

FINAL REPORT

Reactive Electrochemical Membrane (REM) Reactors for the Oxidation of PFAS-Impacted Water

SERDP Project ER18-1491

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List of Acronyms

Acronym	Meaning
AFFFs	aqueous film forming foam
BDD	boron-doped diamond
CNTs	carbon nanotubes
COD	chemical oxidant demand
CV	cyclic voltammetry
DC	direct current
DCE	dichloroethene
DoD	Department of Defense
EPA	Environmental Protection Agency
EIS	electrochemical impedance spectroscopy
GAC	granular activated carbon
GW1	groundwater 1
GW2	groundwater 2
IDW	investigation derived waste
kWh	kilowatt hour
LCA	life cycle assessment
LC-MS	liquid chromatography/mass spectroscopy
LMH	liters per meter squared per hour
MWCNTs	multi-walled carbon nanotubes
OCP	open circuit potential
OD	outside diameter
OH [•]	hydroxyl radicals
PAC	powder activated carbon
PI	principle investigator
PFAS	perfluoroalkyl substance
PFBS	perfluorobutanesulfonic acid
PFOA	perfluorooctanoic acid
PFOS	perfluorooctanesulfonic acid
PFHxS	perfluorohexane sulfonate
PFHpA	perfluoroheptanoic acid
PFNA	perfluoronanoic acid
REM	reactive electrochemical membrane
SDS	sodium dodecyl sulfate
SEM	scanning electron microscopy
SHE	standard hydrogen electrode
SS	stainless steel
TCE	trichloroethene
TOC	total organic carbon
UCMR-3	third unregulated contaminant monitoring rule
USEPA	United States Environmental Protection Agency
UV	ultraviolet
VC	vinyl chloride
XRD	X-ray diffraction

Keywords

Perfluoroalkyl substances; electrochemical oxidation; reactive electrochemical membrane; Ti_4O_7 ; investigation derived waste

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We thank Dr. Todd DeJournett, Dr. James Wang, and David Sherman from Geosyntec Consultants for procuring groundwater samples for this project. We thank Jason Speicher from Willow Grove Naval Base for allowing us to collect groundwater samples for this project. We also thank Dr. Todd DeJournett and Dr. James Wang for useful discussions regarding site remediation.

Abstract

Introduction. This research focused on the development of a novel reactive electrochemical membrane (REM) treatment system for the remediation of perfluoroalkyl substances (PFASs) in liquid samples that were generated from subsurface investigations of PFAS contamination at groundwater sites, known as investigation-derived waste (IDW). The REM is a patented technology developed in PI Chaplin's laboratory that utilizes a conductive, porous ceramic electrode material to electrochemically oxidize PFAS contaminants in a flow-through operation.

Objectives. The overall objective of this work was to develop proof-of-concept data to show that the REM technology is a viable option for the removal of PFASs from liquid IDW samples. Specific technical objectives associated with the work include: 1) development of REMs for destructive PFAS removal in synthetic and IDW water samples; 2) determination of the optimal operational mode; and 3) calculation of energy requirements for the REM-based system for comparison to other technologies.

Technical Approach. The work performed during this project consisted of REM synthesis, a series of bench-scale experimental studies, and a preliminary energy cost assessment. The six PFAS compounds on the USEPA UCMR-3 list were investigated, which included perfluorooctanoic acid (PFOA), perfluorooctanesulfonic acid (PFOS), perfluorononanoic acid (PFNA), perfluorohexanesulfonic acid (PFHxS), perfluoroheptanoic acid (PFHpA), and perfluorobutanesulfonic acid (PFBS). A specific focus on treatment of PFOS and PFOA was made, which allowed comparison of results to the existing literature. Experimental parameters that were explored included: 1) adsorption capacity; 2) necessary residence time in the reactor; 3) reactor operational mode; and 4) energy usage (kWh m^{-3} per log removal of PFAS).

Results. The oxidation of PFOA and PFOS in synthetic solutions indicated that approximately 5-log removal of PFOA and PFOS was achieved in a single pass through the REM (hydraulic residence time ~ 11 s) at applied potentials of 3.3 V/SHE for PFOA and 3.6 V/SHE for PFOS. Permeate concentrations were < 86 ng L $^{-1}$ for PFOA and 35 ng L $^{-1}$ for PFOS, from initial concentrations of 4.14 and 5 mg L $^{-1}$, respectively. Removal rates were as high as 3415 ± 203 $\mu\text{mol m}^{-2} \text{h}^{-1}$ for PFOA and 2436 ± 106 $\mu\text{mol m}^{-2} \text{h}^{-1}$ for PFOS at a permeate flux value of 720 L m $^{-2} \text{h}^{-1}$ (residence time of ~ 3.8 s). The energy consumption (per log removal) to remove PFOA and PFOS to below the detection limits were 5.1 kWh m $^{-3}$ and 6.7 kWh m $^{-3}$, respectively. In addition, non-normalized observed reaction rate constants for this data were calculated as 607 h $^{-1}$ for PFOA and 210 h $^{-1}$ for PFOS. These values are more than two orders of magnitude higher than those reported by other destructive technologies (i.e., ultrasonication, photocatalysis, vacuum UV photolysis, microwave-hydrothermal decomposition). Additional work involving real groundwater samples were also conducted. Results showed that single-pass flow-through mode could achieve only $\sim 50\%$ PFAS destruction, which was attributed to background organic constituents and low solution conductivity. However, operating in recycle-mode with high permeate fluxes achieved $> 99\%$ destruction of the total measured PFASs, with individual concentrations < 61 ng L $^{-1}$. Recycle-mode required a total energy consumption of only 2.9 kWh m $^{-3}$ per log removal, which was significantly lower than other destructive technologies.

Benefits. The high rate constants reported above are the highest reported for electrochemical oxidation of PFASs, and the low energy consumptions are much more favorable than other destructive treatment technologies (i.e., ultrasonication, photocatalysis, vacuum UV photolysis, microwave-hydrothermal decomposition), demonstrating the promise of the REM technology for PFAS treatment. In order to determine the full feasibility of this technology, further research and development is needed, which includes 1) reactor scale-up/optimization; 2) impact of co-contaminants; 3) longevity studies; and 4) life cycle and cost assessments. Completion of this follow-on research is needed before the REM technology can be confidently deployed to remediation sites.

Executive Summary

Introduction

PFASs, including perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS), originating from aqueous film forming foams (AFFFs) pose a serious human health risk. Therefore, the USEPA has established a 70 ng L⁻¹ lifetime health advisory level for PFOA and PFOS,² and several states have set even lower standards (e.g., California and New Jersey: 14 ng L⁻¹ for PFOA and 13 ng L⁻¹ for PFOS).³ The removal of these compounds from groundwater is complicated by low volatility and general lack of reactivity to biodegradation and traditional oxidative treatment processes (e.g., advanced oxidation processes, UV photolysis).⁴ As a result, treatment strategies have mainly used GAC and other sorbents for PFAS removal.⁵⁻¹¹ However, studies have found that desorption of PFASs from GAC (and other sorbents) was nearly irreversible using conventional regeneration methods,⁵ which greatly increases the costs associated with adsorbent-based treatment strategies. PFAS-contaminated groundwater also often contains other co-contaminants, including hydrocarbon surfactants originating from the AFFFs, chlorinated solvents, solvent stabilizers, and fuel components. Therefore, effective remediation technologies should be capable of the simultaneous removal of this diverse group of contaminants, which will be beneficial for on-site treatment of IDWs.

Here, we describe an innovative, destructive treatment strategy for the remediation of PFAS-contaminated IDWs. We have designed a novel REM system that is capable of electrochemical destruction of PFASs and associated co-contaminants. A successful proof of concept of the REM technology will be transformative for groundwater remediation, as it will show that a single, compact technology is capable of providing cost-effective remediation of PFASs in groundwater samples. However, there are several technological challenges that must be met in order to establish proof of concept. These challenges include: 1) demonstration of destructive PFAS removal in IDW water samples to < 70 ng L⁻¹; 2) optimization of the operational mode; and 3) low energy consumption compared to other destructive treatment methods. Overcoming these challenges will indicate that the REM is a viable PFAS remediation technology, where additional research and development focused on scale-up and pilot testing could lead to large-scale treatment systems for site-wide remediation.

Objectives

The proposed research was focused on the development of a novel reactive electrochemical membrane (REM) treatment system for the remediation of perfluoroalkyl substances (PFASs) in liquid samples that were generated from subsurface investigations of PFAS contamination at groundwater sites, known as investigation-derived waste (IDW). Thus, this research is directly in line with the objectives of the SERDP Statement of Need (ERSON-18-L1). The REM technology was developed with consideration towards technical effectiveness, cost effectiveness, and compactness and mobility of the treatment system. The completed Limited Scope project has produced proof-of-concept data that indicates that a REM-based remediation strategy is a viable option for the treatment of IDW liquid samples. The overall objective of this work was to utilize a cost-effective REM for the removal of PFASs from liquid IDW samples collected at contaminated groundwater sites. Specific technical objectives associated with this project included: 1) development of REMs for destructive PFAS removal in IDW water samples to < 70 ng L⁻¹; 2) determination of the optimal operational mode; and 3) calculation of energy requirements for the REM-based system for comparison to other technologies. These objectives were accomplished in this work and thus we have established proof of concept that the REM system is a viable technology for PFAS remediation. Therefore, we are seeking a follow-on project to develop a pilot-scale treatment system to test the long-term effectiveness of PFAS remediation in IDW samples. Deliverables of this follow-on research include: 1) a scaled-up optimized reactor, 2) durable REMs with a projected lifetime of > 10 years; and 3) cost and life cycle assessments for comparison to other technologies. A specific focus of the follow-on research will be to characterize short-chain

PFAS that are produced during REM treatment and to either optimize REM operational parameters to eliminate these products or couple the REM to other post treatment strategies. These deliverables will allow practitioners to evaluate this new technology for implementation at PFAS-contaminated DoD sites, with the goal of creating on-site disposal options to lower the cost of site management.

Technical Approach

The work performed during this project consisted of REM synthesis, a series of bench-scale experimental studies, and a preliminary energy cost assessment. The six PFAS compounds on the USEPA UCMR-3 list were investigated, which included perfluorooctanoic acid (PFOA), perfluorooctanesulfonic acid (PFOS), perfluorononanoic acid (PFNA), perfluorohexanesulfonic acid (PFHxS), perfluoroheptanoic acid (PFHpA), and perfluorobutanesulfonic acid (PFBS). A specific focus on treatment of PFOS and PFOA was made, which allowed comparison of results to the existing literature. Experimental parameters that were explored included: 1) adsorption capacity; 2) necessary residence time in the reactor; 3) reactor operational mode; and 4) energy usage (kWh m^{-3} per log removal of PFAS).

Results and Discussion

Overview of Results. The Limited Scope project had four specific milestones which were used to determine if proof of concept was met. These four milestones and a brief discussion of the primary results are discussed below:

- **Milestone 1:** *Synthesis of sorbent-loaded REMs with high sorption capacities for PFASs (> 10 mg/g of sorbent)*

Results: Sorbed-loaded REMs were synthesized containing MWCNTs and PAC. Although the addition of these sorbent materials resulted in a significant increase in the adsorption of PFAS, they were found to be unstable during anodic polarization. Therefore, the anticipated strategy of using the sorbent-loaded REMs for a 'trap and zap' treatment approach was not explored in further detail. However, preliminary experiments were conducted that indicates that electrosorption of PFOA on to the MWCNT-REM was significantly higher than the REM. These results suggest that an electrosorption step may be included before electrochemical oxidation to concentrate PFASs, but the concept was not explored in detail as it was not a primary focus of the project.

- **Milestone 2:** *Demonstrate the ability of REMs to remove PFASs from an initial concentration of > 400 $\mu\text{g L}^{-1}$ to below the treatment goal of 70 ng L^{-1} in synthetic/real groundwater samples*

Results: This milestone was achieved in both synthetic samples for PFOA and PFOS and for real groundwater samples for a mixture of PFASs.

- **Milestone 3:** *Determination of the most energy efficient operational strategy for PFAS removal in groundwater*

Results: The most efficient operational strategy for PFAS removal from groundwater was found to be a recycle-mode with a high permeate flux. This mode of operation could achieve the treatment goal stated in Milestone 1 for a mixture of PFASs present in groundwater.

- **Milestone 4:** *Determination of the energy costs for achieving the 70 ng L^{-1} treatment goal in PFAS-contaminated groundwater with a target energy usage of < 2.0 kWh m^{-3} of water treated*

Results: An energy usage of 2.9 kWh m^{-3} per log removal of PFAS was measured for the mixture of PFASs in groundwater with the REM operated in recycle-mode. Although this value is slightly higher than the goal, further optimization of the reactor design (e.g., electrode spacing, fluid dynamics) should allow much lower energy consumptions to be realized.

Overall, proof of concept was established, and we are confident that further research into reactor design and process optimization will lead to achieving the energy usage goal (**milestone 4**). It should be noted that the reported energy usage values in our work are the

lowest reported for electrochemical oxidation and approximately an order of magnitude lower than those reported for other destructive technologies (i.e., ultrasonication, photocatalysis, vacuum UV photolysis, microwave-hydrothermal decomposition). The complete results of this project are discussed below in further detail.

PFOA and PFOS Oxidation in Synthetic Solutions. Work in this section focused on **Milestone 2: Demonstrate the ability of REMs to remove PFASs from an initial concentration of $> 400 \mu\text{g L}^{-1}$ to below the treatment goal of 70 ng L^{-1} in synthetic/real groundwater samples.**

The results shown in this section were recently published in *Environmental Science and Technology Letters*.¹ PFOA and PFOS were chosen as model PFASs to test the effectiveness of the REM for electrochemical oxidation. The effect of the applied anodic potential on PFOA/PFOS degradation using the REM at a flux of 240 LMH is shown in **Figure E1**. Oxidation experiments for PFOA were performed at the OCP to 3.3 V/SHE (**Figure E1a**) and for PFOS at the OCP to 3.6 V/SHE (**Figure E1b**). Nearly complete removal was achieved for both compounds in a single pass through the REM with residence times of 11.3 s (3.3 V/SHE

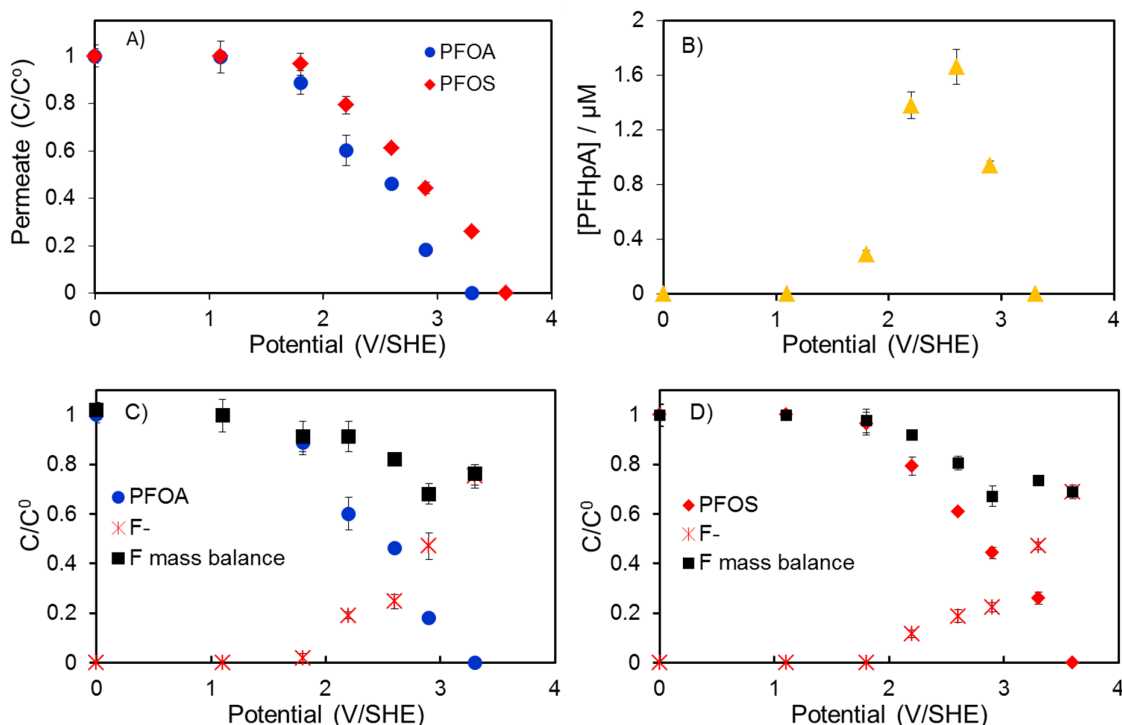


Figure E1. (a) Concentration profile of permeate during the oxidation of PFOA and PFOS on Ti_4O_7 REM. (b) Concentration of PFHpA formed from PFOA oxidation. Fluoride mass balance as a function of potential for (c) PFOA, and (d) PFOS at $J = 240 \text{ LMH}$. (Electrolyte = $100 \text{ mM K}_2\text{HPO}_4$). Concentrations were normalized by initial PFAS concentration. Error bars represent standard deviations about mean values and are contained within data points for some data.¹

for PFOA and 3.6 V/SHE for PFOS). The maximum removal for PFOA was achieved at 3.3 V/SHE with a 4.7 ± 0.05 -log removal and permeate concentrations were below the analytical detection limit (86 ng L^{-1}). The maximum removal for PFOS was achieved at 3.6 V/SHE with a 5.2 ± 0.02 -log removal, and permeate concentrations were below the analytical detection limit (35 ng L^{-1}). The detection limits for PFOA/PFOS were on order with the 70 ng L^{-1} lifetime health advisory level established by the USEPA,² which achieved the goal set forth by **Milestone 2**. However, the permeate concentrations were still higher than standards set forth by several states (e.g., California and New Jersey: 14 ng L^{-1} for PFOA and 13 ng L^{-1} for PFOS).³

