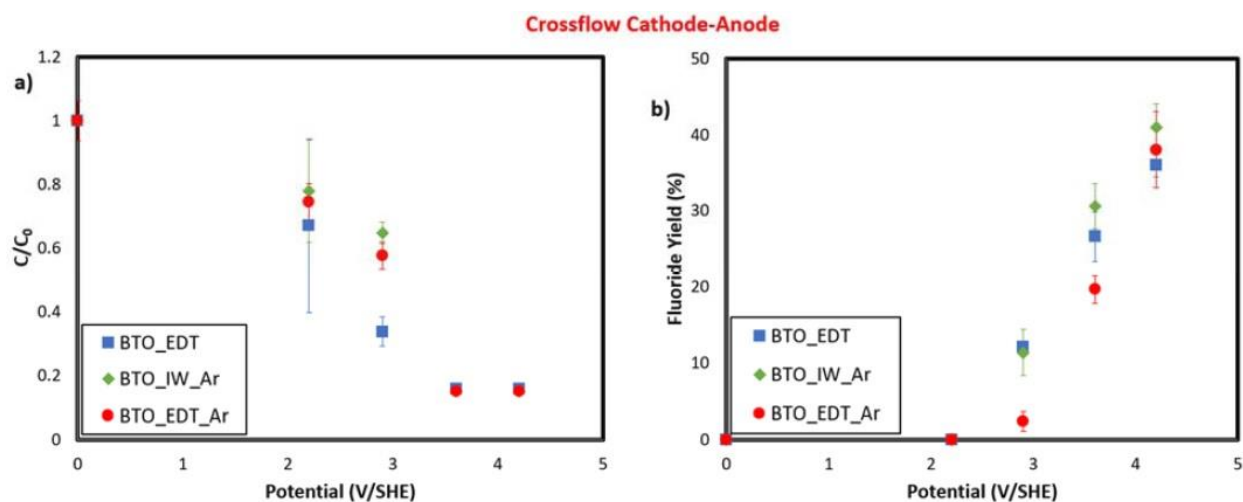


Figure 4 - (a) 6:2 FTS concentration profile, (b) fluoride yield for the 100 μM 6:2 FTS oxidation experiments using BTO/EDT/REM, BTO/IW/REM, and BTO/EDT/Ar/REM at different potentials and at a constant flux of 240 LMH in a CF-CA flow mode of the flow-through reactor in NaClO₄ feed solutions.

As shown in Figs. 5a and b, the 6:2-FTS removal reached 69.3 ± 4.5%, with a fluoride yield of 20.8 ± 2.5% after 2 hours. To analyze Bi and Sn leaching during the experiment, samples were analyzed using inductively coupled plasma mass spectrometry (ICP-MS). The results, depicted in Figs. 5c and d, highlight the significant leaching of Bi within the initial 2 hours of the experiment.

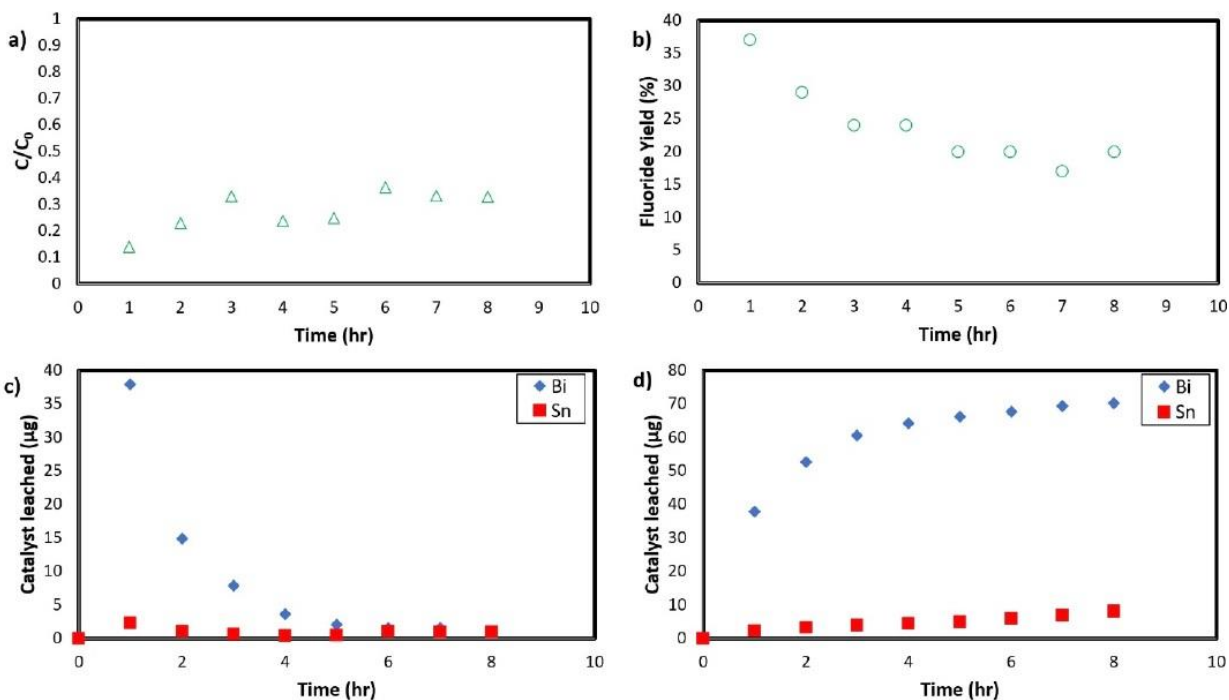


Figure 5 - (a) 6:2 FTS Concentration profile; (b) fluoride yield with time in NaClO_4 electrolytes at $4.2 \text{ V}_{\text{SHE}}$ using BTO/EDT/REM; (c) catalyst leached vs. time and (d) cumulative catalyst leached vs. time for the longevity experiment.

Future work will focus on the study of the catalyst leaching of BTO/IW/REM to determine the most stable catalyst for the 6:2-FTS oxidation experiment. Additionally, the fluoride balance will be calculated through the analysis of short-chained PFASs in the experiment.

Past project reports

1. Quarters 1-5 (April 2019-June 2021): Summary: *NASF Report in Products Finishing; NASF Surface Technology White Papers*, **86** (1), 19 (October 2021); Full paper (With Project Introduction): <http://short.pfonline.com/NASF21Oct1>.
2. Quarter 6 (July-September 2021): Summary: *NASF Report in Products Finishing; NASF Surface Technology White Papers*, **86** (4), 19 (January 2022); Full paper: <http://short.pfonline.com/NASF22Jan2>.
3. Quarters 7-8 (October 2021-March 2022): Summary: *NASF Report in Products Finishing; NASF Surface Technology White Papers*, **86** (11), 19 (August 2022); Full paper: <http://short.pfonline.com/NASF22Aug2>.
4. Quarters 9-12 (April 2022-March 2023): Summary: *NASF Report in Products Finishing; NASF Surface Technology White Papers*, **87** (10), 20 (July 2022); Full paper: <http://short.pfonline.com/NASF23Jul2>.

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About the principal investigator



Dr. Brian P. Chaplin is a Professor in the Department of Chemical Engineering, at the University of Illinois at Chicago. He holds a B. Civil Engineering (1999) and an M.S. (2003) in Civil Engineering from the University of Minnesota and a Ph.D. in Environmental Engineering (2007) from the University of Illinois at Urbana-Champaign.