

FINAL REPORT

Quantification of In Situ Chemical Reductive Defluorination (ISCRD) of Perfluoroalkyl Acids in Groundwater Impacted by AFFFs

SERDP Project ER-2426

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14. ABSTRACT At the start of this ER-2426 project, the primary approach to mitigate PFAS transport and contamination of drinking water was sorbents, which came with challenges to effectively capture shorter chain PFAAs. Longevity and regeneration. The primary goal of this project was to identify reductive technologies amenable for in situ destructive remediation of PFAS with PFOS as the initial focus. This research led to the development of a reductive technology using NiOFeO nanoparticles synthesized onto an activated carbon (AC). The technology was demonstrated in batch and 1-D column reactors to transform and mineralize L- and br-PFAS with fluoride and sometimes sulfite generation and organic intermediates. All PFAS transformed and mineralized to varying degrees. Additional column studies, which best mimic how well this technology may work in the field either as an in situ permeable reactive barrier, above ground treatment (a reactive GAC rather than just a sorptive GAC) or in situ injection are needed to evaluate further transformation and defluorination at increased residence times.					
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ABSTRACT

Introduction and Objectives: At the start of this ER-2426 project, the primary approach to mitigate PFAS transport and contamination of drinking water was sorbents, which came with challenges to effectively capture shorter chain PFAAs. Longevity and regeneration. Very little was known about potential technologies that could destroy PFAS, in particular PFOS, which had been identified as the most recalcitrant PFAS to even abiotic technologies. What we did know at the time was that microbial degradation of PFAS would lead to terminal PFAAs. Also the abiotic technologies that had been evaluated at some level for destruction of PFOS and PFOA were either unsuccessful, had questionable results or were simply not amenable for in situ remediation of groundwater. The large PFAS-contaminated plumes being generated from military bases due to the frequent use of AFFFs called for the need to identify in situ destructive remediation technologies to mitigate PFAS transport offsite. The primary goal of this project was to identify reductive technologies amenable for in situ destructive remediation of PFAS with PFOS as the initial focus.

Technical Approach: We investigated a subset of zero valent metals/bimetal particles alone and associated with a carrier for ease of injection (e.g., synthesized within clay interlayers or onto granulated activated carbon) and a metal-catalyzed Vitamin B12 to defluorinate PFAS (primarily PFOS) as well as a coupled reductive/oxidative (permanganate/persulfate) technology. To different extents depending on success of preliminary experiments, our studies included: (1) quantifying the magnitude, rate, and effectiveness of a technique to defluorinate linear PFOS in aqueous batch reactions within an environmentally relevant PFOS concentration ranges with multiple lines of evidence (PFOS loss, generation of inorganic (fluoride and sulfite) and organic products; (2) characterizing intermediates resulting from incomplete defluorination; and (3) quantify matrix effects; and (4) evaluate defluorination in column studies.

Results: This research led to the development of a reductive technology using Ni^0Fe^0 nanoparticles synthesized onto an activated carbon (AC). The technology was demonstrated in batch and 1-D column reactors to transform and mineralize L- and br-PFAS with fluoride and sometimes sulfite generation and organic intermediates. All PFAS transformed and mineralized to varying degrees. Overall, fluoride generation was greatest for the PFASs with the highest transformation and mineralization observed for PFOS (> 94%). For the PFAAs, transformation rates and % fluoride generated relative to moles of parent transformed decreased with decreasing perfluorocarbon chain length. In addition we exemplified that VB12 technology cannot be enhanced to degrade L-PFASs due to steric hindrances and not activation energy, thus addition of stronger reductants/catalysts will not help. The other bimetal nPdFe^0 , that initially showed promise, did not transform PFOS, but only sorbed and complexed PFOS; PFOS complexation with iron reduces quantifiable PFOS concentrations. We also found that neither PM, persulfate or a combination of the two (ScisoR Technology[®]) can transform PFOS. Apparent PFOS loss appeared to be due to clustering and salting out, which leads to sampling artifacts, thus underestimating PFOS concentrations. Fluoride impurities in reagents used as well as peaks that interfere with proper fluoride quantitation led to wrongly assuming fluoride was being generated.

Benefits: Additional column studies, which best mimic how well this technology may work in the field either as an in situ permeable reactive barrier, above ground treatment (a reactive GAC rather than just a sorptive GAC) or in situ injection are needed to evaluate further transformation and defluorination at increased residence times. Also potential impacts of additional groundwater matrix parameters including non-PFAS co-contaminants likely to be present at AFFF-impacted sites as well as regeneration potential of the nNi^0Fe^0 -AC nanocomposite should be evaluated. Preliminary data indicated that there is potential for in situ regeneration.