The formation of F^- ions was used to calculate the defluorination ratio of PFOA/PFOS (i.e., $[F^- \text{ formed}]/[F \text{ in initial PFAS}] \times 100$) and values were up to $75.3 \pm 4.7 \%$ for PFOA (**Figure E1c**) and $68.9 \pm 2.7 \%$ for PFOS (**Figure E1d**). The total fluorine mass balance was calculated (i.e., $\{[F^-]_{\text{in solution}} + [F]_{\text{in PFAS}}\} / [F]_{\text{in PFAS, initial}}$) and ranged between 68.1 ± 4.1 to $99.7 \pm 0.3 \%$ for PFOA (**Figure E1c**) and between 67.2 ± 4.1 to $99.8 \pm 0.2 \%$ for PFOS (**Figure E1d**). The only fluorocarbon product detected during experiments was perfluoroheptanoic acid (PFHpA) during PFOA oxidation (**Figure E1b**). The maximum concentration of PFHpA formed at a potential of 2.6 V/SHE and decreased at higher potentials, which was attributed to a lowering

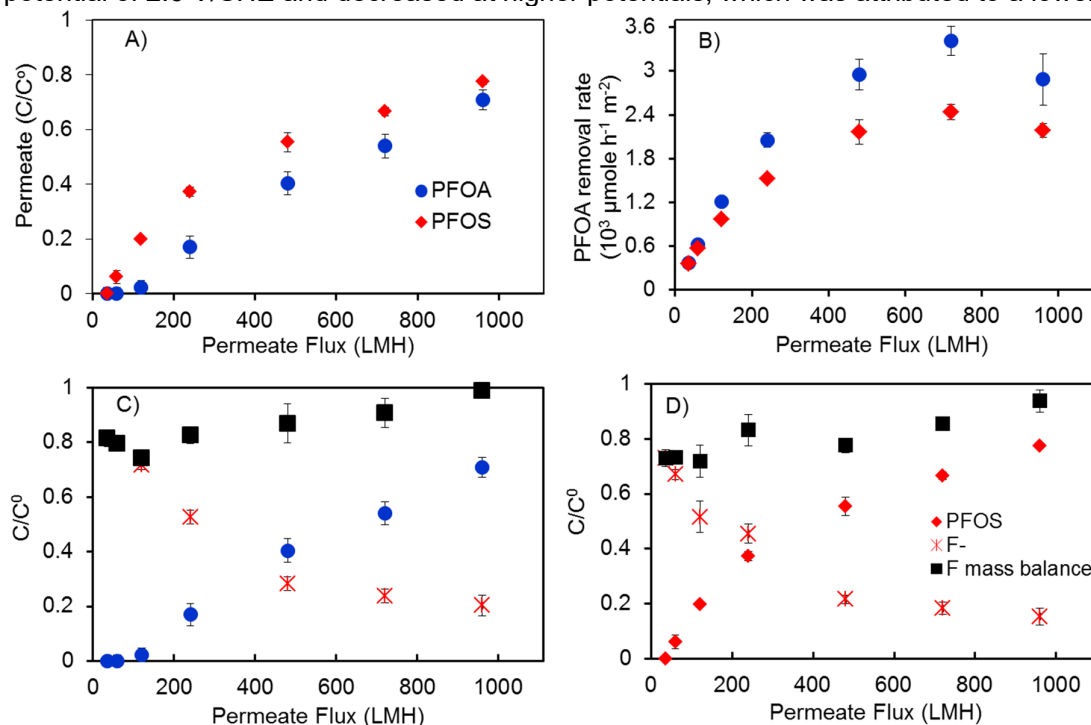


Figure E2. (a) Concentration profile of permeate, (b) Removal rate of PFOA/PFOS during the oxidation on Ti_4O_7 REM at different membrane fluxes. Fluoride mass balance as a function of membrane flux of (c) PFOA, and (d) PFOS (V anode = 2.9 V/SHE, Electrolyte = 100 mM K_2HPO_4). Error bars represent standard deviations about mean values and are contained within data points for some data.¹

of the activation energy for PFHpA oxidation at higher potentials. The fact that the mass balance was $< 100\%$ indicates that shorter chain volatile PFAS products likely formed, which were not analyzed by LC-MS.^{12,13}

Results for the electrochemical oxidation of PFOA/PFOS at a constant anodic potential of 2.9 V/SHE and with different membrane fluxes ($J = 36$ to 960 LMH) are shown in **Figure E2**. These membrane fluxes gave residence times between 75 to 2.8 s. The highest conversions for both compounds were found at $J = 36$ LMH, which again achieved approximately 5-log removal for both compounds (liquid residence time = 75 s). **Figure E2b** contains the calculated PFAS removal rates as a function of J . The maximum removal rates for PFOA/PFOS were obtained at $J = 720$ LMH, with $R_r = 3415 \pm 203 \mu\text{mol m}^{-2} \text{h}^{-1}$ for PFOA and $R_r = 2436 \pm 106 \mu\text{mol m}^{-2} \text{h}^{-1}$ for PFOS. Reaction rate constants were also calculated based on the conversion of PFOA/PFOS as a function of liquid residence time in the REM. Results indicated that the reactions were pseudo first-order, with surface area normalized observed rate constants (k_{obs}) of $1.3 \times 10^{-4} \text{ m s}^{-1}$ for PFOA and $4.4 \times 10^{-5} \text{ m s}^{-1}$ for PFOS. These k_{obs} values were over an order of magnitude higher than previously reported results with Ti_4O_7 and BDD anodes.^{14,15} These significantly improved results were attributed to the flow-through mode operation, which enhanced mass transfer and utilized the high specific surface area of the REM (i.e., $1.3 \times 10^6 \text{ m}^{-1}$). In addition, non-normalized observed reaction rate constants for

this data were calculated as 607 h⁻¹ for PFOA and 210 h⁻¹ for PFOS. These values are more than two orders of magnitude higher than those reported by other destructive technologies (i.e, ultrasonication, photocatalysis, vacuum UV photolysis, microwave-hydrothermal decomposition).¹⁶⁻¹⁹

The defluorination ratios as a function of J were between 20.3% $\pm$ 3.8 at 960 LMH to 81.4% $\pm$ 3.2 at 36 LMH for PFOA (**Figure E2c**) and between 15.5 $\pm$ 2.2 % at 960 LMH to 72.9 $\pm$ 3.1 % at 36 LMH for PFOS (**Figure E2d**). The total fluorine mass balance ranged between 74.1 $\pm$ 0.07 to 98.6 $\pm$ 0.16 % for PFOA (**Figure E2c**) and between 71.7 $\pm$ 5.8 % to 93.8 $\pm$ 4.1 % for PFOS (**Figure E2d**).

PFAS Oxidation in Groundwater Samples. Work in this section focused on addressing Milestones 2 and 3.

Milestone 2: Demonstrate the ability of REMs to remove PFASs from an initial concentration of > 400 $\mu\text{g L}^{-1}$ to below the treatment goal of 70 ng L^{-1} in synthetic/real groundwater samples.

Milestone 3: Determination of the most energy efficient operational strategy for PFAS removal in groundwater.

Two groundwater samples (GW1 and GW2) were treated with the REMs. The general water quality analyses for these samples are shown in **Table E1**. The GW1 sample was collected by Geosyntec Consultants from a client's site in Jacksonville, Florida and did not contain detectable concentrations of PFASs. This sample was spiked with the six different PFASs at concentrations between 1.0 to 2.5 μM . These initial concentrations are shown in **Figure E3** (OCP/Feed data). This experiment was conducted at low flux ($J = 60$ LMH), which gave a hydraulic residence time of $t_r = 45$ s. Control experiments (OCP data) were not significantly different than the original feed samples, indicating that adsorption was minimal. In general, results show the accumulation of shorter chain PFASs (e.g., PFBS, PFHpA, PFHxS), presumably from the oxidation of longer chain PFASs (e.g., PFNA, PFOS). At the highest cell potentials tested (e.g., 8.1 and 10.5 V) total PFAS removal was ~50% (**Figure E3**). The lack of total removal of PFASs was attributed to

Table E1. General water quality analyses for groundwater samples.

Constituent	GW1 mg/L	GW2 mg/L
F ⁻	1.06	15.7
Cl ⁻	51.5	27.1
NO ₃ ⁻	8.18	175
SO ₄ ²⁻	10.8	< 0.1
HPO ₄ ²⁻	7.78	< 0.1
HCO ₃ ⁻	228	87.7
Na ⁺	72.6	25.3
K ⁺	13.7	30.1
Ca ²⁺	25.7	34.5
Mg ²⁺	21.4	8.75
pH	6.8	6.5
Conductivity ($\mu\text{S/cm}$)	788	337
COD (mg/L)	43.3	4.35
Alkalinity (mg/L CaCO ₃)	373	144

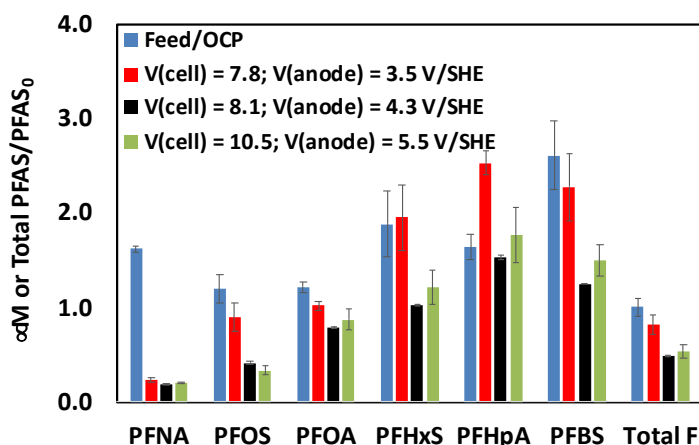


Figure E3. PFAS and total F removal in GW1 sample as a function of cell potential. $J = 60$ LMH

the presence of background organic compounds (COD = 43.3 mg/L) and low solution conductivity (**Table E1**). The background organic compounds can compete with PFASs for reactive sites on the REM, and the low conductivity caused a significant potential drop in solution and therefore reduced the reactive thickness of the REM.

The GW2 sample was obtained from Willow Grove Naval Base in collaboration with Jason

Speicher. The general water quality parameters are shown in Table 1 and PFAS concentrations are shown in **Figure E4a** (Feed/OCP data). Control experiments (OCP data) were not significantly different than the original feed samples, indicating that adsorption was minimal. Operation of the REM in single-pass mode with a low flux ($J = 60$ LMH) resulted in approximately 55% total PFAS removal (**Figure E3a**). Once again, longer chain PFASs were oxidized to shorter chain PFASs, and the background COD and low conductivity inhibited complete oxidation. In order to increase the oxidation rate, the operational mode of the REM was switched to recycle mode. In this mode of operation the solution was continuously recycled through the REM until the target removal was achieved. A flux ($J = 720$ LMH) was chosen that corresponded to the maximum rate observed for PFOA/PFOS oxidation experiments (see **Figure E2b**). Individual final PFAS concentrations were < 61 ng/L and total PFAS concentrations were 274 ng L^{-1} (**Figure E4b**). The percent removals for individual and total PFAS are shown in **Figure E5** and indicate that total PFAS destruction was $> 99\%$. These results indicate that a recycle mode operation with high flux is needed to improve mass transfer and increase contact time with the REM, which resulted in effective oxidation of

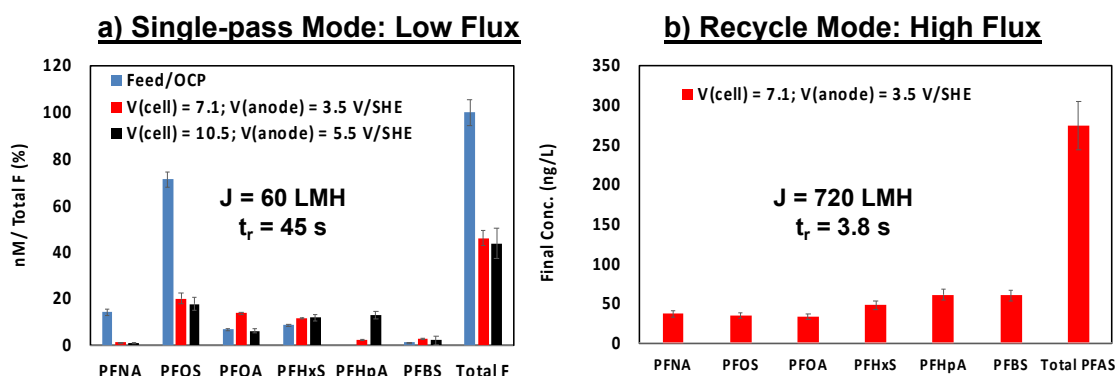


Figure E4. Comparison of electrochemical oxidation of PFASs in GW2 in single-pass versus recycle modes.

PFASs in the groundwater solution. **These experiments achieved both Milestones 2 and 3, as stated above.**

Energy Requirements. Work in this section focused on addressing **Milestone 4: Determination of the energy costs for achieving the 70 ng L^{-1} treatment goal in PFAS-contaminated groundwater with a target energy usage of < 2.0 kWh m^{-3} (per log removal) of water treated.**

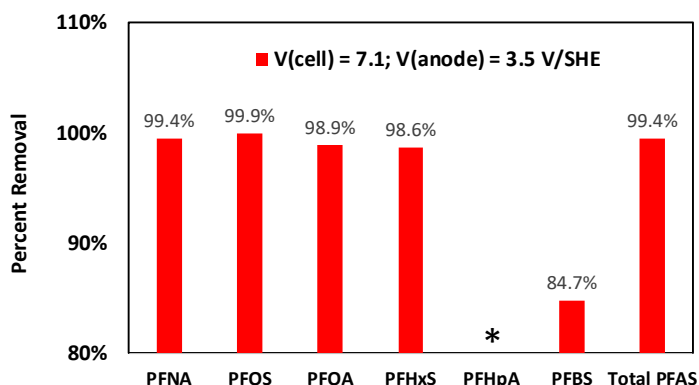


Figure E5. Percent removal of PFAS compounds in GW2.

*PFHpA was not detected in the feed solution, but was produced during treatment to a final concentration of 60 ng/L.

A key issue associated with destructive PFAS remediation technologies is the operational cost. While a complete analysis of operating costs for PFAS remediation technologies could not be found in the existing literature, we have recently summarized the energy consumption per log-removal for various novel technologies for PFOA/PFOS degradation,²⁰ which is also summarized in the Appendix (Table A1). Remediation

technologies that were reviewed include sonolysis,^{16,21,22,23} microwave-hydrothermal,¹⁷ photolysis,²⁴⁻²⁶ photocatalysis,^{27,28,29} and electrochemical oxidation.^{12,14,20,30-38} Direct electrochemical oxidation of PFAS is by far the most energy efficient destructive method reported to date (5 – 132 kWh m⁻³).^{20,30,38,39} Porous Magnéli phase Ti₄O₇ ceramic anodes have shown the lowest energy consumption of 5 kWh/m³ for PFOA and between 6.7 to 32 kWh/m³ for PFOS,^{20,38} further demonstrating the promise of this technology. In this study, the electrode energy requirements for the Ti₄O₇ REM anode to remove 10 µM initial concentrations of PFOA and PFOS to below the detection limits (86 ng L⁻¹ for PFOA and 35 ng L⁻¹ for PFOS) were 5.1 ± 0.1 and 6.7 ± 0.2 kWh m⁻³, respectively. Additionally, it was found that the groundwater samples required 13 – 24 kWh m⁻³ to treat GW1 and 11 – 15 kWh m⁻³ to treat GW2 in single-pass mode. The energy usage decreased to 2.9 kWh m⁻³ to treat GW2 in recycle mode, which was able to decrease individual PFASs to < 61 ng/L. Although the lowest energy consumption observed during this project (i.e., 2.9 kWh m⁻³) was 45% higher than the 2.0 kWh m⁻³ goal, this energy consumption value is the lowest reported in the literature and shows the extreme promise of the REM technology. Further optimization of reactor design and operation will undoubtedly lower the energy consumption of the REM.

Implications for Future Research and Benefits

The high rate constants reported above are the highest reported for electrochemical oxidation of PFASs, and the low energy consumptions are much more favorable than other destructive treatment technologies (i.e, ultrasonication, photocatalysis, vacuum UV photolysis, microwave-hydrothermal decomposition), demonstrating the promise of the REM technology for PFAS treatment. In order to determine the full feasibility of this technology, further research and development is needed, which includes 1) reactor scale-up/optimization; 2) impact of co-contaminants; 3) longevity studies; and 4) life cycle and cost assessments. Completion of this follow-on research is needed before the REM technology can be confidently deployed to remediation sites.

1.0 Objectives

The proposed research was focused on the development of a novel reactive electrochemical membrane (REM) treatment system for the remediation of perfluoroalkyl substances (PFASs) in liquid samples that were generated from subsurface investigations of PFAS contamination at groundwater sites, known as investigation-derived waste (IDW). Thus, this research is directly in line with the objectives of the SERDP Statement of Need (ERSON-18-L1). The REM technology was developed with consideration towards technical effectiveness, cost effectiveness, and compactness and mobility of the treatment system. The completed Limited Scope project has produced proof-of-concept data that indicates that a REM-based remediation strategy is a viable option for the treatment of IDW liquid samples.

The overall objective of this work was to utilize a cost-effective REM for the removal of PFASs from liquid IDW samples collected at contaminated groundwater sites. Specific technical objectives associated with this project included: 1) development of REMs for destructive PFAS removal in IDW water samples to $< 70 \text{ ng L}^{-1}$; 2) determination of the optimal operational mode; and 3) calculation of energy requirements for the REM-based system for comparison to other technologies. These objectives were accomplished in this work and thus we have established proof of concept that the REM system is a viable technology for PFAS remediation. Therefore, we are seeking a follow-on project to develop a pilot-scale treatment system to test the long-term effectiveness of PFAS remediation in IDW samples. Deliverables of this follow-on research include: 1) a scaled-up optimized reactor, 2) durable REMs with a projected lifetime of > 10 years; and 3) cost and life cycle assessments for comparison to other technologies. These deliverables will allow practitioners to evaluate this new technology for implementation at PFAS-contaminated DoD sites, with the goal of creating on-site disposal options to lower the cost of site management.

