EXECUTIVE SUMMARY

Investigating Electrocatalytic and Catalytic Approaches for in situ Treatment of Perfluoroalkyl Contaminants in Groundwater

SERDP Project ER-2424

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TABLE OF CONTENTS

Page

1.0 INTRODUCTION 1
- 1.1 PFAS CHEMISTRY AND SOURCES 1
- 1.2 ELECTROCHEMICAL OXIDATION 2
- 1.3 REDUCTIVE CATALYTIC AND PHOTOCATALYTIC TREATMENT 2

2.0 OBJECTIVES 3

3.0 TECHNICAL APPROACH 5
- 3.1 ELECTROCHEMICAL OXIDATION EXPERIMENTS 5
- 3.2 REDUCTIVE CATALYTIC AND UV PHOTOCATALYTIC TREATMENT EXPERIMENTS 5

4.0 RESULTS AND DISCUSSION 7
- 4.1 ELECTROCHEMICAL OXIDATION EXPERIMENTS 7
- 4.2 B12-CATALYZED REDUCTION 8
- 4.3 REDUCTIVE TREATMENT BY UV-SULFITE 9

5.0 IMPLICATIONS FOR FUTURE RESEARCH AND BENEFITS 11

6.0 LITERATURE CITED 13

LIST OF FIGURES

Page

Figure 1. Representative Structures of PFAS Present in AFFF and at AFFF-impacted Sites. 1
Figure 2. Electrochemical Treatment of PFOA in 1500 mg/L Na2SO4, and (When Added) 167 mg/L NaCl. 7
Figure 3. Proposed Transformation Pathway Based on Electrochemical Treatment of 3M AFFF. 8
Figure 4. Degradation of perfluoro-3,7- dimethyloctanoic acid and the corresponding defluorination data catalyzed by B12 and CoPP complexes. 9

ACRONYMS AND ABBREVIATIONS

AFFF	aqueous film-forming foam
BDD	boron-doped diamond
BDE	bond dissociation energies
DFT	Density Functional Theory
EC	electrochemical
FTA	fluorotelomer acid
LC-QToF-MS	liquid chromatography with quantitative time-of-flight mass spectrometry
MMO	mixed metal oxide
PFAA	perfluoroalkyl acid
PFAS	per- and polyfluoroalkyl substance
PFCA	perfluorocarboxylic acid
PFHxS	perfluorohexane sulfonate
PFOA	perfluorooctanoic acid
PFOS	perfluorooctane sulfonate
PFSA	perfluoroalkyl sulfonic acid
UV	ultraviolet

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1.0 INTRODUCTION

1.1 PFAS CHEMISTRY AND SOURCES

Per- and polyfluoroalkyl substances (PFAS) include a wide range of fluorine-containing compounds. Of particular importance is the perfluorinated subclass of PFAS, referred to as perfluoroalkyl acids (PFAAs) which include perfluorocarboxylates and perfluorosulfonates (Figure 1). Under appropriate chemical or biological conditions, poly-fluorinated PFAS (i.e., not completely perfluorinated) can be converted to much more recalcitrant PFAAs, and thus are often referred to as PFAA precursors. Both PFAAs and PFAA precursors have been used in various formulations of aqueous film-forming foam (AFFF) used by the Department of Defense (DoD) for fire-fighting and fire training (Moody and Field, 1999; Moody et al., 2003; Place and Field, 2012). PFAAs are characterized by an alkane backbone, a terminal functional group, and fluorine atoms at all remaining available positions on the alkane backbone. Some PFAAs, particularly perfluorooctanoic acid (PFOA), are known to originate from the biodegradation of fluorotelomer-based precursors, some of which are present in AFFF (Place and Field, 2012).

