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AESF Research Project #R-120
Final Report

Electrochemical Destruction of Perfluorooctanesulfonate in Electroplating Wastewaters

by
Brian P. Chaplin[**]
Department of Chemical Engineering
University of Illinois at Chicago
Chicago, Illinois, USA

Editor's Note: *Unavoidably interrupted by the SARS CoV-2 pandemic of 2020-21, this NASF-AESF Foundation research project report R-120 has been ongoing since April 2019. Now complete, this report is the final report, reflecting 16 quarters of work.*

1. Overview

Per- and polyfluoroalkyl substances (PFASs) are a class of chemicals that have unique properties that impart oil and water repellency. As a result, PFASs have been used as coatings for textiles, paper products and consumer packaging, as well as for metal plating and in various other industries (*e.g.*, semiconductors, automotive, construction). As a result of the widespread use of PFASs and their resistance to destructive treatment and biodegradation, these compounds are ubiquitous in the environment. There is growing evidence of their toxicity to humans. In response, the Environmental Protection Agency (EPA) has issued a combined Health Advisory Level for perfluorooctanoic acid (PFOA) and perfluorooctanesulfonate (PFOS) of 70 ng/L, and several states have endorsed standards for these and other PFASs. However, due to its ability to act as mist suppressant, PFOS has been used for metal finishing and electroplating applications in the form of tetraethylammonium PFOS salt (CAS #56773-42-3). New formulations have been introduced that utilize other polyfluoralkyl substances (*e.g.*, 6:2 fluorotelomer sulfonate (6:2 FTS)) in place of PFOS. Given the health concerns and emerging regulatory standards of PFASs, reliable low-cost methods for destructive removal of PFOS and other PFASs are greatly needed.

The primary objective of this work was to employ a cost-effective reactive electrochemical membrane (REM) for the removal of PFAS from synthetic electroplating wastewater. The REM, a patented technology, features a conductive ceramic electrode material with micronsized pores that enables the electrochemical oxidation or reduction of contaminants in a flowthrough operation.

The specific technical objectives of the proposed work were:

1. To develop REMs for the destructive removal of PFAS in synthetic electroplating wastewater.
2. To determine the optimal operational mode.
3. To calculate the energy requirements for the REM-based system and compare them to those for GAC adsorption and other technologies.

[*] Corresponding Author (Principal Investigator)
Dr. Brian P. Chaplin, Professor
Dept. of Chemical Engineering
University of Illinois at Chicago
221 Chemical Engineering Building
810 S. Clinton St.
Chicago, IL 60607
Office: (312) 996-0288
Mobile: (217) 369-5529
E-mail: chaplin@uic.edu

Objectives 1 and 2 were successfully achieved. It was determined that a Ti_4O_7 REM coated with a Bi_2O_3-SnO_2 catalyst was effective in oxidizing PFAS to mineral products with short residence times in the electrochemical reactor. Additionally, the most energy-efficient operational mode was identified as a single-pass system utilizing multiple reactor stages in series. However, Objective 3 was not completed due to a fundamental shift in the work plan.

More time was required for catalyst development and stability testing than initially anticipated. Consequently, a comprehensive side-by-side evaluation of the REM system compared to GAC treatment was not performed.

Specific technical questions evaluated in this work are as follows:

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?
Question 3: Will the REMs be a technically effective and cost-efficient remediation strategy for PFAS-containing electroplating wastewater?
Each of these questions are discussed in detail.

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

Work was conducted on the synthesis of reactive electrochemical membranes (REMs), with powder activated carbon (PAC) and multi-walled carbon nanotube (MWCNT) sorbent materials. The PAC-REM and MWCNT-REM materials were tested as a function of the applied anodic potential. These experiments were conducted in a flow-through reactor and effluent solution from the reactor was collected as a function of potential. Results are summarized in Figure 1.

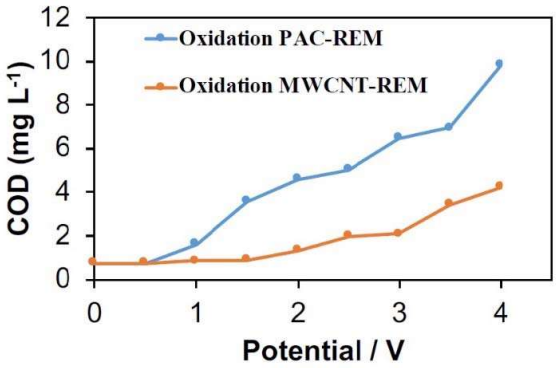

Figure 1 - COD permeate concentrations for PAC-REM and MWCNT-REM as a function of the anodic potential.