2.0 Background

2.1 Introduction. PFASs, including perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS), originating from aqueous film forming foams (AFFFs) pose a serious human health risk. Therefore, the USEPA has established a 70 ng L^{-1} lifetime health advisory level for PFOA and PFOS,² and several states have set even lower standards (e.g., California and New Jersey: 14 ng L^{-1} for PFOA and 13 ng L^{-1} for PFOS).³ The removal of these compounds from groundwater is complicated by low volatility and general lack of reactivity to biodegradation and traditional oxidative treatment processes (e.g., advanced oxidation processes, UV photolysis).⁴ As a result, treatment strategies have mainly used GAC and other sorbents for PFAS removal.⁵⁻¹¹ However, studies have found that desorption of PFASs from GAC (and other sorbents) was nearly irreversible using conventional regeneration methods,⁵ which greatly increases the costs associated with adsorbent-based treatment strategies. PFAS-contaminated groundwater also often contains other co-contaminants, including hydrocarbon surfactants originating from the AFFFs, chlorinated solvents, solvent stabilizers, and fuel components. Therefore, effective remediation technologies should be capable of the simultaneous removal of this diverse group of contaminants, which will be beneficial for on-site treatment of IDWs.

Here, we describe an innovative, destructive treatment strategy for the remediation of PFAS-contaminated IDWs. We have designed a novel REM system that is capable of electrochemical destruction of PFASs and associated co-contaminants. A successful proof of concept of the REM technology will be transformative for groundwater remediation, as it will show that a single, compact technology is capable of providing cost-effective remediation of PFASs in groundwater samples. However, there are several technological challenges that must be met in order to establish proof of concept. These challenges include: 1) demonstration of destructive PFAS removal in IDW water samples to $< 70 \text{ ng L}^{-1}$; 2) optimization of the operational mode; and 3) low energy consumption compared to other destructive treatment methods. Overcoming these challenges will indicate that the REM is a viable PFAS remediation technology, where additional research and development focused on scale-up and pilot testing could lead to large-scale treatment systems for site-wide remediation.

2.2 Reactive Electrochemical Membrane Overview. In this project we have investigated the technical and economic feasibility of using REMs for treatment of liquid IDWs containing PFASs. A schematic of one possible configuration of a REM unit is shown in **Figure 1**. The concentric porous cathode/anode tubes shown in **Figure 1** are made of solid Ti_4O_7 (25 mm cathode OD; 200 mm long; pore size $\sim 1.0 \mu\text{m}$; porosity $\sim 30\%$). The anode and cathode are separated by inert 1 mm thick Viton® o-rings (not shown in figure). This configuration results in minimal electrode spacing (1 mm) and limits power consumption associated with solution resistance. Depending on the treatment objective or the need to remove carbonate scale from the cathode, the anode and cathode can be switched by changing the polarity of the direct current (DC) voltage, without any physical manipulation of the device.

Figure 1 illustrates the use of the REM system for remediation of PFAS-contaminated water in the presence of trichloroethene (TCE) as a co-contaminant. In this configuration TCE is dechlorinated on the cathode to dichloroethene (DCE), then vinyl chloride (VC), and finally to ethene, according to reaction scheme 1.

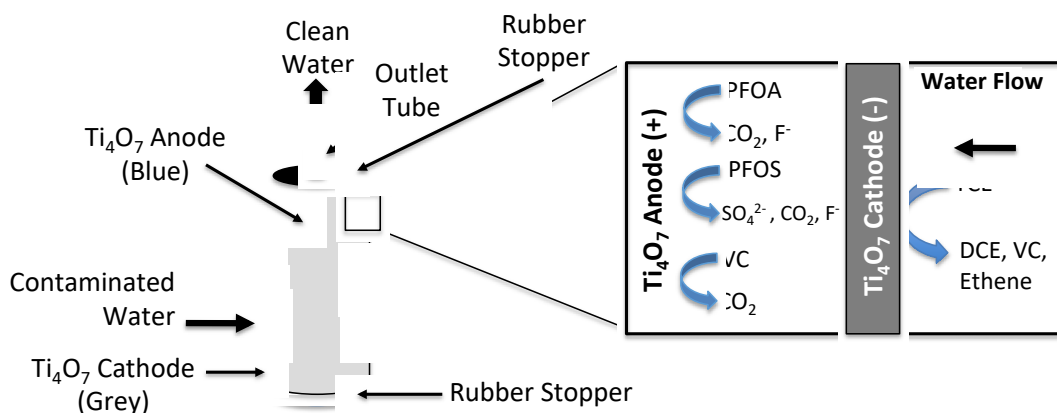
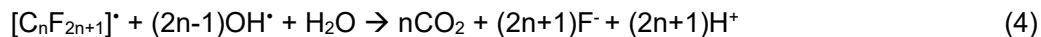


Figure 1. Schematic of a concentric cylindrical REM used for the treatment of PFASs (PFOS, PFOA) in the presence of TCE as a co-contaminant. Dechlorination reactions occur on the cathode, and oxidation of PFASs and cathodic products occur on the anode. Flow configuration is outside-in, dead end, filtration mode.

Residual TCE, DCE, VC, and ethene that may pass through the cathode are oxidized on the anode by a combination of direct electron transfer reactions and reactions with electrochemically generated hydroxyl radicals ($\text{OH}^\bullet$) (reaction 2).



The anodic reaction pathway for PFASs is given in reactions 3 and 4, where X is the functional group (e.g., $\text{X} = \text{COO}$ for PFOA and $\text{X} = \text{SO}_3$ for PFOS).



PFAS oxidation is initiated by a direct electron transfer reaction according to reaction (3), which has been reported to occur at potentials exceeding 2.2 and 2.7 V/SHE for PFOA and PFOS, respectively.^{40,41} The direct electron transfer reaction step is critical, since it has been shown that PFASs are unreactive with $\text{OH}^\bullet$.^{22,42} Once the direct electron transfer reaction occurs, complete mineralization with $\text{OH}^\bullet$ can proceed according to reaction (4).⁴³

Past electrochemical oxidation studies have focused on PFAS removal using parallel plate reactors in recycle mode, where the removal rates were limited primarily by mass transfer to the electrode surface, corresponding to low specific surface area normalized rate constants ($k_{\text{obs}} \sim 1 \times 10^{-5} \text{ m s}^{-1}$).³⁹ Due to the interconnected microporous structure of the REM electrodes, we have achieved very high mass transfer rate constants, using the REM in flow-through mode, which translated to high removal rates for PFASs. This work was focused on utilizing a

novel REM for destructive electrochemical oxidation of PFASs to mineral products (i.e., F^- , CO_2 , H_2O), which will efficiently remediate IDWs and eliminate the need for off-site treatment/disposal. Electrochemical oxidation has recently been shown to be one of few oxidative treatment technologies that is effective for PFAS oxidation.^{34,41}

2.3 Electrochemical Oxidation of PFASs. The requirements for a successful electrode for PFAS oxidation are: 1) stability during anodic and cathodic polarization; 2) ability to generate $OH^\bullet$ via water oxidation; 3) electrodes should be comprised of nontoxic compounds; 4) inexpensive; and 5) ability to fabricate in porous and monolithic geometries for the development of high surface area electrodes that are needed for scale-up to contaminated sites. Very few electrode materials can meet all of these requirements. Over the past decade, the most promising electrodes for electrochemical oxidation are BDD film electrodes.⁴³ They meet the first three criteria stated above, but are prohibitively expensive ($\sim \$7125$ per m^2) (requirement 4) and it is difficult to produce BDD electrodes with complex geometries (requirement 5).⁴⁴ Recent work comparing various electrode materials (i.e., BDD, Ti_4O_7 , Pt, SnO_2) for organic compound oxidation showed that Ti_4O_7 electrodes were comparable to BDD electrodes for efficiency of organic compound oxidation,⁴⁵ but Ti_4O_7 electrodes can be synthesized at extremely low costs. For example, small laboratory batches of Ti_4O_7 electrodes synthesized in PI Chaplin's laboratory cost $\sim \$0.36$ per m^2 (materials cost), which is a fraction of the cost of BDD electrodes.⁴⁴ In recent years Ti_4O_7 electrodes have shown the ability to oxidize several different organic compounds, including recent studies focused on PFAS oxidation (including work from this project).^{1,15,45-51} Ti_4O_7 electrodes are the focal point of the proposed research, and thus are discussed in more detail in the following section.

2.4 Ti_4O_7 Electrodes. The key to developing a REM is the use of porous electrode materials. Stoichiometric titanium dioxide (TiO_2) is an insulator with an electrical conductivity of $\sim 10^{-9}$ S cm^{-1} .⁵² The electronic properties of TiO_2 can be drastically changed by creating oxygen deficiencies in the lattice structure, which is accomplished at temperatures > 900 °C and under a H_2 atmosphere.⁵² This method results in conversion of some $Ti^{(IV)}$ to $Ti^{(III)}$ and n-type semiconductor behavior. Ti_4O_7 has a measured electrical conductivity as high as 166 S cm^{-1} , many orders of magnitude greater than TiO_2 .⁵² In these sub-oxides, crystal rearrangement occurs, which minimizes point oxygen vacancies and makes the electrode very resistant to oxidation and highly suitable as stable anode materials.

The remediation potential of Ti_4O_7 electrodes are very promising, although few relevant studies have been conducted. Ti_4O_7 electrodes can produce $OH^\bullet$ via water oxidation.^{46,48,51,53,54} In contrast, other $OH^\bullet$ producing anodes, such as BDD are expensive and cannot be effectively coated onto highly porous substrates (as stated above). Additional materials that have been researched as electro-active materials for membranes include carbon nanotubes (CNTs)^{55,56} and carbon membranes (graphite) coated with electroactive catalysts.^{57,58} These materials have good electrical conductivity, but do not produce an adequate yield of $OH^\bullet$.^{59,60} Thus, they have limited usefulness for compound oxidation as they can only partially oxidize organics, leading to the formation of polymeric films that passivate the electrode surface.⁵⁹

3.0 Materials and Methods.

The materials and methods used during this project were described in detail in a recent publication, which includes the majority of the results from this project.¹ A brief description of the reactor used in this study and a discussion of additional methods for unpublished results are provided below.

3.1 Electrochemical Oxidation Experiments. Oxidation experiments were performed in a three-electrode flow-through reactor, including a 0.5 cm^2 REM as working electrode (projected surface area), a 0.33 cm^2 stainless steel (SS) as counter electrode, and a leak-free 1 mm diameter Ag/AgCl as reference electrode (Warner Instruments, LF-100). The reactor and REM preparation method used for this project was described in our prior work.⁶¹ The PFAS-containing feed solution was pumped from SS cathode to REM anode. Potential was applied

be included before electrochemical oxidation to concentrate PFASs, but the concept was not explored in detail as it was not a primary focus of the project. Detailed results associated with this milestone are included in Sections 4.2, 4.3, and 4.4.

- **Milestone 2:** *Demonstrate the ability of REMs to remove PFASs from an initial concentration of $> 400 \mu\text{g L}^{-1}$ to below the treatment goal of 70 ng L^{-1} in synthetic/real groundwater samples*
Results: This milestone was achieved in both synthetic samples for PFOA and PFOS and for real groundwater samples for a mixture of PFASs. Detailed results associated with this milestone are included in Sections 4.5 (synthetic solutions) and 4.6 (groundwater solutions).
- **Milestone 3:** *Determination of the most energy efficient operational strategy for PFAS removal in groundwater*
Results: The most efficient operational strategy for PFAS removal from groundwater was found to be a recycle-mode with a high permeate flux. This mode of operation could achieve the treatment goal stated in Milestone 1 for a mixture of PFASs present in groundwater. Detailed results associated with this milestone are included in Section 4.6.
- **Milestone 4:** *Determination of the energy costs for achieving the 70 ng L^{-1} treatment goal in PFAS-contaminated groundwater with a target energy usage of $< 2.0 \text{ kWh m}^{-3}$ of water treated*
Results: An energy usage of 2.9 kWh m^{-3} per log removal of PFAS was measured for the mixture of PFASs in groundwater with the REM operated in recycle-mode. Although this value is slightly higher than the goal, further optimization of the reactor design (e.g., electrode spacing, fluid dynamics) should allow much lower energy consumptions to be realized. Detailed results associated with this milestone are included in Section 4.7.

Overall, proof of concept was established, and we are confident that further research into reactor design and process optimization will lead to achieving the energy usage goal (milestone 4). It should be noted that the reported energy usage values in our work are the lowest reported for electrochemical oxidation and approximately an order of magnitude lower than those reported for other destructive technologies (i.e., ultrasonication, photocatalysis, vacuum UV photolysis, microwave-hydrothermal decomposition). The complete results of this project are discussed below in further detail.

Work in the following three sections focused on addressing **Milestone 1: Synthesis of sorbent-loaded REMs with high sorption capacities for PFASs ($> 10 \text{ mg/g}$ of sorbent)**.

4.2 REM Characterization. The electrodes used in this study were defined as follows: 100% Ti_4O_7 pellet (REM), 10 wt% PAC 90 wt% Ti_4O_7 pellet (PAC-REM), and 10 wt% MWCNT 90 wt% Ti_4O_7 pellet (MWCNT-REM) and were characterized in prior work.⁶² Results indicated that the REMs contained high purity Ti_4O_7 , and Raman spectroscopy analysis indicated that the carbonaceous content was not sufficiently altered during the synthesis process.⁶² The average DI water permeabilities were $806 \pm 14 \text{ L m}^{-2} \text{ hr}^{-1} \text{ bar}^{-1}$ (LMH bar^{-1}) for REM, $589 \pm 16 \text{ LMH bar}^{-1}$ for PAC-REM, and $290 \pm 13 \text{ LMH bar}^{-1}$ for MWCNT-REM.⁶² Conductivity measurements were $935 \pm 14 \text{ S m}^{-1}$ for REM, $1832 \pm 19 \text{ S m}^{-1}$ for PAC-REM, and $2991 \pm 37 \text{ S m}^{-1}$ for MWCNT-REM.⁶² The effective average pore size for REM, PAC-REM, and MWCNT-REM were $0.35 \pm 0.05 \mu\text{m}$, $0.30 \pm 0.04 \mu\text{m}$, and $0.20 \pm 0.04 \mu\text{m}$, respectively.⁶²

4.3 REM Electrochemical Stability. Prior work has shown that Ti_4O_7 is stable during anodic polarization.⁶³ However, the electrochemical stability of the PAC-REM and MWCNT-REM materials have not been investigated. The electrochemical stability of the PAC-REM and MWCNT-REM materials were tested as a function of the applied anodic potential. These experiments were conducted in the flow-through reactor shown in **Figure 2** and effluent

solution from the reactor was collected as a function of potential. Results are summarized in **Figure 3**. Results for the PAC-REM indicated that it began to oxidize at applied potential

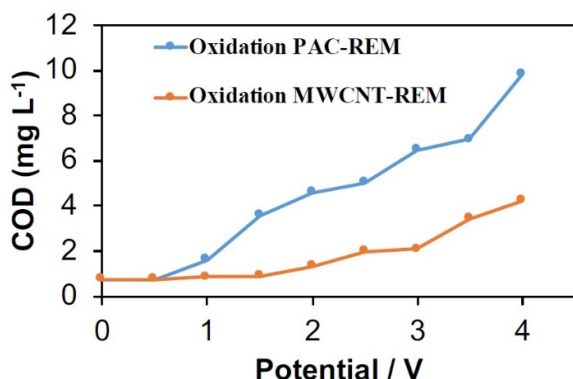


Figure 3. COD permeate concentrations for PAC-REM and MWCNT-REM as a function of the anodic potential (V/SHE). Flow rate = 240 LMH

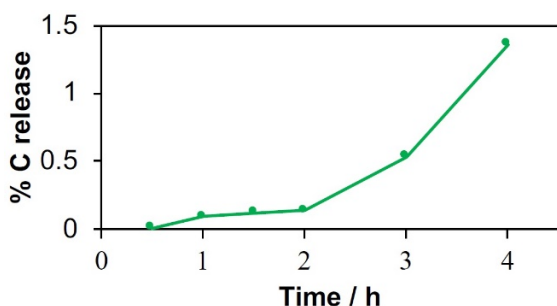


Figure 4. Percent carbon leaching for the MWCNT-REM at a potential of 3.0 V/SHE as a function of time. Flow rate = 240 LMH

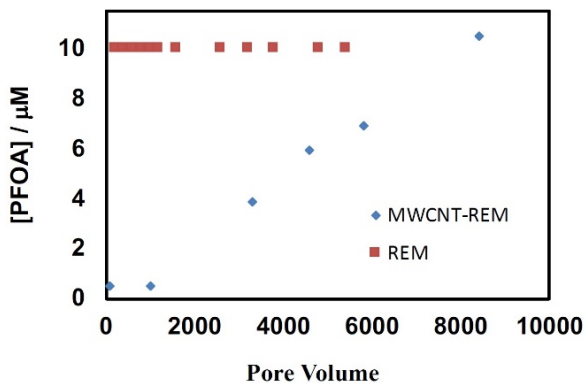


Figure 5. PFOA effluent concentrations as a function of pore volumes processed in the REMs with an applied potential of 0.5 V/SHE. Influent PFOA concentration of 10 μM and a flow rate of 240 $\text{L m}^{-2} \text{h}^{-1}$.

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. Results for the MWCNT-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 (i.e., does leaching slow with time), an additional experiment was conducted at 3.0 V/SHE over a four-hour period. Results are shown in **Figure 4** 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. Upstream adsorption followed by downstream oxidation is being explored.

4.4 Electrostatic PFAS Adsorption.

Electrostatic adsorption of PFOA was investigated to determine if an adsorption step prior to electrochemical oxidation could be used to concentrate PFASs prior to electrochemical oxidation. Two flow-through electrode materials were investigated, including a Ti_4O_7 REM and a MWCNT- Ti_4O_7 REM. These REMs were polarized at an anodic potential of 0.5 V/SHE, which was a potential where the MWCNT-REM was stable.