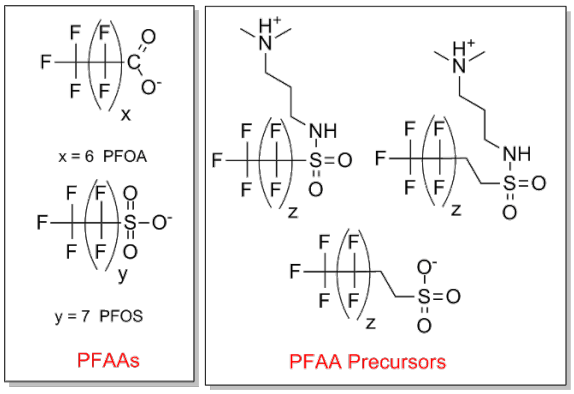

Figure 1. Representative Structures of PFAS Present in AFFF and at AFFF-impacted Sites.

While some attention has recently been focused on the remediation of PFAAs such as perfluoroctane sulfonate (PFOS) and PFOA, considerably less attention has been given to PFAA precursors. Evidence from the project team's (the team) site investigation at Ellsworth AFB, which included analysis of PFAA in soil and groundwater as well as direct measurement of specific PFAA precursors and oxidizable PFAA precursors (measured through the formation of perfluorocarboxylates in the laboratory using persulfate; Houtz and Sedlak, 2012), suggests that *in situ* transformation of PFAA precursors to PFAAs is likely and may be facilitated by processes such as air biosparging (McGuire et al., 2014). In the team's investigation of the site, samples collected from locations outside the zone of influence of these remedial activities showed much higher levels of PFAA precursors. ***With respect to remediation, these data suggest that any* in situ *treatment for PFAAs must also be capable of treating the PFAA precursors, as these chemicals may be an important source of PFAAs at AFFF-impacted sites.***

1.2 ELECTROCHEMICAL OXIDATION

An alternative and particularly promising approach for treatment of PFOS, PFOA, and other PFAS is via electrocatalytic oxidation at mixed metal oxide (MMO) or boron-doped diamond (BDD) anodes (Carter and Farrell, 2008; Ochiai et al., 2011, Zhuo et al., 2011). Of particular note are the results of Zhou et al. (2011), who demonstrated the use of MMO on titanium anodes for treatment of PFOA in electrolyte solution. These reactions occur via an initial step of direct electron transfer at the anode; electrochemically generated oxidants may also facilitate the oxidation of fluorinated daughter products or precursor compounds. The generation of oxidants provides added benefit, as these oxidants (i.e., hydroxyl radical, chlorine) can be effective for removal of hydrocarbon or chlorinated solvent co-contaminants that often are co-mingled with PFASs, such as the plume observed during the team's investigation at Ellsworth AFB. When using BDD anodes, substantial quantities of perchlorate were also formed from chloride present in the groundwater being treated.

1.3 REDUCTIVE CATALYTIC AND PHOTOCATALYTIC TREATMENT

As highly halogenated chemicals, PFAS may also be subject to reductive transformation in the presence of suitably strong reducing agents or catalysts. Recently, Ochoa-Herrera et al. (2008) observed >70% fluoride ion (F^-) release from a mixture of branched PFOS isomers by reaction with Vitamin B12 (a corrin-Co^{III} complex, catalyst precursor) and Ti^{III} citrate (reductant) (Ochoa-Herrera et al., 2008). While B12 is a naturally occurring enzyme co-factor, this finding also suggests a strategy for synthetic catalysts based upon Co-corrin complexes that may be effective in promoting reductive transformation of PFAS. A second approach to achieve reductive transformation of PFAS involved ultraviolet (UV) generation of strongly reducing hydrated electrons (e_{aq}^-, NHE = -2.9 V), which have been shown to be effective in degrading individual PFAA structures, including PFOS and PFOA (Buxton et al., 1988; Gu et al., 2017, 2016; Herbert and Coons, 2017; Park et al., 2011, 2009; Qu et al., 2016, 2010; Song et al., 2013). These short-lived reactive species can be generated via UV excitation of an appropriate sensitizer species (e.g., iodide, 3-indole acetic acid, nitrilotriacetic acid, sulfite) (Park et al., 2009; Song et al., 2013; Sun et al., 2018; Tian et al., 2016). Here, the team focuses on use of sulfite. While the UV-sulfite process has been demonstrated to be effective in transforming individual PFAS compounds, the efficacy of this process for treatment of the broader range of PFAS mixtures present in AFFF-impacted waters is unknown. Most importantly, little is known about the effectiveness of UV-sulfite treatment for structures beyond the perfluorocarboxylic acids (PFCAs) and perfluoroalkyl sulfonic acids (PFSAs) for which reference standards are available to quantify directly.