ABBREVIATIONS AND ACRONYMS

ABTS	2,2'-Azino-bis(3-ethylbenzothiazoline-6-sulfuric acid)
AFB	Air Force Base
AFFF	Aqueous film forming foam
AOTs	Advanced oxidation technologies
br-	Branched
ECD	Electrochemical detection
ECF	Electrofluorination
F ⁻	Fluoride
F	Fluorine
Fe ⁰	Zero valent iron
FTS	Fluorotelomer sulfonate
HCl	Hydrochloric acid
HDPE	High density polyethylene
HPLC	High performance liquid chromatography
IC	Ion chromatography
L-	Linear
LC-MS/MS	Liquid chromatography tandem mass spectrometry
Mg	Magnesium
N ₂	Nitrogen
NaOH	Sodium hydroxide
NH ₄ OH	Ammonium hydroxide
Na ₂ SO ₄	Sodium sulfate
Ni	Nickel
NP	Nanoparticle
nZn	Nano-zinc
Pd	Palladium
PFAS	Perfluoroalkyl substances
PFBA	Perfluorobutanoate
PFBS	Perfluorobutane sulfonate
PFCAs	Perfluorinated carboxylates
PFHpA	Perfluoroheptanoate
PFHpS	Perfluoroheptane sulfonate
PFHxA	Perfluorohexanoate
PFHxS	Perfluorohexane sulfonate
PFNA	Perfluorononanoate
PFNS	Perfluorononane sulfonate
PFOA	Perfluorooctanoate
PFOS	Perfluorooctane sulfonate
PFPeA	Perfluoropentanoate
PFSAs	Perfluoroalkyl sulfonates
pK _a	Acid dissociation constant
PM	Permanganate
PRB	Permeable Reactive Barrier
PV	Pore Volume
QToF	Quadrupole time of flight
SO ₃ ²⁻	Sulfite
SO ₄ ²⁻	Sulfate

SI	Supplemental Information
TOP	Total oxidizable precursor
VB12	Vitamin B12
Wt%	weight %
XRD	xray diffraction
XPS	x-ray photoelectron spectroscopy

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EXECUTIVE SUMMARY

Introduction

At the time of the ER-2426 project, capture with activated carbon was the only technology being used for removal of PFAA contaminated groundwater (NRC Report, 2012). However, this approach commonly results in only limited remediation and typically requires decades of operation. Because of this, the U.S. Air Force, which had the most PFAS-contaminated sites among DOD-associated sites, had endeavored to apply in situ destructive technologies whenever possible. However, no such treatment methods were available for the entire range of PFAS. Advanced oxidative technologies have been demonstrated with some success for PFOA and other PFAAs, but not for PFOS (both in literature review and our own research). Similarly, to the best of our knowledge, biological treatment had not been demonstrated effective for either perfluorooctanoic acid (PFOA) or PFOS. Methods that have been demonstrated as effective for both PFOA and PFOS required conditions that were not applicable for use in situ, including high temperature, pressure, the presence of UV light, or the lack of dispersed treatment (such as in the case of an electrode treatment). Therefore, the overarching goal of this research was to identify an in situ chemical reductive defluorination (ISCRD) technology that could destroy PFAAs in AFFF-impacted groundwater with an initial focus on PFOS. Specific question posed included:

- *What degree of defluorination (especially for L-PFOS) can be achieved with the various reductive techniques that are amenable for in situ use?*
- *What are the reaction mechanisms and pathways (intermediates) for PFOS defluorination using the proposed reductive techniques?*
- *For techniques where fluoride generation is the greatest, do perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonic acids (PFSAs) defluorinate to a similar extent and through a similar pathway?*
- *For techniques where fluoride generation is the greatest, how is defluorination potential affected by various solution parameters (pH, electrolyte composition, redox potential) and co-contaminants likely to be associated with AFFF-contaminated groundwater?*
- *For the techniques where fluoride generation is the greatest, how does the presence of porous media affect defluorination potential and reductant reactivity?*
- *How can the overall effectiveness and remediation success be increased by a treatment train approach; how amenable are intermediates to other remediation processes?*

Objectives

The following technical objectives (tasks) were defined to address the questions posed:

1. Quantify the degree of PFOS defluorination that can be achieved with selected abiotic reductive techniques
2. Characterize rates, intermediates, and pathways
3. Evaluate enhanced delivery techniques of bimetal reductants
4. Quantify key solution and porous media effects on defluorination
5. Assess permeable bimetal reactive barrier potential
6. Probe degradation potential of intermediates by other remediation processes in support of treatment train strategies.