Results for the PAC-REM indicated that the carbon began to oxidize at applied potential values higher than 0.5 V_{SHE}. The COD value increased continuously from 0.76 mg/L at 0.5 V_{SHE} to 9.81 mg/L at 4.0 V_{SHE}.

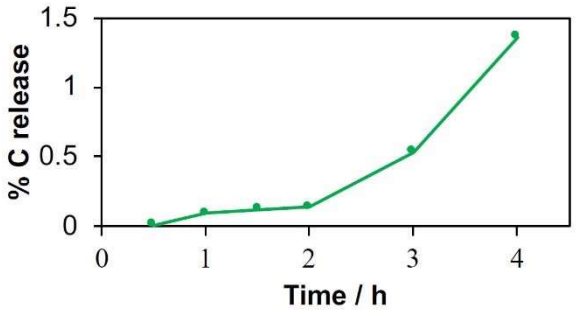

Figure 2 - Percent carbon leaching for the MWCNT-REM at a potential of 3.0 V_{SHE} as a function of time.

Results for the MWCN- REM were more promising, but carbon leaching was still observed. For example, COD values in the effluent reached as high as 4.2 mg/L at an applied voltage of 4.0 V_{SHE}. These results indicated that the composite REMs were not stable under anodic conditions. To determine if the MWCNT-REM stability would improve with longer operation times, an additional experiment was conducted at 3.0 V_{SHE} over a four-hour period. Results are shown in Figure 2 and indicate that stability of the MWCNT- REM deteriorated over time.

Effluent COD levels were as high as 455 mg/L after 4 hours, which amounted to approximately 1.5% of the total carbon content. Thus, it is apparent that these composite REMs are not appropriate for PFAS oxidation. Therefore, other strategies are needed to remove and treat PFAS. Upstream adsorption followed by downstream oxidation is one possible strategy.

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

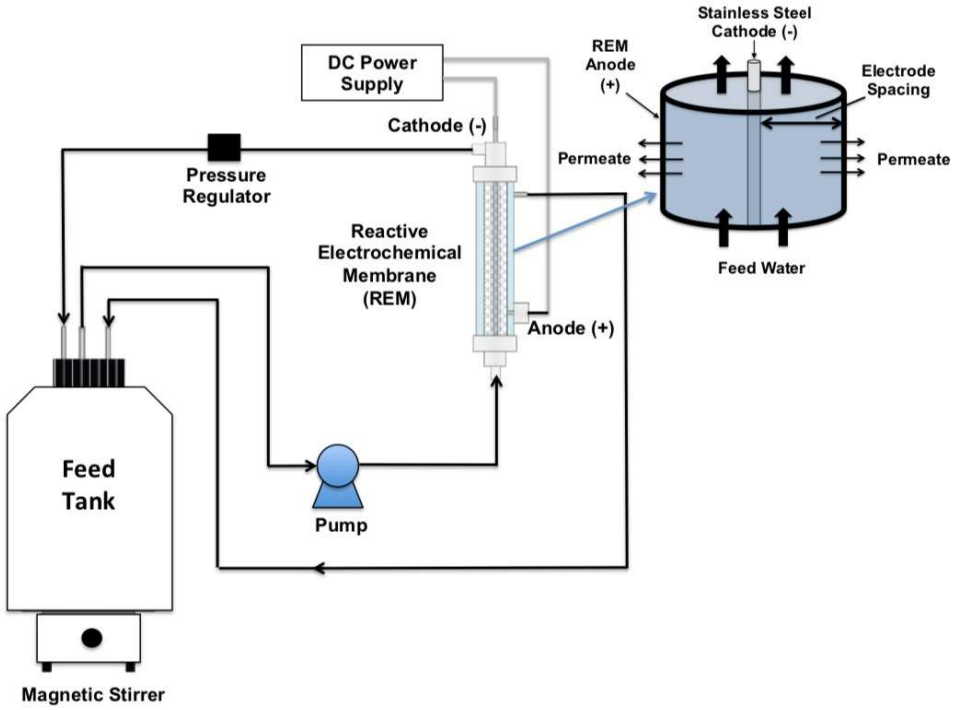

Figure 3 - Schematic of setup for testing crossflow operation mode in (1) 100% recycle of both permeate and feed and (2) Single-pass.