2.0 OBJECTIVES

The overall goal of this research was to develop and assess the use of electrocatalytic and catalytic/photocatalytic approaches for treatment of PFAS in groundwater. For this effort, the team's focus was initially on two parallel treatment approaches that rely on catalytic metals. The first approach relied on the use of MMO and BDD anodes for the catalytic oxidation of PFAS in electrochemical (EC) systems. The second approach involved the use of supported rhodium (Rh)-based catalysts to facilitate reductive hydrodefluorination of PFAS; this second approach had potential for treatment as a permeable reactive barrier, or as an *in situ* source area treatment technology. Initial testing of this second reductive approach indicated that treatment would not be effective, so the reductive approach was modified to focus on two approaches that showed early promise for reductive transformation of PFAS: (1) application of B12 and related cobalt corrin complexes as homogeneous catalysts, and (2) application of UV-sulfite for generation of hydrated electrons (e_{aq}^-). Thus, this study focused on PFAS treatment via:

1. Electrochemical oxidation
2. Reduction using B12-catalyzed reaction
3. Reduction using the UV-sulfite process

To attain the overall project goal, the following specific objectives were developed:

- Measure the degradation kinetics of representative PFASs during electrochemical oxidation treatment and B12-catalyzed and UV-sulfite reductive treatment processes.
- Identify PFAS transformation products and elucidate the controlling reaction mechanisms.
- Determine the optimal anode formulations for treatment.
- Determine the influence of current density on electrochemical treatment performance.
- Evaluate the impacts of co-contaminants and groundwater geochemistry on treatment effectiveness and anode longevity.
- Demonstrate that the wide range of PFAS, including perfluoroalkyl acid precursors, can be effectively treated using the proposed strategies.
- Evaluate the overall potential for treatment using both the oxidative and reductive technologies.

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3.0 TECHNICAL APPROACH

3.1 ELECTROCHEMICAL OXIDATION EXPERIMENTS

Electrochemical oxidation experiments were performed using a small bench-scale system. Various commercially available anode materials were evaluated (i.e., MMO and BDD anodes from multiple vendors) and both undivided and divided cell configurations were evaluated. Experiments were performed over a range of applied current densities in both simple electrolytes (e.g., sodium sulfate, sodium chloride) and in natural groundwater. In addition, both individual PFAA compounds were evaluated, as well as complex PFAS mixtures associated with AFFF-impacted groundwaters and diluted 3M AFFF solutions. PFAS treatment was evaluated with respect to transformation of suspected PFAA precursors (when present), removal of PFAAs, fluoride generation, and overall energy demand. Generation of perchlorate, as well as the ability to subsequently biologically reduce the generated perchlorate, was also evaluated as part of this study.

3.2 REDUCTIVE CATALYTIC AND UV PHOTOCATALYTIC TREATMENT EXPERIMENTS

Experiments evaluating PFAS reduction catalyzed by B12 and structurally related corrin complexes were conducted in batch experiments performed under strict anaerobic conditions in a glovebox environment. Replicate batch reactors were prepared with individual perfluorocarboxylate structures together with cobalt catalyst, bulk reducing agent (Ti^{III}-citrate), and pH buffer. Reactions were monitored for a period of 15 days, monitoring both fluoride ion release (by ion chromatography) and degradation of the parent PFAS structures (by high resolution liquid chromatography with quantitative time-of-flight mass spectrometry (LC-QToF-MS) analysis). Experimental results were complemented with Density Functional Theory (DFT) to calculate molecular descriptors that would be predictive of PFAS reactivity with the cobalt complexes.