Results are shown in **Figure 5** and indicate that the Ti_4O_7 REM did not provide any adsorption capacity for PFOA. However, significant adsorption was observed for the MWCNT-REM. PFOA breakthrough occurred at over 2000 pore volumes and effluent concentrations did not reach influent concentration until approximately 10000 pore volumes. These results indicate

that after further optimization an electrosorption step prior to electrochemical oxidation could prove to be an effective treatment strategy for PFAS remediation, but since it was not a major task of this project, further optimization was not pursued at this time.

4.5 PFOA and PFOS Oxidation in Synthetic Solutions. Work in this section focused on **Milestone 2: Demonstrate the ability of REMs to remove PFASs from an initial concentration of $> 400 \mu\text{g L}^{-1}$ to below the treatment goal of 70 ng L^{-1} in synthetic/real groundwater samples.**

The results shown in this section were recently published in *Environmental Science and Technology Letters*.¹ PFOA and PFOS were chosen as model PFASs to test the effectiveness of the REM for electrochemical oxidation. The effect of the applied anodic potential on PFOA/PFOS degradation using the REM at a flux of 240 LMH is shown in **Figure 6**. Oxidation experiments for PFOA were performed at the OCP to 3.3 V/SHE (**Figure 6a**) and for PFOS at the OCP to 3.6 V/SHE (**Figure 6b**). Nearly complete removal was achieved for both

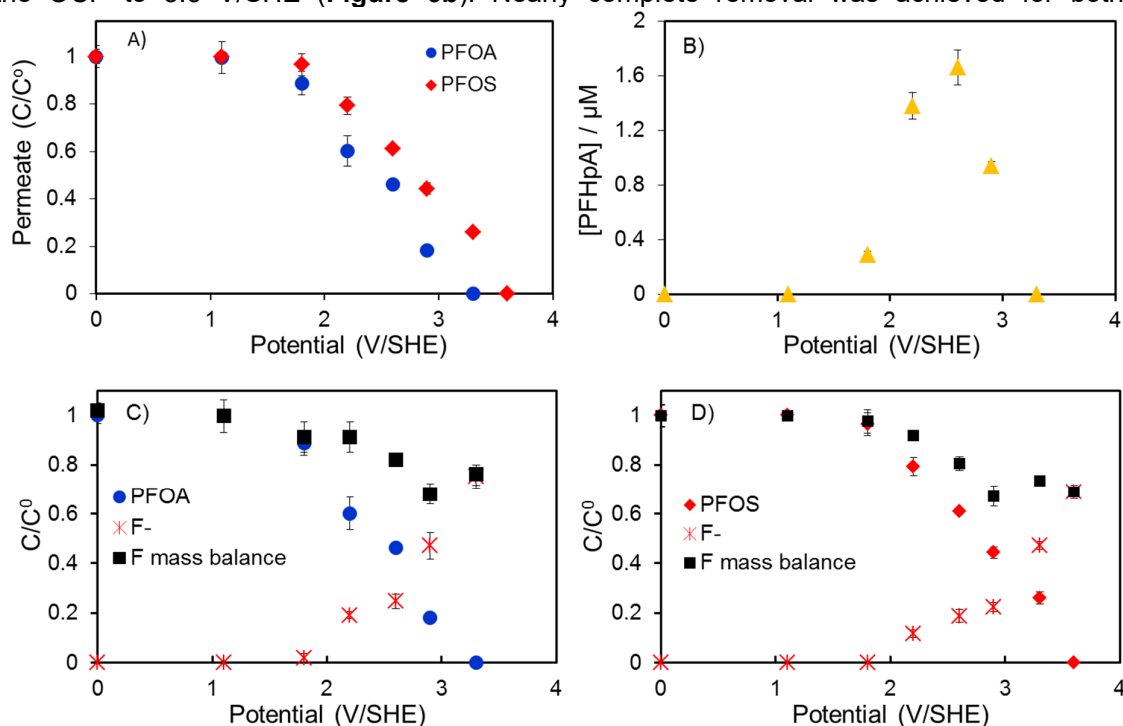


Figure 6. (a) Concentration profile of permeate during the oxidation of PFOA and PFOS on Ti_4O_7 REM. (b) Concentration of PFHpA formed from PFOA oxidation. Fluoride mass balance as a function of potential for (c) PFOA, and (d) PFOS at $J = 240 \text{ LMH}$. (Electrolyte = $100 \text{ mM K}_2\text{HPO}_4$). Concentrations were normalized by initial PFAS concentration. Error bars represent standard deviations about mean values and are contained within data points for some data.¹

compounds in a single pass through the REM with residence times of 11.3 s (3.3 V/SHE for PFOA and 3.6 V/SHE for PFOS). The removal of PFOA was 39.8 ± 6.5 , 53.7 ± 0.2 , and 81.8 ± 2.0 % at anodic potentials of 2.2, 2.6 and 2.9 V/SHE, respectively. The maximum removal for PFOA was achieved at 3.3 V/SHE with a 4.7 ± 0.05 -log removal and permeate concentrations were below the analytical detection limit (86 ng L^{-1}). For PFOS, the removal was 20.7 ± 4.5 , 38.9 ± 0.6 , 55.7 ± 5.3 , and 73.9 ± 0.4 % at anodic potentials of 2.2, 2.6, 2.9, and 3.3 V/SHE, respectively. The maximum removal for PFOS was achieved at 3.6 V/SHE with a 5.2 ± 0.02 -log removal, and permeate concentrations were below the analytical detection limit (35 ng L^{-1}). The detection limits for PFOA/PFOS were on order with the 70 ng L^{-1} lifetime health advisory level established by the USEPA,² which achieved the goal set forth by **Milestone 2**. However, the permeate concentrations were still higher than standards set forth by several states (e.g., California and New Jersey: 14 ng L^{-1} for PFOA and 13 ng L^{-1} for PFOS).³ For all anodic potentials tested, PFOA showed higher conversion compared to PFOS, which is consistent with previous experimental and theoretical studies.³⁹ In addition, the observed removal of PFOA/PFOS at potentials of $\sim 2.0 \text{ V/SHE}$ in the REM system was attributed to the very high specific surface area of the electrode ($\sim 1 \times 10^6 \text{ m}^{-1}$), which allowed the slow reaction kinetics that were occurring at these potentials to yield a non-negligible

change in concentration. By contrast, previous work in batch reactor systems with low specific surface area electrodes did not achieve measurable PFAS removal until potentials exceeded 2.5 V/SHE.⁶⁴

The formation of F^- ions was used to calculate the defluorination ratio of PFOA/PFOS (i.e., $[F^- \text{ formed}]/[F \text{ in initial PFAS}] \times 100$) and values were up to $75.3 \pm 4.7 \%$ for PFOA (**Figure 6c**) and $68.9 \pm 2.7 \%$ for PFOS (**Figure 6d**). The total fluorine mass balance was calculated (i.e., $\{[F^-]_{\text{in solution}} + [F]_{\text{in PFAS}}\} / [F]_{\text{in PFAS, initial}}$) and ranged between 68.1 ± 4.1 to $99.7 \pm 0.3 \%$ for PFOA (**Figure 6c**) and between 67.2 ± 4.1 to $99.8 \pm 0.2 \%$ for PFOS (**Figure 6d**). For conditions where PFASs were oxidized to below the analytical detection limits, mass balances were 76.3% for PFOA and 68.9% for PFOS. The only fluorocarbon product detected during experiments was perfluoroheptanoic acid (PFHpA) during PFOA oxidation (**Figure 6b**). The maximum concentration of PFHpA formed at a potential of 2.6 V/SHE and decreased at higher potentials, which was attributed to a lowering of the activation energy for PFHpA oxidation at higher potentials. The fact that the mass balance was $< 100\%$ indicates that shorter chain volatile PFAS products likely formed, which were not analyzed by LC-MS.^{12,13}

Results for the electrochemical oxidation of PFOA/PFOS at a constant anodic potential of 2.9 V/SHE and with different membrane fluxes ($J = 36$ to 960 LMH) are shown in **Figure 7**. These membrane fluxes gave residence times between 75 to 2.8 s. The highest conversions for both compounds were found at $J = 36$ LMH, which again achieved approximately 5-log removal for both compounds (liquid residence time = 75 s). **Figure 7b** contains the calculated

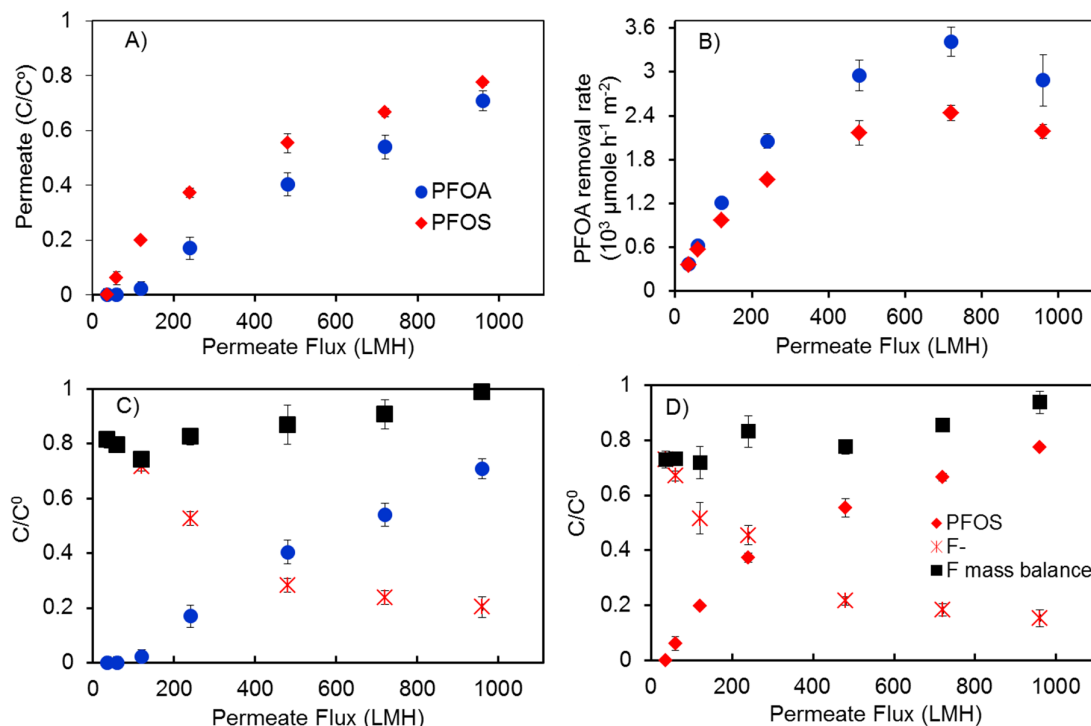


Figure 7. (a) Concentration profile of permeate, (b) Removal rate of PFOA/PFOS during the oxidation on Ti_4O_7 REM at different membrane fluxes. Fluoride mass balance as a function of membrane flux of (c) PFOA, and (d) PFOS (V anode = 2.9 V/SHE, Electrolyte = 100 mM K_2HPO_4). Error bars represent standard deviations about mean values and are contained within data points for some data.¹

PFAS removal rates as a function of J . The maximum removal rates for PFOA/PFOS were obtained at $J = 720$ LMH, with $R_r = 3415 \pm 203 \mu\text{mol m}^{-2} \text{ h}^{-1}$ for PFOA and $R_r = 2436 \pm 106 \mu\text{mol m}^{-2} \text{ h}^{-1}$ for PFOS. Rates decreased at higher J values for both compounds, which is consistent with prior work for compound oxidation in the REM and was attributed to an increased current efficiency for oxygen evolution at higher J values, which was facilitated by sweeping of O_2 bubbles from the REM surface.⁵¹ Reaction rate constants were also calculated

based on the conversion of PFOA/PFOS as a function of liquid residence time in the REM (**Figure 8**). Results indicated that the reactions were pseudo first-order, with surface area normalized observed rate constants (k_{obs}) of $1.3 \times 10^{-4} \text{ m s}^{-1}$ for PFOA and $4.4 \times 10^{-5} \text{ m s}^{-1}$ for PFOS. These k_{obs} values were over an order of magnitude higher than previously reported results with Ti_4O_7 and BDD anodes, with liquid residence times of $< 45 \text{ s}$ in our study compared to several hours in previous work.^{14,15} These significantly improved results were attributed to the flow-through mode operation, which enhanced mass transfer and utilized the high specific surface area of the REM (i.e., $1.3 \times 10^6 \text{ m}^{-1}$). In addition, non-normalized observed reaction rate constants for this data were calculated as 607 h^{-1} for PFOA and 210 h^{-1} for PFOS. These values are more than two orders of magnitude higher than those reported by other destructive technologies (i.e., ultrasonication, photocatalysis, vacuum UV photolysis, microwave-hydrothermal decomposition).¹⁶⁻¹⁹

The defluorination ratios as a function of J were between $20.3\% \pm 3.8$ at 960 LMH to $81.4\% \pm 3.2$ at 36 LMH for PFOA (**Figure 7c**) and between $15.5 \pm 2.2\%$ at 960 LMH to $72.9 \pm 3.1\%$ at 36 LMH for PFOS (**Figure 7d**).

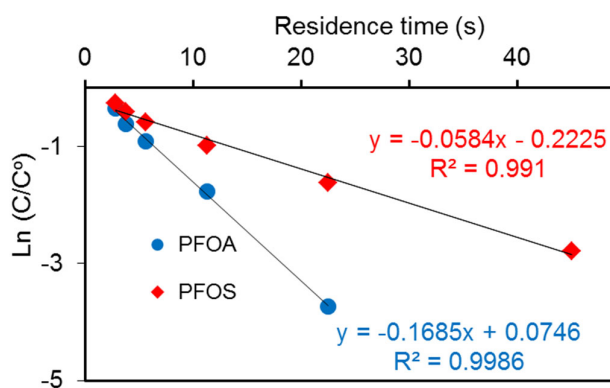
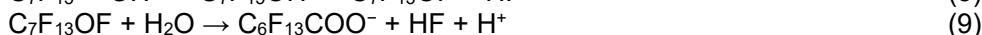


Figure 8. The linear regression of the Napierian logarithm of permeate concentration profile as function of residence time in the REM.¹

The total fluorine mass balance ranged between 74.1 ± 0.07 to $98.6 \pm 0.16\%$ for PFOA (**Figure 7c**) and between $71.7 \pm 5.8\%$ to $93.8 \pm 4.1\%$ for PFOS (**Figure 7d**). For conditions where PFASs were oxidized to below the analytical detection limits, mass balances were $79.6\text{--}81.4\%$ for PFOA ($J = 36$ and 60 LMH) and $73.0\text{--}73.1\%$ for PFOS ($J = 36$ and 60 LMH). In general, the mass balance increased with J due to a lower overall PFAS conversion. The only fluorocarbon product detected was PFHpA during PFOA oxidation (**Figure 9**). The maximum PFHpA concentration was observed at $J = 480 \text{ LMH}$, which coincided

approximately with the highest PFOA removal rate.

The detection of PFHpA during PFOA oxidation suggests that the sequential unzipping reaction mechanisms proposed prior may be occurring.¹² This mechanism results in the progressive loss of CF_2 molecules.^{14,34,65} For PFOA these reaction steps are shown in reactions 6 to 9. The rate-limiting step is the formation of a perfluorinated alkyl radical *via* direct electron transfer (reaction 6).¹³ The $\text{C}_7\text{F}_{15}\text{COO}^\bullet$ radical then undergoes Kolbe decarboxylation to produce $\text{C}_7\text{F}_{15}^\bullet$ (reaction 7). The $\text{C}_7\text{F}_{15}^\bullet$ species then reacts with $\text{OH}^\bullet$ to form $\text{C}_7\text{F}_{15}\text{OH}$ followed by HF elimination (reaction 8). The last step involves hydrolysis to generate PFHpA (reaction 9). This CF_2 unzipping cycle is repeated until PFASs are completely mineralized to CO_2 and HF. A similar mechanism is thought to occur for PFOS, where the initial direct electron transfer step results in cleavage of the $-\text{SO}_3$ group to form a perfluoroalkyl radical, which then follows the reaction sequence shown in reactions 8 and 9.¹²



The formation of PFHpA and other short-chain PFASs (inferred by < 100% mass balance) is consistent with reports that short-chain PFASs are more difficult to oxidize, which has been

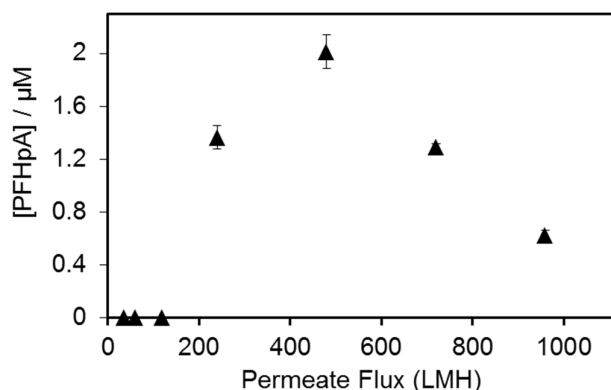


Figure 9. Concentration of PFHpA formed from PFOA oxidation as a function of membrane flux at an anode potential of 2.9 V/SHE (Electrolyte = 100 mM K_2HPO_4).¹

Table 1. General water quality analyses for groundwater samples.

Constituent	GW1 mg/L	GW2 mg/L
F ⁻	1.06	15.7
Cl ⁻	51.5	27.1
NO ₃ ⁻	8.18	175
SO ₄ ²⁻	10.8	< 0.1
HPO ₄ ²⁻	7.78	< 0.1
HCO ₃ ⁻	228	87.7
Na ⁺	72.6	25.3
K ⁺	13.7	30.1
Ca ²⁺	25.7	34.5
Mg ²⁺	21.4	8.75
pH	6.8	6.5
Conductivity (μS/cm)	788	337
COD (mg/L)	43.3	4.35
Alkalinity (mg/L CaCO ₃)	373	144

oxidation of longer chain PFASs (e.g., PFNA, PFOS). At the highest cell potentials tested (e.g., 8.1 and 10.5 V) total PFAS removal was ~50% (**Figure 10**). The lack of total removal of PFASs was attributed to the presence of background organic compounds (COD = 43.3 mg/L) and low solution conductivity (**Table 1**). The background organic compounds can compete with PFASs for reactive sites on the REM, and the low conductivity caused a significant potential drop in solution and therefore reduced the reactive thickness of the REM.