Several reactor designs were evaluated, including dead-end filtration and crossflow filtration in two modes: (1) 100% recycle and (2) single-pass. Dead-end filtration was deemed unfeasible due to excessive bubble formation from water electrolysis, which blocked the electrode surface. In contrast, the crossflow mode successfully swept bubbles off the electrode, preventing blockage. Figure 3 shows schematics of the crossflow setup in both 100% recycle and single-pass modes.

Experimental tests revealed that the single-pass mode was more energy-efficient. The 100% recycle mode, however, was less efficient due to increased energy consumption from pumping, as the permeate stream reintroduced PFAS into the feed reservoir.

Depending on the PFAS concentration in the feed solution and the treatment goals, multiple REM reactors in series may be required. Figure 4 (p. 15) illustrates a possible configuration for these reactors. Each reactor stage can achieve ~ 1-log PFAS removal based on the applied potential and permeate flux. Given that energy requirements in complex solutions can increase significantly, it may be more cost-effective to redirect the permeate stream to the front of the treatment train (*e.g.*, for sorbent treatment) once PFAS concentrations reach sub-µg/L levels. Further testing is needed, in combination with sorbent technologies, to determine the optimal configuration of the treatment train, particularly the ideal PFAS concentration to achieve before sending the permeate stream back to the adsorption stage.

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

Experimental tests demonstrated that Bi_2O_3-SnO_2 catalysts deposited on REMs were effective anode materials for destroying PFAS in electroplating wastewater. However, the development and stability testing of the catalysts took significantly longer than expected, preventing a comprehensive side-by-side comparison of the REM system with GAC treatment, which is needed for a cost analysis. Details of the experimental work are provided on page 15.

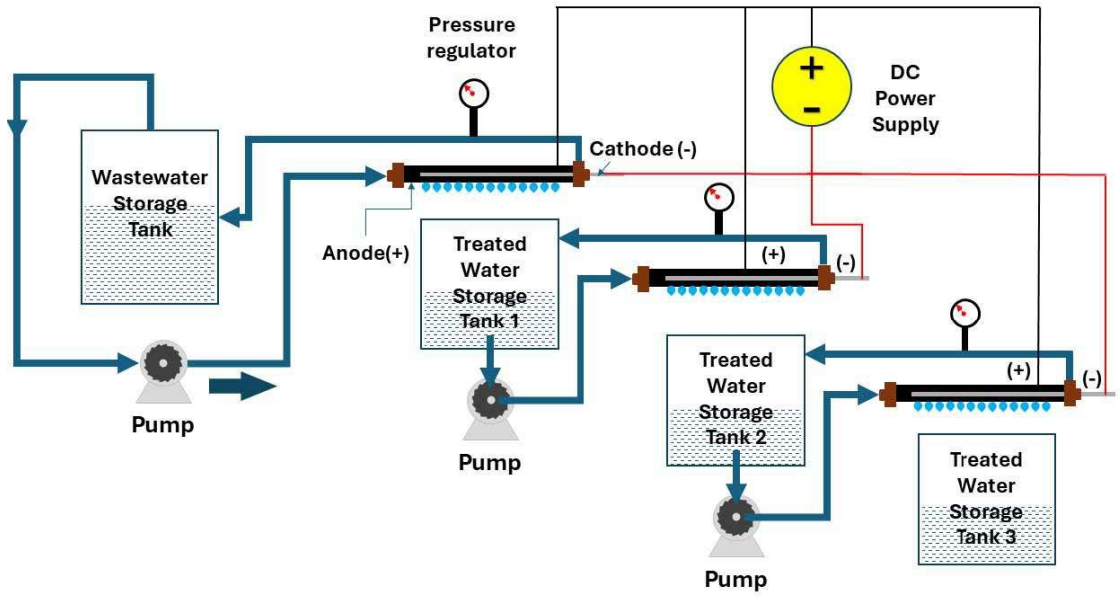

Figure 4 - Schematic of electrochemical treatment with multiple REM reactors in series: (1) 100% Recycle, (2) Single-pass.