UV-sulfite treatment experiments were performed using a quartz immersion well photoreactor incorporating an 18 W low pressure Hg UV lamp that irradiates at 254 nm. Sodium sulfite was provided as a UV sensitizer to generate hydrated electrons (e_{aq}^-) upon irradiation. Solution pH was typically buffered at 9.5 using 5 mM $NaHCO_3$. Experiments examined the treatment of individual PFAA structures (PFOS, PFOA, PFHxS), treatment of AFFF diluted in pH buffered solution (typically diluted 1-to-60,000 fold to mimic groundwater PFAS concentrations), and treatment of AFFF-impacted groundwater collected from DoD facilities. High resolution LC-QToF-MS analysis was used to monitor degradation of individual PFAS in the different mixtures. In selected experiments, fluoride ion release was monitored using ion selective electrode measurements. UV-only and dark control reactions were included to verify that transformation results principally from UV generation of hydrated electrons. Experiments also examined reactivity of suspected precursors that generate PFAAs as reaction byproducts during treatment.

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4.0 RESULTS AND DISCUSSION

4.1 ELECTROCHEMICAL OXIDATION EXPERIMENTS

Initial electrode screening experiments indicated that BDD anodes, as opposed to a wide variety of MMO anodes, were the most effective for treating PFOS and PFOA. Subsequent experiments showed that substantial removal and defluorination of PFOA (Figure 2) and PFOS occurred, and overall treatment was a function of the applied current density. Treatment in electrolyte was similar to that observed in natural groundwater. Although substantial generation of perchlorate and chlorate occurred due to the oxidation of chloride, subsequent biotic treatment (via addition of electron donor) facilitated the reductive treatment of the electrochemically generated perchlorate.

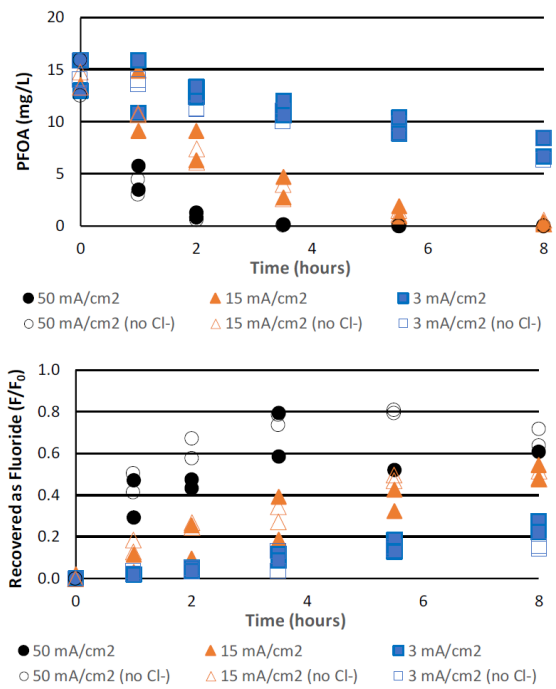

Figure 2. Electrochemical Treatment of PFOA in 1500 mg/L Na_2SO_4, and (When Added) 167 mg/L NaCl.

Additional EC experiments using 3M AFFF-spiked water provided insight into the complex oxidation pathway for the suspected PFAA precursors (Figure 3).