The GW2 sample was obtained from Willow Grove Naval Base in collaboration with Jason Speicher. The general water quality parameters are shown in Table 1 and PFAS concentrations are shown in **Figure 11a** (Feed/OCP data). Control experiments (OCP data) were not significantly different than the original feed samples, indicating that adsorption was minimal. Operation of the REM in single-pass mode with a low flux ($J = 60$ LMH) resulted in approximately 55% total PFAS removal (**Figure 11a**). Once again, longer chain PFASs were oxidized to shorter chain PFASs, and the background COD and low conductivity inhibited

attributed to a decrease in hydrophobicity with a decrease in chain length.⁶⁶ However, further investigation into the reaction mechanisms of PFASs on multiple electrode types through both experimental and theoretical studies are needed to support this hypothesis.

4.6 PFAS Oxidation in Groundwater Samples. Work in this section focused on addressing Milestones 2 and 3.

Milestone 2: *Demonstrate the ability of REMs to remove PFASs from an initial concentration of > 400 μg L⁻¹ to below the treatment goal of 70 ng L⁻¹ in synthetic/real groundwater samples.*

Milestone 3: *Determination of the most energy efficient operational strategy for PFAS removal in groundwater.*

Two groundwater samples (GW1 and GW2) were treated with the REMs. The general water quality analyses for these samples are shown in **Table 1**. The GW1 sample was collected by Geosyntec Consultants from a client's site in Jacksonville, Florida and did not contain detectable concentrations of PFASs. This sample was spiked with the six different PFASs at concentrations between 1.0 to 2.5 μM. These initial concentrations are shown in **Figure 10** (OCP data). This experiment was conducted at low flux ($J = 60$ LMH), which gave a hydraulic residence time of $t_r = 45$ s. Control experiments (OCP data) were not significantly different than the original samples, indicating that adsorption was minimal. In general, results show the accumulation of shorter chain PFASs (e.g., PFBS, PFHpA, PFHxS), presumably from the

complete oxidation. In order to increase the oxidation rate, the operational mode of the REM

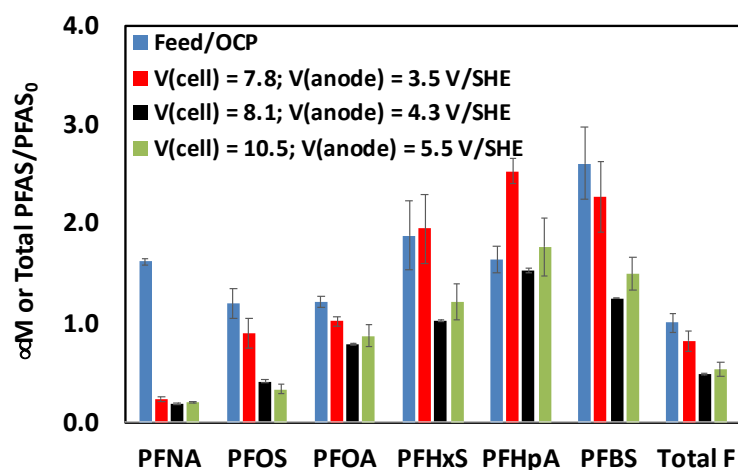


Figure 10. PFAS and total F removal in GW1 sample as a function of cell potential. $J = 60$ LMH

was switched to recycle mode. In this mode of operation the solution was continuously recycled through the REM until the target removal was achieved. A flux ($J = 720$ LMH) was chosen that corresponded to the maximum rate observed for PFOA/PFOS oxidation experiments (see **Figure 7b**). Individual final PFAS concentrations were < 61 ng/L and total PFAS concentrations were 274 ng L^{-1} (**Figure 11b**). The percent removals for individual and total PFAS

are shown in **Figure 12** and indicate that total PFAS destruction was $> 99\%$. These results indicate that a recycle mode operation with high flux is needed to improve mass transfer and increase contact time with the REM, which resulted in effective oxidation of PFASs in the

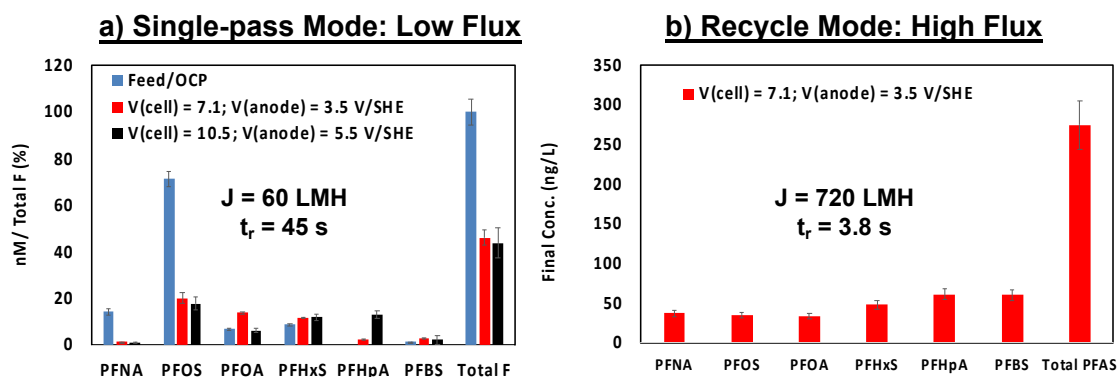


Figure 11. Comparison of electrochemical oxidation of PFASs in GW2 in single-pass versus recycle modes.

groundwater solution. **These experiments achieved both Milestones 2 and 3, as stated above.**

4.7 Energy Requirements. Work in this section focused on addressing **Milestone 4: Determination of the energy costs for achieving the 70 ng L^{-1} treatment goal in PFAS-contaminated groundwater with a target energy usage of < 2.0 kWh m^{-3} (per log removal) of water treated.**

A key issue associated with destructive PFAS remediation technologies is the operational cost. While a complete analysis of operating costs for PFAS remediation technologies could not be found in the existing literature, we have recently summarized the energy consumption per log-removal for various novel technologies for PFOA/PFOS degradation,²⁰ which is also summarized in the Appendix (Table A1). Remediation technologies that were reviewed include sonolysis,^{16,21,22,23} microwave-hydrothermal,¹⁷ photolysis,²⁴⁻²⁶ photocatalysis,^{27,28,29} and electrochemical oxidation.^{12,14,20,30-38} In general, sonolysis has the highest energy

consumption (1475 to 4045 kWh/m³).^{23,67} A significant energy demand was also reported for

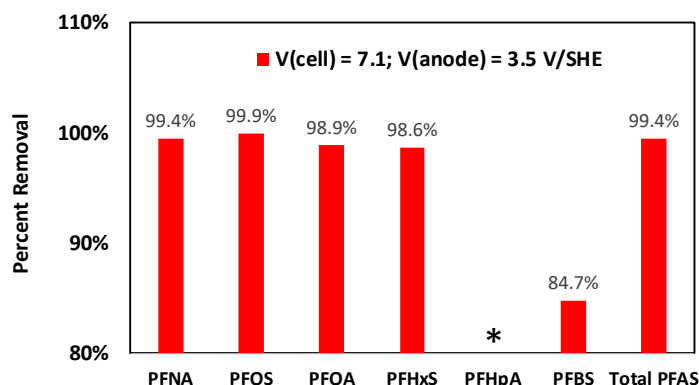


Figure 12. Percent removal of PFAS compounds in GW2.

*PFHpA was not detected in the feed solution, but was produced during treatment to a final concentration of 60 ng/L.

microwave-hydrothermal (2599 kWh m⁻³)¹⁷ and photolysis/boiling (1177 kWh/m³).²⁶ While the UV/KI photoreduction method has a much lower energy consumption (95 kWh/m³), it has a relatively long treatment time (14 h) and requires anaerobic conditions.⁶⁸ Using a TiO₂ photocatalyst in the presence of O₃ can significantly reduce energy consumption (37 kWh/m³).²⁹ However, direct electrochemical oxidation of PFAS is by far the most energy efficient destructive method reported to date (5 –

132 kWh m⁻³) and does not require the addition of chemicals or the removal of dissolved oxygen.^{20,30,38,39} Porous Magnéli phase Ti₄O₇ ceramic anodes have shown the lowest energy consumption of 5 kWh/m³ for PFOA and between 6.7 to 32 kWh/m³ for PFOS,^{20,38} further demonstrating the promise of this technology. In this study, the electrode energy requirements (Table 2) for the Ti₄O₇ REM anode to remove 10 µM initial concentrations of PFOA and PFOS to below the detection limits (86 ng L⁻¹ for PFOA and 35 ng L⁻¹ for PFOS) were 5.1 ± 0.1 and 6.7 ± 0.2 kWh m⁻³, respectively. Additionally, it was found that the groundwater samples required 13 –24 kWh m⁻³ to treat GW1 and 11 –15 kWh m⁻³ to treat GW2 in single-pass mode. The energy usage decreased to 2.9 kWh m⁻³ to treat GW2 in recycle mode, which was able to decrease individual PFASs to < 61 ng/L. Although the lowest energy consumption observed during this project (i.e., 2.9 kWh m⁻³) was 45% higher than the 2.0 kWh m⁻³ goal, this energy consumption value is the lowest reported in the literature and shows the extreme promise of the REM technology. Further optimization of reactor design and operation will undoubtedly lower the energy consumption of the REM.

Table 2. Energy consumption (E, kWh m⁻³) for PFOA and PFOS by electrochemical oxidation using Ti₄O₇ REM (Energy calculated per log removal according to equation ()).

Potential (V/SHE)*		1.1	1.8	2.2	2.6	2.9	3.3	3.6
PFOA	E (kWh m ⁻³)	205 ± 14	40.2 ± 5.8	17.2 ± 3.7	23.3 ± 0.1	19.4 ± 1.3	5.1 ± 0.1	-
	Removal (%)	0.3 ± 0.1	11.2 ± 4.9	39.8 ± 6.5	53.7 ± 0.2	81.8 ± 2.0	99.9 ± 2.0	-
PFOS	E (kWh m ⁻³)	535 ± 72	77.6 ± 8.0	33.7 ± 5.4	34.6 ± 0.4	39.4 ± 2.5	49.0 ± 0.2	6.7 ± 0.2
	Removal (%)	-	3.4 ± 0.3	20.7 ± 3.6	38.9 ± 0.4	55.7 ± 2.4	74 ± 15	99.9 ± 2.3
J (LMH) [§]		36	60	120	240	480	720	960
PFOA	E (kWh m ⁻³)	13.3 ± 2.5	9.2 ± 2.5	17.0 ± 2.8	18.9 ± 2.5	21.1 ± 2.5	22.5 ± 1.8	31.9 ± 4.6
	Removal (%)	99.9 ± 2.4	99.9 ± 2.4	97.6 ± 2.4	82.9 ± 4.1	59.6 ± 4.3	46.0 ± 4.3	29.2 ± 3.5
PFOS	E (kWh m ⁻³)	12.3 ± 0.5	43.3 ± 0.5	39.4 ± 0.5	33.9 ± 1.5	32.3 ± 3.5	34.1 ± 1.8	43.1 ± 6.6
	Removal (%)	99.9 ± 2.4	93.9 ± 2.4	80.1 ± 0.4	62.7 ± 1.6	44.6 ± 3.4	33.4 ± 1.4	22.5 ± 0.9

* The experiment was carried out at a constant permeate flux of 240 LMH.

[§] The experiment was carried out at a constant applied potential of 2.9 V/SHE.

5.0 Conclusions and Implications for Future Research.

5.1 Conclusions and Assessment of Proof of Concept. The completed Limited Scope project has produced proof-of-concept data that indicates that a REM-based remediation strategy is a viable option for the treatment of IDW liquid samples. The overall objectives of the research were met, which include: 1) development of REMs for destructive PFAS removal in IDW water samples to $< 70 \text{ ng L}^{-1}$; 2) determination of the optimal operational mode; and 3) calculation of energy requirements for the REM-based system for comparison to other technologies. Specific milestones were partially satisfied and as a result some reprioritization of the research was necessary. For example, **Milestone 1** was focused on developing sorbent-loaded REMs for simultaneous adsorption/oxidation of PFASs. Although these REMs were successfully fabricated and showed adsorption capacity for PFAS, the carbon sorbents were not electrochemically stable under anodic polarization, so pure Ti_4O_7 REMs were used for all subsequent work. **Milestone 2** was met, which involves achieving the 70 ng L^{-1} treatment goal for PFASs in both synthetic and real groundwater samples. **Milestone 3** was also met by the determination that a recycle mode operation was the most efficient for PFAS removal. **Milestone 4** was not achieved, as the goal for energy usage during electrochemical oxidation was 2.0 kWh m^{-3} and results from this project could achieve an energy consumption of 2.9 kWh m^{-3} . However, the energy consumption reported here is the lowest reported in the literature for electrochemical oxidation and orders of magnitude lower than other destructive treatment technologies. Therefore, the project was deemed a success and follow-on research will be sought to improve reactor design and optimization as stated below.

5.2 Objectives for Follow-on Research. Based on the results of this study, several areas of follow-on research are proposed, which include: 1) Reactor design/optimization; 2) Impact of co-contaminants; 3) Longevity studies; and 4) Life cycle and cost analyses. Specific technical questions and hypotheses to be tested are stated below:

Question 1: Can the optimization of reactor design lead to a technology that can remediate PFASs to below the ng/L regulatory standards with low energy consumption?

Hypothesis 1: It is hypothesized that a combination of reactive transport modeling and experimental validation will allow a highly effective and energy efficient (Energy $< 2.0 \text{ kWh m}^{-3}$) reactor to be developed.

Question 2: Can the REM effectively oxidize both PFASs and various organic co-contaminants?

Hypothesis 2: It is hypothesized that, while energy consumptions may increase in certain solutions, the REM can effectively oxidize all organic contaminants. PFASs are among the most oxidative resistant contaminants of environmental concern. Therefore, other co-contaminants (e.g., chlorinated solvents, fuel components) will be oxidized more easily than PFASs.

Question 3: Can a prototype REM-based PFAS remediation strategy be developed that can operate long-term under a realistic treatment scenario?

Hypothesis 3: It is hypothesized that REMs and other reactor components will prove to be sufficiently stable under anodic/cathodic polarization, which will be assessed by accelerated life testing.

Question 4: Will the REM-based treatment strategy be competitive from a cost and environmental standpoint with respect to existing technologies?

Hypothesis 4: It is hypothesized that REMs can be synthesized at low costs, operate under low energy requirements, and will prove to be sufficiently stable so they will be both a technically effective and cost-efficient remediation strategy for PFAS-contaminated groundwater. The combination of rigorous experimental bench-scale testing and cost and life cycle assessments will be used to test this hypothesis.

5.2.1 Reactor Design/Optimization. Work described in this section will test *Hypothesis 1*. In the Limited Scope project 1 cm² pellet shaped REMs were used in flow-through mode (see **Figure 2**). This decision was made to expediate the testing process in order to obtain proof of concept data for this short-term project. Follow-on research will focus on scaling up the electrochemical reactor. PI Chaplin has developed tubular micro- and ultra-filtration REMs in prior work,^{48,49,51,69} and these REMs will be utilized in follow-on research. The REMs have high membrane flux (3000 to 5000 L m⁻² h⁻¹ bar⁻¹ (LMH bar⁻¹)),⁵¹ and synthesis was accomplished by the thermal reduction (1050 °C/100% H₂) of TiO₂ ceramic membrane precursors. **Figure 13a** shows a photograph of the TiO₂ membrane (beige) and thermally reduced Ti₄O₇ membrane (bluish-black). The reduction resulted in a 10⁸-fold increase in the conductivity from 2.6 x 10⁻⁵ to 1.0 x 10³ S m⁻¹ (**Figure 13a**) and XRD measurements confirmed near complete conversion to Ti₄O₇ (**Figure 13b**). Cross-sectional SEM analysis provided in **Figure 13c** shows a thin active layer (~ 50 μm, ~0.1 μm pore diameter) overlying the support (~ 2 mm, ~1.0 μm pore diameter). This pore structure allows for very high membrane permeation fluxes (**Figure 13d**).

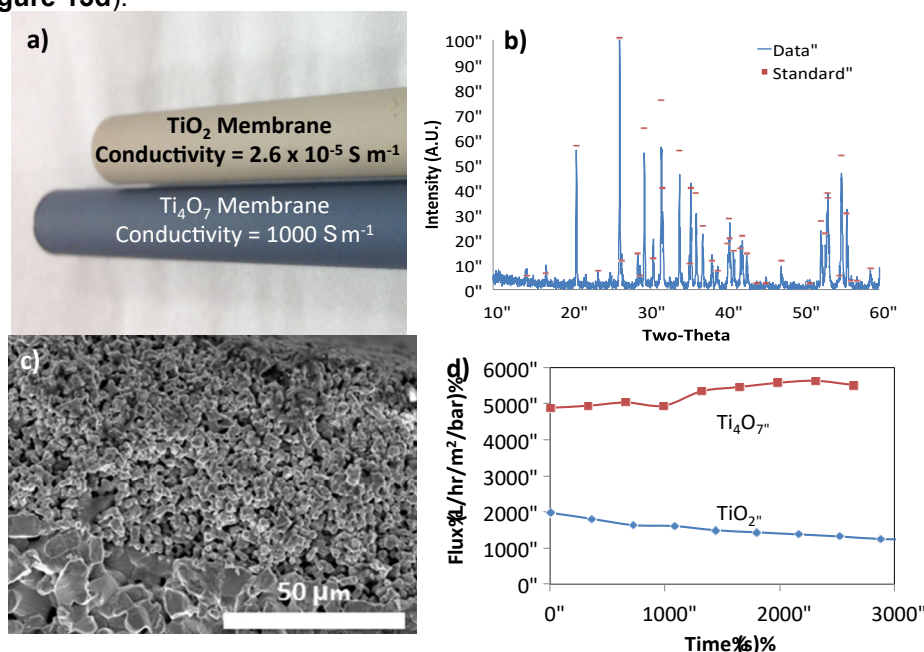


Figure 13. (a) Image of the TiO₂ and Ti₄O₇ cylindrical REM, with measured conductivity values. (b) XRD data of Ti₄O₇ REM with standards. (c) SEM image of REM. (d) Measured flux data.