Table 1 - General water quality parameters for electroplating wastewater sample.

Constituents	Conc. (mM)
Calcium	0.594
Sodium	61.5
Magnesium	0.650
Ammonium	1.57
Chloride	24.7
Fluoride	0.90
Nitrate	0.81
Sulfate	13.9
Bicarbonate	6.12
pH	7.35
COD	50 mg/L
Conductivity	6.3 mS/cm

The electroplating wastewater had a total PFAS concentration of 228 µg/L, primarily composed of 6:2 FTS (220 µg/L), with smaller amounts of 4:2 FTS, PFHpA, PFHxA, and PFOS. General water quality parameters, including NaCl and Na_2SO_4 concentrations, a pH of 7.35, and a COD of 50 mg/L, are detailed in Table 1.

Electrochemical oxidation was tested in a REM system at constant flux (240 L/m²/hr) with applied potentials of 2.2, 2.9, and 3.6 V_{SHE}. COD reduction results indicated decreases of 10%, 24%, and 83%, demonstrating effective oxidation of organics.

A subsequent experiment using synthetic wastewater (0.5 µM 6:2 FTS) with similar ionic content (as shown in Table 1) but without bulk organics showed fluoride levels increasing with potential, reaching 75% defluorination of 6:2 FTS (Figure 5).

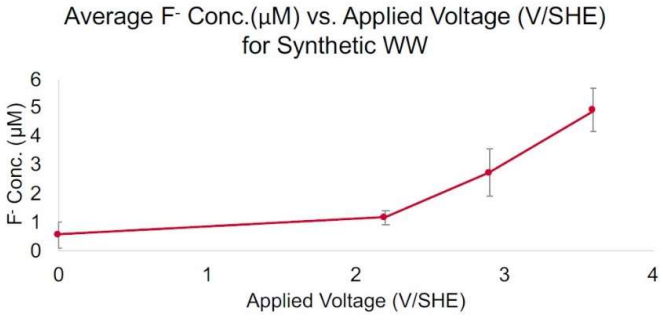

Figure 5 - Fluoride analysis for 0.5 mM 6:2 FTS oxidation in synthetic wastewater sample as a function of potential. Residence time ~ 11 s.

Another synthetic sample with concentrated 6:2 FTS (40 µM) was tested, resulting in 66-83% removal at varying potentials. However, short-chain PFAS byproducts formed, with their concentrations peaking at 2.9 V_{SHE} and then decreasing at 3.6 V_{SHE} (Figure 6). These results suggest that concentrating PFAS in wastewater may be an effective treatment strategy, but using multiple REM reactors in series are necessary to prevent the accumulation of short-chain PFAS byproducts.

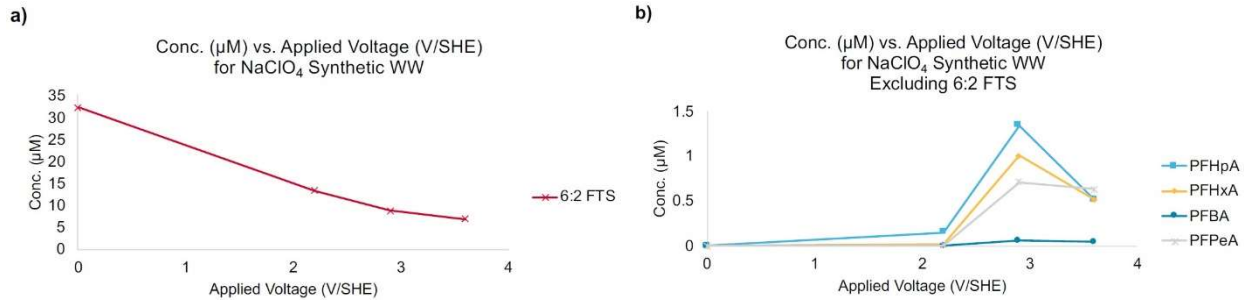

Figure 6 – (a) Concentration of 6:2 FTS as a function of the applied potential. Initial concentration of 6:2 FTS = 40 mM; (b) products from 6:2 FTS as a function of the applied potential.