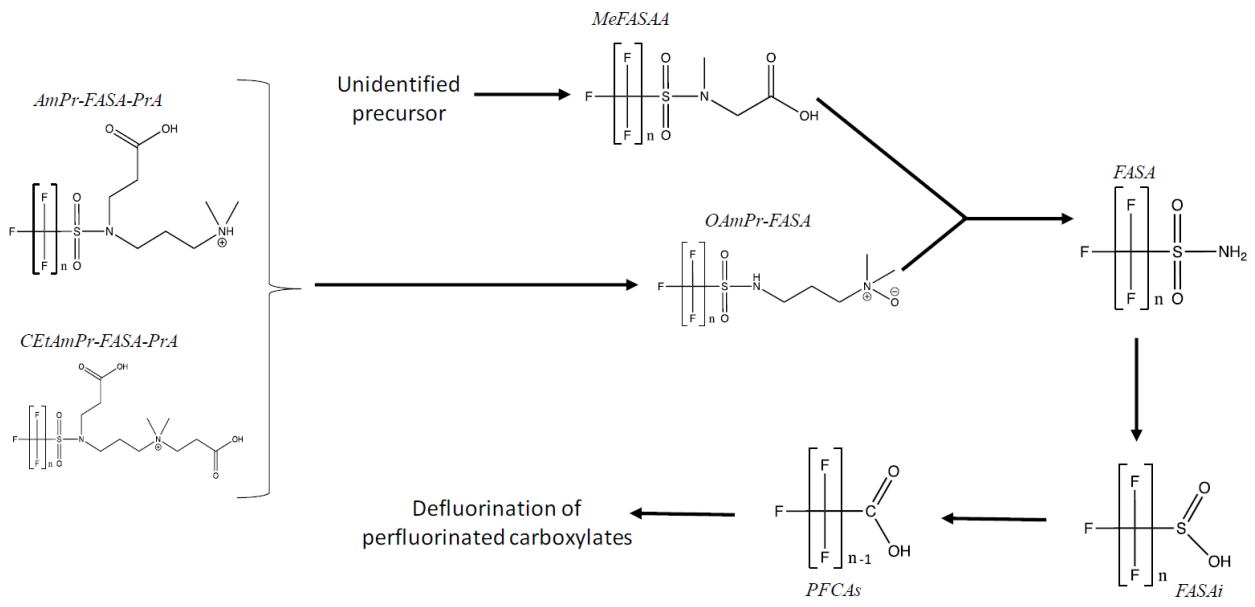

Figure 3. Proposed Transformation Pathway Based on Electrochemical Treatment of 3M AFFF.

Solid lines point to compounds that showed a transient increase during electrochemical treatment.

Interestingly, the oxidation pathway observed in historically AFFF-impacted groundwater did not result in the transient generation of PFAAs as observed in Figure 3, despite the fact that abundant PFAA precursors were present and the fact that fluoride generation indicated that substantial defluorination of precursors occurred. These results highlight the complexity of understanding oxidation pathways and fluorine mass balances when performing EC oxidation on AFFF-impacted waters.

4.2 B12-CATALYZED REDUCTION

Experiments demonstrated reductive transformation of branched PFAS catalyzed by B12 and structurally related cobalt-corrin (CoPP) complexes (Figure 4). Experimental results and theoretical calculations revealed correlations between the extent of PFAS defluorination, the local C−F bonding environment, and calculated bond dissociation energies (BDEs). In general, BDEs for tertiary C−F bonds < secondary C−F bonds < primary C−F bonds. A tertiary C−F bond adjacent to three fluorinated carbons (or two fluorinated carbons and one carboxyl group) had a relatively low BDE that permits an initial defluorination to occur. Neither B12 or CoPP complexes induced significant defluorination in linear perfluorooctanoic acid (PFOA; no tertiary C−F bond) or a perfluoroalkyl ether carboxylic acid (tertiary C−F BDEs too high). Thus, the current complexes have limited utility in treating legacy mixtures of PFAS that are predominantly linear in nature. That said, these results do open new lines of research, including (1) designing branched PFAS and cobalt complexes that promote complete defluorination in natural and engineered systems, and (2) evaluating potential impacts of branched PFAS in biological systems where B12 is present.