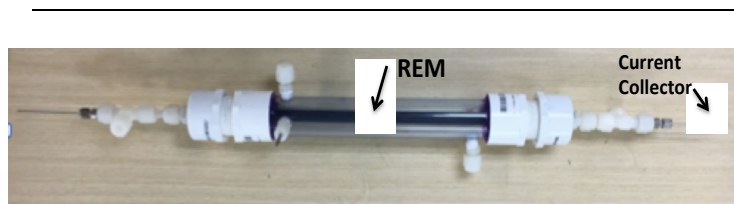


Figure 14. REM for bench-scale electrochemical testing.

Work will focus on optimizing the reactor design and performance. A prototype system has been developed (**Figure 14**), but further work is needed to optimize the electrode placement (which will reduce the energy consumption)

and flow dynamics (which will increase the conversion efficiency). Based on work in the Limited Scope project this reactor will be designed to operate in recycle-mode with a high crossflow velocity. Reactor optimization will be guided by reactive transport modeling utilizing COMSOL Multiphysics and validated by experiments. The REM reactor will be developed with consideration towards technical effectiveness, cost effectiveness, and compactness and

mobility of the treatment system. Metrics for success will be achieving effluent PFAS concentrations of $< 70 \text{ ng L}^{-1}$ in treated groundwater samples with minimal energy consumption. A specific focus will be placed on minimizing the formation of shorter chain PFAS, which will likely dictate operational parameters of the REM system.

5.2.2 Impact of Co-contaminants. Work described in this section will test *Hypothesis 2*. Various co-contaminants may exist with PFASs at groundwater remediation sites. These co-contaminants include hydrocarbon surfactants originating from the AFFFs, chlorinated solvents, solvent stabilizers, and fuel components. To test the efficiency of PFAS + co-contaminant removal, the reactor discussed in the previous section will be challenged with several different groundwater samples from contaminated sites. The removal of PFASs and these co-contaminants will be assessed and further optimization of the reactor will be performed as necessary. During these experiments, the production of unwanted side products will be monitored (e.g., aldehydes, chlorate, perchlorate, phosgene, chloroform, and other halogenated organics) and appropriate post treatment strategies will be investigated as needed.

5.2.3 Longevity Studies. Work described in this section will test *Hypothesis 3*. Research will focus on assessing the longevity of the REM reactor at the bench-scale using PFAS-contaminated groundwater samples. The specific objective of this task is to determine the dimensional stability of the REM reactor with respect to anodic and cathodic polarization conditions. PI Chaplin has experience with electrode longevity testing from prior projects,^{70,71} and recently it was demonstrated that the REM was effective for 50 cycles of fouling and regeneration on a project focused on whey protein separation with an ultrafiltration REM developed in his laboratory (see Appendix, Figure A1).

The standard technique for comparing the stability of different electrodes is the accelerated life test (ALT). The ALT is conducted at current densities that are one to two orders of magnitude greater than those used in normal operation. High current densities (e.g., $> 100 \text{ mA/cm}^2$) are used in order to reach the point of electrode failure in a test that lasts less than several weeks.⁷² Batch experiments will be performed in groundwater samples to determine the failure rates of the REMs related to anode passivation. The galvanostatic tests will be interrupted periodically in order to perform CV and EIS scans using water oxidation and the $\text{K}_4\text{Fe}(\text{CN})_6/\text{K}_3\text{Fe}(\text{CN})_6$ redox couple as a model of inner and outer sphere electron transfer reactions, respectively, and for XRD analysis to quantify oxygen incorporation to the REM and catalyst stability. One set of experiments will be performed under only anodic OR cathodic polarization and a second set of experiments will be conducted under alternating anodic/cathodic polarization to investigate the effect of reverse polarity on electrode life. The service life of the REM will be estimated by a linear extrapolation to the normal operating current density (determined in Sections 5.2.1 and 5.2.2), which is considered a low estimate of service life.⁷³ A service life of > 10 years is set as a goal for this work.

5.2.4 Life Cycle/Cost Assessments. Work described in this section will test *Hypothesis 4* and will compare the costs and environmental impacts for the removal of PFASs using the final REM design and compare it to other technologies (e.g., membrane, ion exchange, GAC adsorption). Data for these analyses will be obtained from the experimental work and from reported literature data for other treatment technologies. We will determine capital, operating, and maintenance costs on a per mole of contaminant basis. Environmental impacts will be assessed by a life cycle assessment (LCA). LCAs have been previously performed on GAC adsorption in water and wastewater treatment and groundwater remediation strategies,⁷⁴⁻⁷⁸ but not for the remediation of PFASs. We will use SimaPro for the LCA using a cradle to grave analysis and the triple bottom line. This framework assesses sustainability by evaluating impacts to the economy, environment, and society. The economic sustainability will be determined by assessing the capital, operating, maintenance, and disposal costs. The environmental sustainability will be determined by assessing the environmental impacts of each process, taking into account the extraction and processing of raw materials, manufacturing, transportation and distribution, treatment operation, and final waste disposal. The societal sustainability will be determined by health improvement and jobs created. The

SimaPro software will allow us to evaluate these parameters using the International Standard Organization 14000 impact factors, which are internationally accepted standards for environmental impact assessment. The power of SimaPro is that it contains nearly all the publicly available databases necessary to make comparisons between different processes.

6.0 Literature Cited

- (1) Le, T. X. H.; Haflich, H.; Shah, A. D.; Chaplin, B. P., Energy-Efficient Electrochemical Oxidation of Perfluoroalkyl Substances Using a Ti_4O_7 Reactive Electrochemical Membrane Anode. *Environmental Science & Technology Letters* **2019**, *6*, (8), 504-510.
- (2) Regulations, Guidance, and Advisories for Per- and Polyfluoroalkyl Substances (PFAS). U.S. Environmental Protection Agency: Washington, DC. In.
- (3) Per- and Polyfluoroalkyl Substances (PFAS) State Drinking Water Program Challenges. <https://www.asdwa.org/pfas/> (accessed July 16, 2019). In.
- (4) Schroder, H. F.; Meesters, R. J. W., Stability of fluorinated surfactants in advanced oxidation processes - A follow up of degradation products using flow injection-mass spectrometry, liquid chromatography-mass spectrometry and liquid chromatography-multiple stage mass spectrometry. *Journal of Chromatography A* **2005**, *1082*, (1), 110-119.
- (5) Carter, K. E.; Farrell, J., Removal of Perfluorooctane and Perfluorobutane Sulfonate from Water via Carbon Adsorption and Ion Exchange. *Separation Science and Technology* **2010**, *45*, (6), 762-767.
- (6) Zhang, D.; Luo, Q.; Gao, B.; Chiang, S.-Y. D.; Woodward, D.; Huang, Q., Sorption of perfluorooctanoic acid, perfluorooctane sulfonate and perfluoroheptanoic acid on granular activated carbon. *Chemosphere* **2016**, *144*, 2336-2342.
- (7) Zhao, D.; Cheng, J.; Vecitis, C. D.; Hoffmann, M. R., Sorption of Perfluorochemicals to Granular Activated Carbon in the Presence of Ultrasound. *J. Phys. Chem. A* **2011**, *115*, (11), 2250-2257.
- (8) Eschauzier, C.; Beerendonk, E.; Scholte-Veenendaal, P.; De Voogt, P., Impact of Treatment Processes on the Removal of Perfluoroalkyl Acids from the Drinking Water Production Chain. *Environmental Science & Technology* **2012**, *46*, (3), 1708-1715.
- (9) Pramanik, B. K.; Pramanik, S. K.; Suja, F., A comparative study of coagulation, granular- and powdered-activated carbon for the removal of perfluorooctane sulfonate and perfluorooctanoate in drinking water treatment. *Environmental Technology* **2015**, *36*, (20), 2610-2617.
- (10) Yao, Y.; Volchek, K.; Brown, C. E.; Robinson, A.; Obal, T., Comparative study on adsorption of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) by different adsorbents in water. *Water Science and Technology* **2014**, *70*, (12), 1983-1991.
- (11) Yu, Q.; Zhang, R. Q.; Deng, S. B.; Huang, J.; Yu, G., Sorption of perfluorooctane sulfonate and perfluorooctanoate on activated carbons and resin: Kinetic and isotherm study. *Water Research* **2009**, *43*, (4), 1150-1158.
- (12) Niu, J.; Lin, H.; Xu, J.; Wu, H.; Li, Y., Electrochemical Mineralization of Perfluorocarboxylic Acids (PFCAs) by Ce-Doped Modified Porous Nanocrystalline PbO_2 Film Electrode. *Environmental Science & Technology* **2012**, *46*, (18), 10191-10198.
- (13) Niu, J.; Lin, H.; Gong, C.; Sun, X., Theoretical and Experimental Insights into the Electrochemical Mineralization Mechanism of Perfluorooctanoic Acid. *Environ. Sci. Technol.* **2013**, *47*, (24), 14341-14349.
- (14) Ochiai, T.; Iizuka, Y.; Nakata, K.; Murakami, T.; Tryk, D. A.; Fujishima, A.; Koide, Y.; Morito, Y., Efficient electrochemical decomposition of perfluorocarboxylic acids by the use of a boron-doped diamond electrode. *Diamond and Related Materials* **2011**, *20*, (2), 64-67.
- (15) Lin, H.; Niu, J. F.; Liang, S. T.; Wang, C.; Wang, Y. J.; Jin, F. Y.; Luo, Q.; Huang, Q. G., Development of macroporous Magneli phase Ti_4O_7 ceramic materials: As an efficient

anode for mineralization of poly- and perfluoroalkyl substances. *Chemical Engineering Journal* **2018**, *354*, 1058-1067.

(16) Vecitis, C. D.; Park, H.; Cheng, J.; Mader, B. T.; Hoffmann, M. R., Enhancement of Perfluorooctanoate and Perfluorooctanesulfonate Activity at Acoustic Cavitation Bubble Interfaces. *Journal of Physical Chemistry C* **2008**, *112*, (43), 16850-16857.

(17) Lee, Y. C.; Lo, S. L.; Chiueh, P. T.; Chang, D. G., Efficient decomposition of perfluorocarboxylic acids in aqueous solution using microwave-induced persulfate. *Water Research* **2009**, *43*, (11), 2811-2816.

(18) Lo, S.-L. W., C.-H.; Lee, Y.-C.; Chen, M.-J.; Kuo, J., Decomposition of Perfluorooctanoic Acid by Ultraviolet Light Irradiation with Pb-Modified Titanium Dioxide. *J. Hazard. Mater.* **2016**, *303*, 111-118. *J. Hazard. Mater.* **2016**, *303*, 111-118.

(19) Jin, L. Z., P. , Photochemical Decomposition of Perfluorooctane Sulfonate (PFOS) in an Anoxic Alkaline Solution by 185 nm Vacuum Ultraviolet. *Chem. Eng. J.* **2015**, *280*, 241-247.

(20) Le, T. X. H.; Haflich, H.; Shah, A. D.; Chaplin, B. P., Energy-Efficient Electrochemical Oxidation of Perfluoroalkyl Substances using a Ti₄O₇ Reactive Electrochemical Membrane Anode. *Environ Sci Technol Lett* **2019**, *6*, (8), 504-510.

(21) Cheng, J.; Vecitis, C. D.; Park, H.; Mader, B. T.; Hoffmann, M. R., Sonochemical Degradation of Perfluorooctane Sulfonate (PFOS) and Perfluorooctanoate (PFOA) in Groundwater: Kinetic Effects of Matrix Inorganics. *Environmental Science & Technology* **2010**, *44*, (1), 445-450.

(22) Schroder, F.; Meesters, R., Stability of fluorinated surfactants in advanced oxidation processes: A follow up of degradation products using flow injection-mass spectrometry, liquid chromatography-mass spectrometry and liquid chromatography-multiple stage mass spectrometry. *J. Chromatogr. A* **2005**, *1082*, 110-119.

(23) Lin, J. C.; Hu, C. Y.; Lo, S. L., Effect of surfactants on the degradation of perfluorooctanoic acid (PFOA) by ultrasonic (US) treatment. *Ultrasonics Sonochemistry* **2016**, *28*, 130-135.

(24) Hori, H.; Hayakawa, E.; Einaga, H.; Kutsuna, S.; Koike, K.; Ibusuki, T.; Kiatagawa, H.; Arakawa, R., Decomposition of environmentally persistent perfluorooctanoic acid in water by photochemical approaches. *Environmental Science & Technology* **2004**, *38*, (22), 6118-6124.

(25) Chen, J.; Zhang, P. Y.; Liu, J., Photodegradation of perfluorooctanoic acid by 185 nm vacuum ultraviolet light. *Journal of Environmental Sciences* **2007**, *19*, (4), 387-390.

(26) Lyu, X. J.; Li, W. W.; Lam, P. K. S.; Yu, H. Q., Boiling significantly promotes photodegradation of perfluorooctane sulfonate. *Chemosphere* **2015**, *138*, 324-327.

(27) Li, X. Y.; Zhang, P. Y.; Jin, L.; Shao, T.; Li, Z. M.; Cao, J. J., Efficient Photocatalytic Decomposition of Perfluorooctanoic Acid by Indium Oxide and Its Mechanism. *Environmental Science & Technology* **2012**, *46*, (10), 5528-5534.

(28) Li, Z. M.; Zhang, P. Y.; Shao, T.; Li, X. Y., In₂O₃ nanoporous nanosphere: A highly efficient photocatalyst for decomposition of perfluorooctanoic acid. *Applied Catalysis B-Environmental* **2012**, *125*, 350-357.

(29) Huang, J. Y.; Wang, X.; Pan, Z. Q.; Li, X. K.; Ling, Y.; Li, L. S., Efficient degradation of perfluorooctanoic acid (PFOA) by photocatalytic ozonation. *Chemical Engineering Journal* **2016**, *296*, 329-334.

(30) Schaefer, C. E.; Andaya, C.; Burant, A.; Condee, C. W.; Urtiaga, A.; Strathmann, T. J.; Higgins, C. P., Electrochemical treatment of perfluorooctanoic acid and perfluorooctane sulfonate: Insights into mechanisms and application to groundwater treatment. *Chemical Engineering Journal* **2017**, *317*, 424-432.

(31) Schaefer, C. E.; Andaya, C.; Urtiaga, A.; McKenzie, E. R.; Higgins, C. P., Electrochemical treatment of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid

(PFOS) in groundwater impacted by aqueous film forming foams (AFFFs). *Journal of Hazardous Materials* **2015**, 295, 170-175.

(32) Zhuo, Q. F.; Xiang, Q.; Yi, H.; Zhang, Z. K.; Yang, B.; Cui, K.; Bing, X. Y.; Xu, Z. C.; Liang, X. L.; Guo, Q. W.; Yang, R., Electrochemical oxidation of PFOA in aqueous solution using highly hydrophobic modified PbO₂ electrodes. *Journal of Electroanalytical Chemistry* **2017**, 801, 235-243.

(33) Xu, Z. Y., Y.; Liu, H.; Niu, J., Highly Efficient and Stable Zr-Doped Nanocrystalline PbO₂ Electrode for Mineralization of Perfluorooctanoic Acid in a Sequential Treatment System. *Sci. Total Environ.* **2017**, 579, 1600-1607.

(34) Lin, H.; Niu, J.; Ding, S.; Zhang, L., Electrochemical degradation of perfluorooctanoic acid (PFOA) by Ti/SnO₂-Sb, Ti/SnO₂-Sb/PbO₂ and Ti/SnO₂-Sb/MnO₂ anodes. *Water Research* **2012**, 46, (7), 2281-2289.

(35) Zhuo, Q.; Deng, S.; Yang, B.; Huang, J.; Yu, G., Efficient Electrochemical Oxidation of Perfluorooctanoate Using a Ti/SnO₂-Sb-Bi Anode. *Environmental Science & Technology* **2011**, 45, (7), 2973-2979.

(36) Yang, B.; Jiang, C. J.; Yu, G.; Zhuo, Q. F.; Deng, S. B.; Wu, J. H.; Zhang, H., Highly efficient electrochemical degradation of perfluorooctanoic acid (PFOA) by F-doped Ti/SnO₂ electrode. *Journal of Hazardous Materials* **2015**, 299, 417-424.

(37) Wang, Y. G., J.; Wang, Y.; Zhao, G.; Fan, J.; Zhao, H., Fabrication of Novel SnO₂-Sb/carbon Aerogel Electrode for Ultrasonic Electrochemical Oxidation of Perfluorooctanoate with High Catalytic Efficiency. *Appl. Catal. B Environ.* **2013**, 136-137, 278-286.

(38) Lin, H. N., J.; Liang, S.; Wang, C.; Wang, Y.; Jin, F.; Luo, Q.; Huang, Q., Development of Macroporous Magnéli Phase Ti₄O₇ Ceramic Materials: As an Efficient Anode for Mineralization of Poly- and Perfluoroalkyl Substances. *Chem. Eng. J.* **2018**, 354, 354.

(39) Niu, J.; Li, Y.; Shang, E.; Xu, Z.; Liu, J., Electrochemical oxidation of perfluorinated compounds in water. *Chemosphere* **2016**, 146, 526-38.

(40) Jawando, W.; Gayen, P.; Chaplin, B. P., The effects of surface oxidation and fluorination of boron-doped diamond anodes on perchlorate formation and organic compound oxidation. *Electrochimica Acta* **2015**, 174, 1067-1078.