Longevity experiments were also conducted to assess the stability of the Bi_2O_3-SnO_2 catalyst. Two different catalyst deposition methods were conducted. The first used electrodeposition followed by thermal oxidation (BTO_EDT). The second used the incipient wetness method followed by calcination in an inert gas (BTO_IW). As shown in Figure 7a, the 6:2-FTS removal reached 90% for the BTO_IW catalyst, with a fluoride yield of ~40% (Figure 7b). The BTO-EDT catalyst initially showed ~90% 6:2-FTS removal, but removal declined over the 8-hr experiment (Figure 7a) and fluoride yield decreased (Figure 7b). To analyze Bi and Sn leaching during the experiment, samples were analyzed using inductively coupled plasma mass spectrometry. The results, depicted in Figures 7c and 7d, highlight the significant leaching of Bi within the first hour of the experiment. Leaching was minimal after this point, so future work is needed to study long-term catalyst leaching over extended time periods. Furthermore, more work is necessary to stabilize the catalyst.

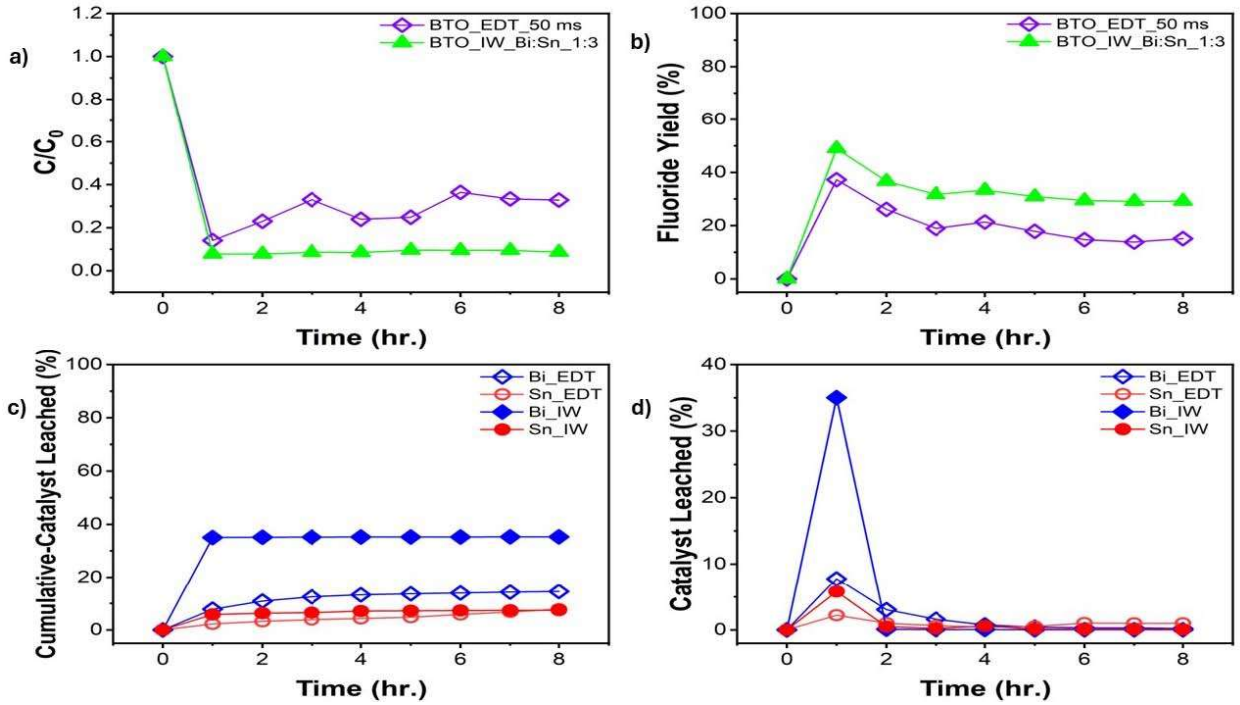

Figure 7 - (a) 6:2-FTS concentration profile; (b) Fluoride yield with time in $NaClO_4$ electrolytes at 4.2 V_{SHE} using BTO/EDT/50ms and BTO/IW/Bi:Sn/1:3; (c) percentage of cumulative catalyst leached vs time in %; (d) percentage of catalyst leached vs time for the longevity experiment.

About the author

Dr. Brian P. Chaplin is Associate 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.