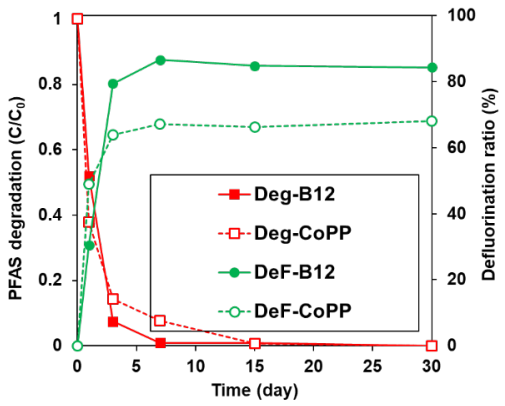

Figure 4. Degradation of perfluoro-3,7- dimethyloctanoic acid and the corresponding defluorination data catalyzed by B12 and CoPP complexes.

Reaction conditions: PFAS (0.1 mM), Co catalyst (0.25 mM), Ti^{III} citrate (~36 mM), and carbonate buffer (~40 mM) pH 9.0; 70°C.

4.3 REDUCTIVE TREATMENT BY UV-SULFITE

Here, UV-sulfite treatment was applied to an AFFF mixture diluted in buffered electrolyte matrix to characterize reactions between hydrated electrons (e_{aq}^-) and different PFAS structures (>40) identified by high resolution LC-QTOF-MS analysis. Results of these experiments show that individual PFAA structures (PFOS, PFOA, and PFHxS) present in the AFFF mixture are degraded at measured reaction rates similar to rates measured in individual-solute experiments, validating that the rate constants the team measured for diverse structures in the AFFF mixture are representative of rates that would occur in isolation. Results show that PFAS reactivity varies widely among PFAS structures present in AFFF. Whereas some structures, including PFCAs like PFOA, long-chain PFSAs like PFOS and some precursor species of PFAAs are readily broken down upon UV sulfite treatment, some other structures, most notably the short-chain PFSAs like perfluorobutane sulfonate and fluorotelomer acid species (FTAs) are much less reactive during UV-sulfite treatment (Figure 5). These trends are consistent with results from fluoride release measurements where the extent of fluoride ion release from the PFAS was incomplete (up to 53% of the fluorine content of the AFFF during reactions).

In addition, temporal data indicates that selected PFSAs, PFCAs, and FTAs can form as intermediates or stable end-products due to UV-sulfite treatment of PFAA precursors. Thus, these results indicate that while treatment with UV-sulfite can be effective for treating PFOS and PFOA down to the United States Environmental Protection Agency's recently released lifetime health advisory levels (HALs), remediation of the wider diversity of PFAS identified at DoD sites will be more challenging. UV-sulfite treatment experiments were also conducted with AFFF-impacted groundwater collected from DoD facilities. Results of this work confirms successful PFAS treatment in a variety of groundwater matrices. Rates of individual PFAS destruction in groundwater are similar or greater than those observed in lab-spiked solutions, suggesting promise for remedial applications. Structure-reactivity trends also reveal mechanistic insights that can be applied to predict reactivity with a wider range of potential undiscovered PFAS structures.