(41) Carter, K. E.; Farrell, J., Oxidative destruction of perfluorooctane sulfonate using boron-doped diamond film electrodes. *Environ. Sci. Technol.* **2008**, 42, (16), 6111-6115.

(42) Moriwaki, H.; Takagi, Y.; Tanaka, M.; Tsuruho, K.; Okitsu, K.; Maeda, Y., Sonochemical decomposition of perfluorooctane sulfonate and perfluorooctanoic acid. *Environmental Science & Technology* **2005**, 39, (9), 3388-3392.

(43) Chaplin, B. P., Critical Review of Electrochemical Advanced Oxidation Processes for Water Treatment Applications. *Environ. Sci.: Processes Impacts* **2014**, 16, (6), 1182-1203.

(44) Chaplin, B. P., The Prospect of Electrochemical Technologies Advancing Worldwide Water Treatment. *Accounts of Chemical Research* **2019**, 52, (3), 596-604.

(45) Bejan, D.; Malcolm, J. D.; Morrison, L.; Bunce, N. J., Mechanistic investigation of the conductive ceramic Ebonex® as an anode material. *Electrochim. Acta* **2009**, 54, (23), 5548-5556.

(46) Chen, G.; Betterton, E. A.; Arnold, R. G., Electrolytic Oxidation of Trichloroethylene Using a Ceramic Anode. *J. Appl. Electrochem.* **1999**, 29, (8), 961-970.

(47) Scialdone, O.; Galia, A.; Filardo, G., Electrochemical incineration of 1,2-dichloroethane: Effect of the electrode material. *Electrochimica Acta* **2008**, 53, (24), 7220-7225.

(48) Zaky, A. M.; Chaplin, B. P., Porous Substoichiometric TiO₂ Anodes as Reactive Electrochemical Membranes for Water Treatment. *Environmental Science & Technology* **2013**, 47, (12), 6554-6563.

(49) Zaky, A. M.; Chaplin, B. P., Mechanism of p-Substituted Phenol Oxidation at a Ti₄O₇ Reactive Electrochemical Membrane. *Environ. Sci. Technol.* **2014**, 48, (10), 5857-5867.

- (50) Santos, M. C.; Elabd, Y. A.; Jing, Y.; Chaplin, B. P.; Fang, L., Highly porous Ti₄O₇ reactive electrochemical water filtration membranes fabricated via electrospinning/electrospraying. *AIChE Journal* **2016**, *62*, (2), 508-524.
- (51) Guo, L.; Jing, Y.; Chaplin, B. P., Development and Characterization of Ultrafiltration TiO₂ Magneli Phase Reactive Electrochemical Membranes. *Environmental Science & Technology* **2016**, *50*, (3), 1428-1436.
- (52) Hayfield, P. C. S., Development of a New Material - Monolithic Ti₄O₇ Ebonex® Ceramic. In Royal Society of Chemistry: Cambridge, UK, 2002.
- (53) Bejan, D.; Guinea, E.; Bunce, N. J., On the nature of the hydroxyl radicals produced at boron-doped diamond and Ebonex® anodes. *Electrochim. Acta* **2012**, *69*, 275-281.
- (54) Kesselman, J. M.; Weres, O.; Lewis, N. S.; Hoffmann, M. R., Electrochemical production of hydroxyl radical at polycrystalline Nb-doped TiO₂ electrodes and estimation of the partitioning between hydroxyl radical and direct Hole oxidation pathways. *Journal of Physical Chemistry B* **1997**, *101*, (14), 2637-2643.
- (55) Vecitis, C. D.; Gao, G.; Liu, H., Electrochemical Carbon Nanotube Filter for Adsorption, Desorption, and Oxidation of Aqueous Dyes and Anions. *Journal of Physical Chemistry C* **2011**, *115*, (9), 3621-3629.
- (56) Vecitis, C. D.; Schnoor, M. H.; Rahaman, M. S.; Schiffman, J. D.; Elimelech, M., Electrochemical Multiwalled Carbon Nanotube Filter for Viral and Bacterial Removal and Inactivation. *Environmental Science & Technology* **2011**, *45*, (8), 3672-3679.
- (57) Yang, Y.; Li, J. X.; Wang, H.; Song, X. K.; Wang, T. H.; He, B. Q.; Liang, X. P.; Ngo, H. H., An Electrocatalytic Membrane Reactor with Self-Cleaning Function for Industrial Wastewater Treatment. *Angewandte Chemie-International Edition* **2011**, *50*, (9), 2148-2150.
- (58) Yang, Y.; Wang, H.; Li, J.; He, B.; Wang, T.; Liao, S., Novel Functionalized Nano-TiO₂ Loading Electrocatalytic Membrane for Oily Wastewater Treatment. *Environ Sci Technol* **2012**, *46*, (12), 6815-6821.
- (59) Gao, G. D.; Vecitis, C. D., Doped Carbon Nanotube Networks for Electrochemical Filtration of Aqueous Phenol: Electrolyte Precipitation and Phenol Polymerization. *Acs Applied Materials & Interfaces* **2012**, *4*, (3), 1478-1489.
- (60) Rueffer, M.; Bejan, D.; Bunce, N. J., Graphite: An active or an inactive anode? *Electrochimica Acta* **2011**, *56*, (5), 2246-2253.
- (61) Nayak, S.; Chaplin, B. P., Fabrication and characterization of porous, conductive, monolithic Ti₄O₇ electrodes. *Electrochimica Acta* **2018**, *263*, 299-310.
- (62) Almassi, S.; Li, Z.; Xu, W. Q.; Pu, C. C.; Zeng, T.; Chaplin, B. P., Simultaneous Adsorption and Electrochemical Reduction of N-Nitrosodimethylamine Using Carbon-Ti₄O₇ Composite Reactive Electrochemical Membranes. *Environmental Science & Technology* **2019**, *53*, (2), 928-937.
- (63) Jing, Y.; Almassi, S.; Mehraeen, S.; LeSuer, R. J.; Chaplin, B. P., The roles of oxygen vacancies, electrolyte composition, lattice structure, and doping density on the electrochemical reactivity of Magneli phase TiO₂ anodes. *Journal of Materials Chemistry A* **2018**, *6*, (46), 23828-23839.
- (64) Zhuo, Q.; Deng, S.; Yang, B.; Huang, J.; Wang, B.; Zhang, T.; Yu, G., Degradation of perfluorinated compounds on a boron-doped diamond electrode. *Electrochimica Acta* **2012**, *77*, 17-22.
- (65) Wang, S. Y., Q.; Chen, F.; Sun, J.; Luo, K.; Yao, F.; Wang, X.; Wang, D.; Li, X.; Zeng, G., Photocatalytic Degradation of Perfluorooctanoic Acid and Perfluorooctane Sulfonate in Water: A Critical Review. *Chem. Eng. J.* **2017**, *328*, 927-942.
- (66) Zhuo, Q. F.; Luo, M. Q.; Guo, Q. W.; Yu, G.; Deng, S. B.; Xu, Z. C.; Yang, B.; Liang, X. L., Electrochemical Oxidation of Environmentally Persistent Perfluorooctane Sulfonate by a Novel Lead Dioxide Anode. *Electrochimica Acta* **2016**, *213*, 358-367.

- (67) Moriwaki, H.; Takagi, Y.; Tanaka, M.; Tsuruho, K.; Okitsu, K.; Maeda, Y., Sonochemical decomposition of perfluorooctane sulfonate and perfluorooctanoic acid. *Environ. Sci. Technol.* **2005**, *39*, 3388-3392.
- (68) Qu, Y.; Zhang, C. J.; Li, F.; Chen, J.; Zhou, Q., Photo-reductive defluorination of perfluorooctanoic acid in water. *Water Research* **2010**, *44*, (9), 2939-2947.
- (69) Guo, L.; Ding, K.; Rockne, K.; Duran, M.; Chaplin, B. P., Bacteria inactivation at a sub-stoichiometric titanium dioxide reactive electrochemical membrane. *Journal of Hazardous Materials* **2016**, *319*, 137-146.
- (70) Chaplin, B. P.; Wylie, I.; Zheng, H.; Carlisle, J. A.; Farrell, J., Characterization of the Performance and Failure Mechanisms of Boron-doped Diamond Ultrananocrystalline Diamond Electrodes. *J. Appl. Electrochem.* **2011**, *41*, (11), 1329-1340.
- (71) Chaplin, B. P.; Hubler, D. K.; Farrell, J., Understanding anodic wear at boron doped diamond film electrodes. *Electrochim. Acta* **2013**, *89*, 122-131.
- (72) Pletcher, D.; Walsh, F. C., Industrial Electrochemistry. In 2nd ed.; Kluwer: Dordrecht, Netherlands, 1990.
- (73) Chen, X. M.; Chen, G. H., Stable Ti/RuO₂-Sb₂O₅-SnO₂ electrodes for O₂ evolution. *Electrochimica Acta* **2005**, *50*, (20), 4155-4159.
- (74) Mousel, D.; Palmowski, L.; Pinnekamp, J., Energy demand for elimination of organic micropollutants in municipal wastewater treatment plants. *Science of the Total Environment* **2017**, *575*, 1139-1149.
- (75) Huggins, T. M.; Haeger, A.; Biffinger, J. C.; Ren, Z. J., Granular biochar compared with activated carbon for wastewater treatment and resource recovery. *Water Research* **2016**, *94*, 225-232.
- (76) Jeswani, H. K.; Gujba, H.; Brown, N. W.; Roberts, E. P. L.; Azapagic, A., Removal of organic compounds from water: life cycle environmental impacts and economic costs of the Arvia process compared to granulated activated carbon. *Journal of Cleaner Production* **2015**, *89*, 203-213.
- (77) Munoz, I.; Peral, J.; Ayllon, J. A.; Malato, S.; Martin, M. J.; Perrot, J. Y.; Vincent, M.; Domenech, X., Life-cycle assessment of a coupled advanced oxidation-biological process for wastewater treatment: Comparison with granular activated carbon adsorption. *Environmental Engineering Science* **2007**, *24*, (5), 638-651.
- (78) Bayer, P.; Finkel, M., Life cycle assessment of active and passive groundwater remediation technologies. *Journal of Contaminant Hydrology* **2006**, *83*, (3-4), 171-199.

Appendices

Table A1. Comparison of energy consumption of reported technologies for PFOA/PFOS degradation. Energy usage calculated per log removal.

Technique	Conc. (mg L ⁻¹)	Experimental Conditions	Removal efficiency of PFASs	Energy usage (kWh m⁻³)	Ref.
PFOA					
Sonolysis	0.01	358 kHz, power density of 250 W L ⁻¹ , 10 °C,	100 % in 150 min	208	1
Sonolysis	10	200W, 20 °C, argon atmosphere	85 % in 60 min	4045	2
Sonolysis	0.1	354 kHz, power density of 250 W L ⁻¹ , 10 °C, argon atmosphere	95 % in 140 min	448	3
Microwave / S ₂ O ₈ ²⁻	105	70 W, 90 °C, 50 mM S ₂ O ₈ ²⁻	99.3 % in 4 h	2599	4
Ultrasonication /CTAB	50	150 W, 40 kHz, 25 °C, 0.12 mM CTAB	79 % in 2 h	1475	5
Photolysis	559	pH = 3.7, N ₂ atm., λ = 254 nm, 200 W	89.5 % in 72 h	6687243	6
Photolysis	41	pH = 3.7, 40 °C, N ₂ atm., λ = 185 nm, 15 W	61.7 % in 2 h	90	7
Photocatalysis/ In ₂ O ₃	41	pH = 4, 0.5 g L ⁻¹ In ₂ O ₃ , 25 °C, λ = 254 nm, 23 W	82 % in 4 h	309	8
Photocatalysis/ In ₂ O ₃	30	pH = 3.9, 0.5 g L ⁻¹ In ₂ O ₃ , 25 °C, λ = 254 nm, 23 W	100 % in 3 h	230	9
Photocatalysis/ sulfite	8.3	pH = 10.3, 25 °C, N ₂ atm., λ = 254 nm, [SO ₃ ²⁻] ₀ = 10 mM, 10 W	100 % in 24 h	400	10
Photocatalysis/ sulfite	16	pH = 9.2, [SO ₃ ²⁻] ₀ = 10 mM, [DO] ₀ = ~5 mg L ⁻¹ , 250W	100 % in 10 min	556	11
Photocatalysis/ sulfite	8.3	pH = 10.3, 25 °C, N ₂ atm., λ = 254 nm, [SO ₃ ²⁻] ₀ = 10 mM, 10 W	100 % in 24 h	400	10
Photocatalysis/ sulfite	16	pH = 9.2, [SO ₃ ²⁻] ₀ = 10 mM, [DO] ₀ = ~5 mg L ⁻¹ , 250W	100 % in 10 min	556	10
Photocatalysis/ Carbonate	50	pH = 8.96–8.3, 40 mM HCO ₃ ⁻ , 0.075% H ₂ O ₂ , λ = 254 nm, 400 W	100 % in 12 h	800	12
Photocatalysis /S ₂ O ₈ ²⁻	559	pH = 2–3, 50 mM S ₂ O ₈ ²⁻ , λ = 254 nm, 200 W	100 % in 4 h	12121	13
Photocatalysis/ Cu–TiO ₂	50	pH = 5, 0.5 g L ⁻¹ , Cu–TiO ₂ , λ = 254 nm, 400 W	91% in 12 h	4173	14
Photocatalysis/ Pb–TiO ₂	50	pH = 5, 0.5 g L ⁻¹ , Pb–TiO ₂ , λ = 254 nm, 400 W	99.9 % in 12 h	1455	15
Photocatalysis/ Pt–TiO ₂	60	pH = 3, 0.5 g L ⁻¹ , Pt–TiO ₂ , λ = 365 nm, 125 W	100 % in 7 h	1458	16
Photocatalysis/ TiO ₂ -MWCNT	30	pH = 5, 1.6 g L ⁻¹ , TiO ₂ -MWCNT, λ = 365 nm, 300 W	94 % in 8 h	7857	17
Photocatalysis/ TiO ₂ -O ₃	10	0.2 g TiO ₂ , 25 mg h ⁻¹ O ₃ , λ = 254 nm, 28 W	100 % in 4 h	37	18
Photocatalysis/ TiO ₂ -rGO	100	pH = 3.8, 0.1 g L ⁻¹ TiO ₂ -rGO, 150 W	93 % in 12 h	1559	19

Photocatalysis/ TiO ₂ -Oxalic acid	10	0.5 g L ⁻¹ TiO ₂ , 3 mM H ₂ C ₂ O ₄ , N ₂ atm., λ = 254 nm, 23 W	86.7 % in 3 h	158	20
Photocatalysis/ Fenton	8.3	pH = 3, 32 mM H ₂ O ₂ , 2 mM Fe ²⁺ , λ = 254 nm, 9 W	95.2 % in 5 h	171	21
Photocatalysis/ SiC/Graphene	50	pH = 7.0, 0.5 g L ⁻¹ , λ = 254 nm, 5 W	58.5 % in 8 h	1309	22
Photocatalysis/ KI	10	0.3 mM KI, N ₂ atm., pH = 9.0, λ = 254 nm, 15 W	100 % in 14 h	95	23
Photocatalysis/ β -Ga ₂ O ₃	31	pH = 4.8, 0.5 g L ⁻¹ β -Ga ₂ O ₃ , 2 mM Fe ²⁺ , λ = 254 nm, 15 W	98.8 % in 3 h	234	24
Echem. Oxid.	100	Zr-PbO ₂ anode, current density = 10 mA cm ⁻²	97 % in 90 min	44	25
Echem. Oxid.	100	Ti/SnO ₂ -Sb/PbO ₂ anode, current density = 10 mA cm ⁻²	91.1 % in 90 min	96	26
Echem. Oxid.	100	pH = 3, Ti/SnO ₂ -Sb ₂ O ₅ /PbO ₂ -PVDF (1.0 wt%) anode, current density = 40 mA cm ⁻²	92.1 % in 180 min	144	27
Echem. Oxid.	50	Ti/SnO ₂ -Sb-Bi anode, current density, power density of 13.04 W L ⁻¹	99 % in 2 h	13	28
Echem. Oxid.	100	Ce-PbO ₂ anode, current density = 20 mA cm ⁻²	96.7 % in 90 min	30	29
Echem. Oxid.	100	Ti/SnO ₂ -F anode, current density = 20 mA cm ⁻²	99 % in 30 min	45	30
Ultrasonic Echem. Oxid.	100	SnO ₂ -Sb/Carbon anode, current density = 20 mA cm ⁻² , 33 kHz, 50W	91 % in 5 h	3985	31
Echem. Oxid.	207	Ti ₄ O ₇ anode, current density = 5 mA cm ⁻²	> 99.9 % in 2 h	5	32
Echem. Oxid.	15	BDD anode, current density = 15 mA cm ⁻²	> 90 % in 8 h	113	33
Echem. Oxid.	0.013	Ti/RuO ₂ anode, current density = 10 mA cm ⁻²	~ 95 % in 8 h	76	34
Echem. Oxid.	4.14	Ti ₄ O ₇ REM anode, V anode = 3.3 V/SHE	> 99.9 % at J = 240 LMH	5.1	<i>Present study</i>
PFOS					
Sonolysis	0.01	358 kHz, power density of 250 W L ⁻¹ , 10 °C,	98 % in 180 min	441	1
Sonolysis	10	200W, 20 °C, argon atmosphere	48 % in 58 min	11345	2
Sonolysis	0.1	354 kHz, power density of 250 W L ⁻¹ , 10 °C, argon atmosphere	72 % in 140 min	1055	3
Boiling	18.6	pH = 7, 102 °C, 6 mM PBS, 25 mL min ⁻¹ O ₂ /N ₂ , λ = 254 nm, 500 W	98 % in 4 h	1177	35
Photolysis	20	38-50 °C, N ₂ atm., λ = 254 nm, 32 W	68 % in 10 days	20693	36
Photocatalysis/ Alkaline 2- propanol	20	38-50 °C, 90 μ M NaOH, N ₂ atm., λ = 254 nm, 32 W	92 % in 10 days	9335	36
Photolysis	18.6	100 °C, pH = 11.8, λ = 254 nm, 500 W	99.8 % in 4 h	3705	37

Photolysis	10	25 °C, pH = 12.8, λ = 185 nm, 23 W	95.3 % in 72 h	3118	38
Echem. Oxid.	50	Ti ₄ O ₇ anode, current density = 5 mA cm ⁻²	93.1 % in 3 h	32	32
Echem. Oxid.	46.45	Ti/TiO ₂ -NTs/Ag ₂ O/PbO ₂ anode, current density = 30 mA cm ⁻²	74.87 % in 3h	65	39
Echem. Oxid.	0.018	Ti/RuO ₂ anode, current density = 10 mA cm ⁻²	~ 95 % in 8 h	76	34
Echem. Oxid.	5	Ti ₄ O ₇ REM anode, V anode = 3.6 V/SHE	> 99.9 % at J = 240 LMH	6.7	<i>Present study</i>

atm. = atmosphere

CTAB = Hexadecyl trimethyl ammonium bromide

DO = Dissolved Oxygen

Echem. Oxid. = Electrochemical Oxidation

PVDF = Polyvinylidene Fluoride

PBS = Phosphate Buffer Solution

References

- (1) Vecitis, C. D.; Park, H.; Cheng, J.; Mader, B. T.; Hoffmann, M. R. Kinetics and Mechanism of the Sonolytic Conversion of the Aqueous Perfluorinated Surfactants, Perfluorooctanoate (PFOA), and Perfluorooctane Sulfonate (PFOS) into Inorganic Products. *J. Phys. Chem. A* **2008**, *112*, 4261–4270. <https://doi.org/10.1021/jp801081y>.
- (2) Moriwaki, H.; Takagi, Y.; Tanaka, M.; Tsuruho, K.; Okitsu, K.; Maeda, Y. Sonochemical Decomposition of Perfluorooctane Sulfonate and Perfluorooctanoic Acid. *Environ. Sci. Technol.* **2005**, *39* (9), 3388–3392. <https://doi.org/10.1021/es040342v>.
- (3) Cheng, J.; Vecitis, C. D.; Park, H.; Mader, B. T.; Hoffmann, M. R. Sonochemical Degradation of Perfluorooctane Sulfonate (PFOS) and Perfluorooctanoate (PFOA) in Groundwater: Kinetic Effects of Matrix Inorganics. *Environ. Sci. Technol.* **2010**, *44* (1), 445–450. <https://doi.org/10.1021/es902651g>.
- (4) Lee, Y. C.; Lo, S. L.; Chiueh, P. Te; Chang, D. G. Efficient Decomposition of Perfluorocarboxylic Acids in Aqueous Solution Using Microwave-Induced Persulfate. *Water Res.* **2009**, *43* (11), 2811–2816. <https://doi.org/10.1016/j.watres.2009.03.052>.
- (5) Lin, J. C.; Hu, C. Y.; Lo, S. L. Effect of Surfactants on the Degradation of Perfluorooctanoic Acid (PFOA) by Ultrasonic (US) Treatment. *Ultrason. Sonochem.* **2016**, *28*, 130–135. <https://doi.org/10.1016/j.ultsonch.2015.07.007>.
- (6) Hori, H.; Hayakawa, E.; Einaga, H.; Kutsuna, S.; Koike, K.; Ibusuki, T.; Kiatagawa, H.; Arakawa, R. Decomposition of Environmentally Persistent Perfluorooctanoic Acid in Water by Photochemical Approaches. *Environ. Sci. Technol.* **2004**, *38* (22), 6118–6124. <https://doi.org/10.1021/es049719n>.
- (7) CHEN, J.; ZHANG, P. yi; LIU, J. Photodegradation of Perfluorooctanoic Acid by 185 Nm Vacuum Ultraviolet Light. *J. Environ. Sci.* **2007**, *19* (4), 387–390. [https://doi.org/10.1016/S1001-0742\(07\)60064-3](https://doi.org/10.1016/S1001-0742(07)60064-3).
- (8) Li, X.; Zhang, P.; Jin, L.; Shao, T.; Li, Z.; Cao, J. Efficient Photocatalytic Decomposition of Perfluorooctanoic Acid by Indium Oxide and Its Mechanism. *Environ. Sci. Technol.* **2012**, *46* (10), 5528–5534. <https://doi.org/10.1021/es204279u>.
- (9) Li, Z.; Zhang, P.; Shao, T.; Li, X. In₂O₃ Nanoporous Nanosphere: A Highly Efficient Photocatalyst for Decomposition of Perfluorooctanoic Acid. *Appl. Catal. B Environ.* **2012**, *125*, 350–357. <https://doi.org/10.1016/j.apcatb.2012.06.017>.
- (10) Song, Z.; Tang, H.; Wang, N.; Zhu, L. Reductive Defluorination of Perfluorooctanoic Acid by Hydrated Electrons in a Sulfite-Mediated UV Photochemical System. *J. Hazard.*

- Mater.* **2013**, *262*, 332–338. <https://doi.org/10.1016/j.jhazmat.2013.08.059>.
- (11) Gu, Y.; Liu, T.; Zhang, Q.; Dong, W. Efficient Decomposition of Perfluorooctanoic Acid by a High Photon Flux UV/Sulfite Process: Kinetics and Associated Toxicity. *Chem. Eng. J.* **2017**, *326*, 1125–1133. <https://doi.org/10.1016/j.cej.2017.05.156>.
 - (12) Phan Thi, L. A.; Do, H. T.; Lee, Y. C.; Lo, S. L. Photochemical Decomposition of Perfluorooctanoic Acids in Aqueous Carbonate Solution with UV Irradiation. *Chem. Eng. J.* **2013**, *221*, 258–263. <https://doi.org/10.1016/j.cej.2013.01.084>.
 - (13) Hori, H.; Yamamoto, A.; Hayakawa, E.; Taniyasu, S.; Yamashita, N.; Kutsuna, S.; Kiatagawa, H.; Arakawa, R. Efficient Decomposition of Environmentally Persistent Perfluorocarboxylic Acids by Use of Persulfate as a Photochemical Oxidant. *Environ. Sci. Technol.* **2005**, *39* (7), 2383–2388. <https://doi.org/10.1021/es0484754>.
 - (14) Chen, M. J.; Lo, S. L.; Lee, Y. C.; Huang, C. C. Photocatalytic Decomposition of Perfluorooctanoic Acid by Transition-Metal Modified Titanium Dioxide. *J. Hazard. Mater.* **2015**, *288*, 168–175. <https://doi.org/10.1016/j.jhazmat.2015.02.004>.
 - (15) Lo, S.-L.; Wu, C.-H.; Lee, Y.-C.; Chen, M.-J.; Kuo, J. Decomposition of Perfluorooctanoic Acid by Ultraviolet Light Irradiation with Pb-Modified Titanium Dioxide. *J. Hazard. Mater.* **2015**, *303*, 111–118. <https://doi.org/10.1016/j.jhazmat.2015.10.011>.
 - (16) Sun, L.; Liu, Q.; Huang, W.; Li, M.; Yu, Z. Photocatalytic Decomposition of Perfluorooctanoic Acid by Noble Metallic Nanoparticles Modified TiO₂. *Chem. Eng. J.* **2015**, *286*, 232–238. <https://doi.org/10.1016/j.cej.2015.10.037>.
 - (17) Song, C.; Chen, P.; Wang, C.; Zhu, L. Photodegradation of Perfluorooctanoic Acid by Synthesized TiO₂-MWCNT Composites under 365nm UV Irradiation. *Chemosphere* **2012**, *86* (8), 853–859. <https://doi.org/10.1016/j.chemosphere.2011.11.034>.
 - (18) Li, L.; Pan, Z.; Ling, Y.; Huang, J.; Li, X.; Wang, X. Efficient Degradation of Perfluorooctanoic Acid (PFOA) by Photocatalytic Ozonation. *Chem. Eng. J.* **2016**, *296*, 329–334. <https://doi.org/10.1016/j.cej.2016.03.116>.
 - (19) Gomez-Ruiz, B.; Ribao, P.; Diban, N.; Rivero, M. J.; Ortiz, I.; Urtiaga, A. Photocatalytic Degradation and Mineralization of Perfluorooctanoic Acid (PFOA) Using a Composite TiO₂-rGO Catalyst. *J. Hazard. Mater.* **2018**, *344*, 950–957. <https://doi.org/10.1016/j.jhazmat.2017.11.048>.
 - (20) Wang, Y.; Zhang, P. Photocatalytic Decomposition of Perfluorooctanoic Acid (PFOA) by TiO₂ in the Presence of Oxalic Acid. *J. Hazard. Mater.* **2011**, *192* (3), 1869–1875. <https://doi.org/10.1016/j.jhazmat.2011.07.026>.
 - (21) Ohno, M.; Ito, M.; Ohkura, R.; Mino, A. E. R.; Kose, T.; Okuda, T.; Nakai, S.; Kawata, K.; Nishijima, W. Photochemical Decomposition of Perfluorooctanoic Acid Mediated by Iron in Strongly Acidic Conditions. *J. Hazard. Mater.* **2014**, *268* (2014), 150–155. <https://doi.org/10.1016/j.jhazmat.2013.12.059>.
 - (22) Huang, D.; Yin, L.; Niu, J. Photoinduced Hydrodefluorination Mechanisms of Perfluorooctanoic Acid by the SiC/Graphene Catalyst. *Environ. Sci. Technol.* **2016**, *50* (11), 5857–5863. <https://doi.org/10.1021/acs.est.6b00652>.
 - (23) Qu, Y.; Zhang, C.; Li, F.; Chen, J.; Zhou, Q. Photo-Reductive Defluorination of Perfluorooctanoic Acid in Water. *Water Res.* **2010**, *44* (9), 2939–2947. <https://doi.org/10.1016/j.watres.2010.02.019>.
 - (24) Zhao, B.; Lv, M.; Zhou, L. Photocatalytic Degradation of Perfluorooctanoic Acid with β -Ga₂O₃ in Anoxic Aqueous Solution. *J. Environ. Sci.* **2012**, *24* (4), 774–780. [https://doi.org/10.1016/S1001-0742\(11\)60818-8](https://doi.org/10.1016/S1001-0742(11)60818-8).
 - (25) Xu, Z.; Yu, Y.; Liu, H.; Niu, J. Highly Efficient and Stable Zr-Doped Nanocrystalline PbO₂ Electrode for Mineralization of Perfluorooctanoic Acid in a Sequential Treatment System. *Sci. Total Environ.* **2017**, *579*, 1600–1607.

- <https://doi.org/10.1016/j.scitotenv.2016.11.180>.
- (26) Lin, H.; Niu, J.; Ding, S.; Zhang, L. Electrochemical Degradation of Perfluorooctanoic Acid (PFOA) by Ti/SnO₂-Sb, Ti/SnO₂-Sb/PbO₂ and Ti/SnO₂-Sb/MnO₂ Anodes. *Water Res.* **2012**, *46* (7), 2281–2289. <https://doi.org/10.1016/j.watres.2012.01.053>.
 - (27) Zhuo, Q.; Xiang, Q.; Yi, H.; Zhang, Z.; Yang, B.; Cui, K.; Bing, X.; Xu, Z.; Liang, X.; Guo, Q.; et al. Electrochemical Oxidation of PFOA in Aqueous Solution Using Highly Hydrophobic Modified PbO₂ Electrodes. *J. Electroanal. Chem.* **2017**, *801* (July), 235–243. <https://doi.org/10.1016/j.jelechem.2017.07.018>.
 - (28) Zhuo, Q.; Deng, S.; Yang, B.; Huang, J.; Yu, G. Efficient Electrochemical Oxidation of Perfluorooctanoate Using a Ti/SnO₂-Sb-Bi Anode. *Environ. Sci. Technol.* **2011**, *45* (7), 2973–2979. <https://doi.org/10.1021/es1024542>.
 - (29) Niu, J.; Lin, H.; Xu, J.; Wu, H.; Li, Y. Electrochemical Mineralization of Perfluorocarboxylic Acids (PFCAs) by Ce-Doped Modified Porous Nanocrystalline PbO₂ Film Electrode. *Environ. Sci. Technol.* **2012**, *46* (18), 10191–10198. <https://doi.org/10.1021/es302148z>.
 - (30) Yang, B.; Jiang, C.; Yu, G.; Zhuo, Q.; Deng, S.; Wu, J.; Zhang, H. Highly Efficient Electrochemical Degradation of Perfluorooctanoic Acid (PFOA) by F-Doped Ti/SnO₂ Electrode. *J. Hazard. Mater.* **2015**, *299*, 417–424. <https://doi.org/10.1016/j.jhazmat.2015.06.033>.
 - (31) Wang, Y.; Gao, J.; Wang, Y.; Zhao, G.; Fan, J.; Zhao, H. Fabrication of Novel SnO₂-Sb/Carbon Aerogel Electrode for Ultrasonic Electrochemical Oxidation of Perfluorooctanoate with High Catalytic Efficiency. *Appl. Catal. B Environ.* **2013**, *136–137*, 278–286. <https://doi.org/10.1016/j.apcatb.2013.02.013>.
 - (32) Lin, H.; Niu, J.; Liang, S.; Wang, C.; Wang, Y.; Jin, F.; Luo, Q.; Huang, Q. Development of Macroporous Magnéli Phase Ti₄O₇ Ceramic Materials: As an Efficient Anode for Mineralization of Poly- and Perfluoroalkyl Substances. *Chem. Eng. J.* **2018**, *354*, 1058–1067. <https://doi.org/10.1016/j.cej.2018.07.210>.
 - (33) Schaefer, C. E.; Andaya, C.; Burant, A.; Condee, C. W.; Urtiaga, A.; Strathmann, T. J.; Higgins, C. P. Electrochemical Treatment of Perfluorooctanoic Acid and Perfluorooctane Sulfonate: Insights into Mechanisms and Application to Groundwater Treatment. *Chem. Eng. J.* **2017**, *317*, 424–432. <https://doi.org/10.1016/j.cej.2017.02.107>.
 - (34) Schaefer, C. E.; Andaya, C.; Urtiaga, A.; McKenzie, E. R.; Higgins, C. P. Electrochemical Treatment of Perfluorooctanoic Acid (PFOA) and Perfluorooctane Sulfonic Acid (PFOS) in Groundwater Impacted by Aqueous Film Forming Foams (AFFFs). *J. Hazard. Mater.* **2015**, *295*, 170–175. <https://doi.org/10.1016/j.jhazmat.2015.04.024>.
 - (35) Lyu, X. J.; Li, W. W.; Lam, P. K. S.; Yu, H. Q. Boiling Significantly Promotes Photodegradation of Perfluorooctane Sulfonate. *Chemosphere* **2015**, *138*, 324–327. <https://doi.org/10.1016/j.chemosphere.2015.06.027>.
 - (36) Yamamoto, T.; Noma, Y.; Sakai, S. I.; Shibata, Y. Photodegradation of Perfluorooctane Sulfonate by UV Irradiation in Water and Alkaline 2-Propanol. *Environ. Sci. Technol.* **2007**, *41* (16), 5660–5665. <https://doi.org/10.1021/es0706504>.
 - (37) Lyu, X. J.; Li, W. W.; Lam, P. K. S.; Yu, H. Q. Insights into Perfluorooctane Sulfonate Photodegradation in a Catalyst-Free Aqueous Solution. *Sci. Rep.* **2015**, *5*, 1–6. <https://doi.org/10.1038/srep09353>.
 - (38) Jin, L.; Zhang, P. Photochemical Decomposition of Perfluorooctane Sulfonate (PFOS) in an Anoxic Alkaline Solution by 185nm Vacuum Ultraviolet. *Chem. Eng. J.* **2015**, *280*, 241–247. <https://doi.org/10.1016/j.cej.2015.06.022>.
 - (39) Zhuo, Q.; Luo, M.; Guo, Q.; Yu, G.; Deng, S.; Xu, Z.; Yang, B.; Liang, X.

Electrochemical Oxidation of Environmentally Persistent Perfluorooctane Sulfonate by a Novel Lead Dioxide Anode. *Electrochim. Acta* **2016**, *213*, 358–367. <https://doi.org/10.1016/j.electacta.2016.07.005>.

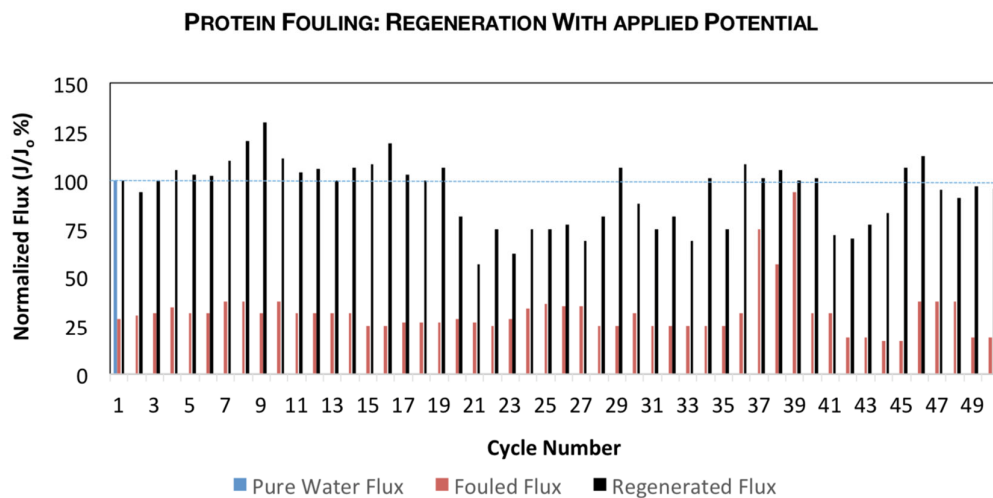


Figure A1. Consecutive fouling/regeneration cycling of an ultrafiltration REM fouled with a 0.05 wt% whey protein solution. Regenerated using backwash + anodic potential on the membrane using 0.6 A direct current. The cost of regeneration was ~\$0.04/m². The average flux recovery was 93.8% (standard deviation = 16.3%).