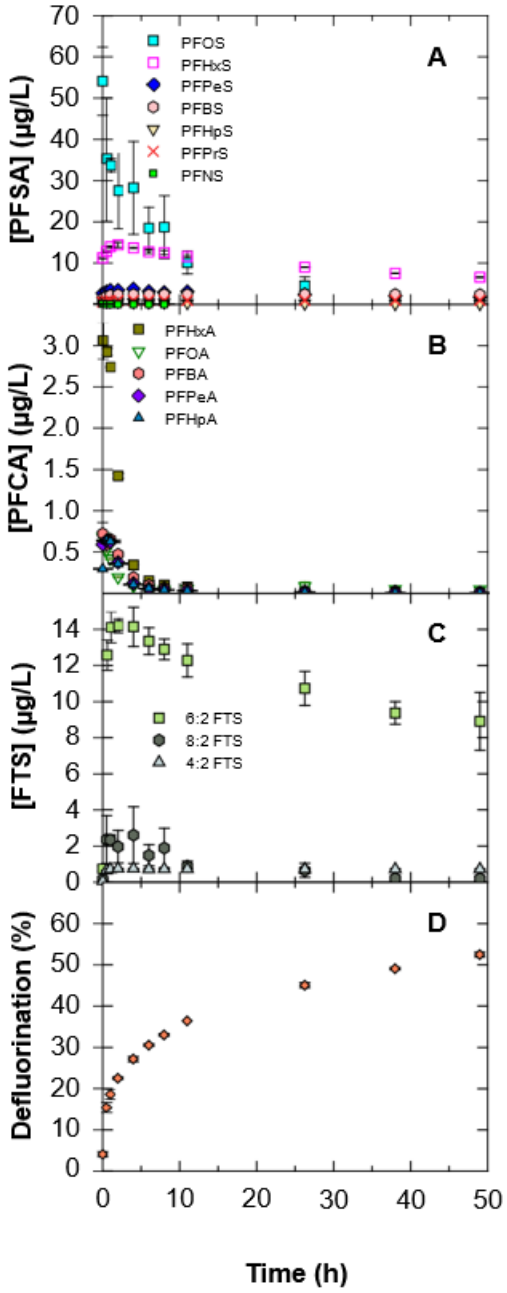

Figure 5. Reaction Timecourse Data for UV-sulfite Treatment of PFAS Detected in AFFF by Targeted Analysis.

(A) PFOS and related PFSAs, (B) PFOA and related PFCAs, and (C) FTSs. Panel (D) Shows the percent of total fluorine released as F- during treatment with UV-sulfite. Reaction conditions: AFFF (1-to-60,000 dilution), 10 mM Na2SO3, 5 mM NaHCO3 (pH0 = 9.5).

5.0 IMPLICATIONS FOR FUTURE RESEARCH AND BENEFITS

Together, results from the EC oxidation, B12, and UV-sulfite studies suggest that these technologies show promise, but have challenges, for remedial application. EC oxidation is effective for the wide range of PFAS typically present in AFFF formulations, even in the presence of other organic contaminants. However, substantial energy is expended related to the oxidation of suspected PFAA precursors. Approaches to develop more energy efficient and cost-effective approaches for these initial oxidation steps would likely benefit the EC approach. In addition, BDD anodes are expensive compared to other anodes typically used in the industry, so development of more inexpensive anodes, or methods to increase the effective surface area of BDD anodes, are likely needed to promote widespread application of this technology. Finally, perchlorate generation is problematic from both a Coulombic efficiency perspective, as well as a health/regulatory perspective. While applications in the absence of chloride (e.g., treatment of PFAS in chloride-free ion exchange regeneration solutions) may provide an excellent opportunity for EC oxidation of PFASs, methods to effectively eliminate this problematic reaction or to readily reduce the perchlorate once formed (e.g., via biotic treatment) require further demonstration.

UV-sulfite treatment is effective for some classes of PFAS, but others, most notably short-chain sulfonic acid and fluorotelomer acid structures, are found to be unreactive with hydrated electrons. Fortunately, short chain analogues that appear most recalcitrant are also considered to pose much less health risks than long-chain analogues. Still, this process is much more effective than the more commonly applied persulfate-based oxidation technologies that are only effective at oxidizing perfluorocarboxylic acid structures and PFAA precursors. One potential strategy worth investigating in the future is a sequential persulfate-UV-sulfite treatment where a wide range of PFAA precursors can first be oxidized to perfluorocarboxylate structures, which should then be amenable to rapid reduction by UV-sulfite treatment (results presented here show that perfluorocarboxylates are highly reactive regardless of chain length). Like EC treatment, UV-sulfite treatment with conventional low pressure Hg lamps is energy intensive, likely limiting applications to concentrate stream management applications. That said, the technology will also benefit from ongoing research into more efficient light sources (e.g., UV LEDs) that direct a larger fraction of input energy to UV photons (and not lost as head) and identification of sensitizers that produce hydrated electrons with greater quantum efficiencies (i.e., fraction of UV photons resulting in generation of hydrated electrons).

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