Technical Approach

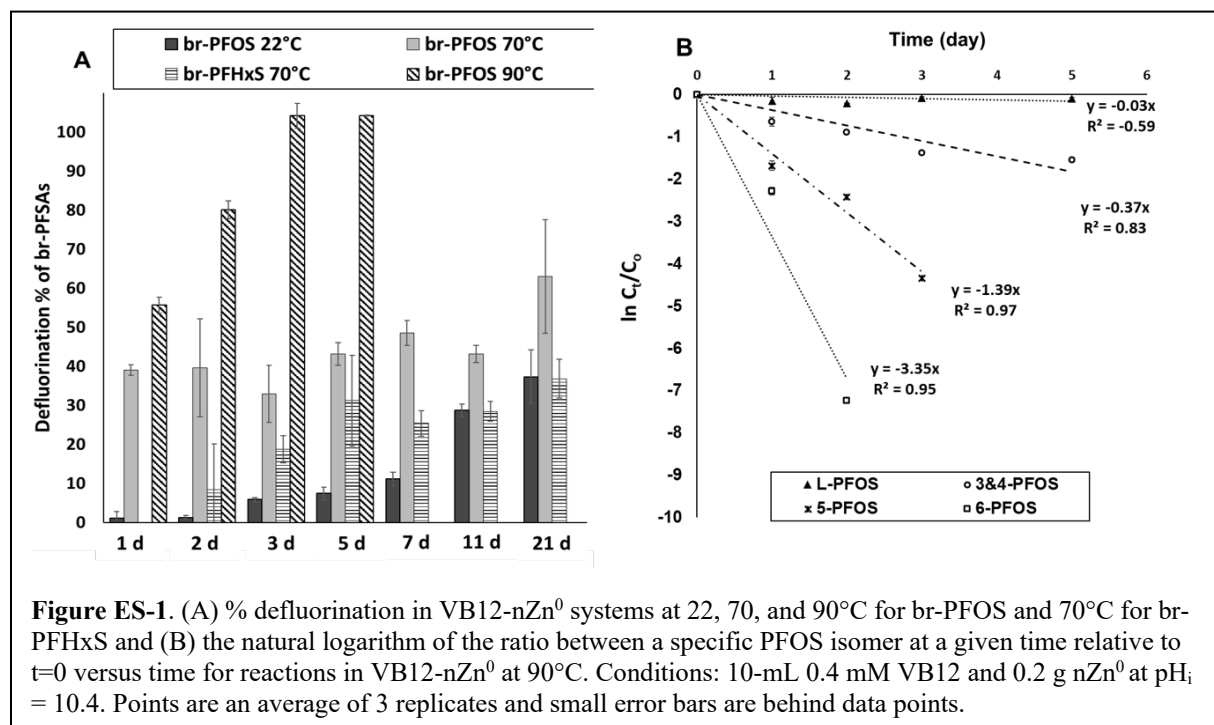
A multiple lines-of-evidence approach was taken with each technology explored. First, we quantified the loss of the target PFOS for several different reductive approaches in batch reactors. The reductive approaches investigated included vitamin B12 systems with nano-Fe⁰ and micro-Zn⁰ catalysts; Pd/micro-Mg⁰, Pd/nFe⁰ and Ni⁰/nFe⁰ bimetals of which in some cases, the bimetals were synthesized within a 2:1 clay support; nano Ni⁰Fe⁰, PdNiFe⁰, CuNiFe⁰, MgNiFe⁰ particles synthesized onto an activated carbon (AC) support; nNi⁰Fe⁰ and Fe⁰ on an AC-magnetite (Fe₃O₄) platform; and reductive/oxidative permanganate-based systems. Almost all work was done in high-density polyethylene (HDPE) or glass batch reactors except for the nNiFe⁰-AC work, which included 1-D column studies. Each technology suite being explored required some associated method development such that we could accurately quantify target parent PFAS and PFAS isomers where possible/appropriate, accurately quantify fluoride and sulfite metabolites where applicable, and identify organic metabolites with quantitation when possible, and ensure an exhaustive extraction of PFAAs towards achieving a fluorine mole balance. If PFOS mass recovered was less than the initial PFOS mass introduced, then generation of fluoride and in some cases sulfite (after oxidative conversion to sulfate) was quantified using ion chromatography with electrochemical detection (**Task 1**). We optimized the inorganic anion analyses to ensure separation of early eluting fluoride from other early eluting byproducts (e.g., acetate and formate). For technologies that showed fluoride generation, additional analysis was done (**Task 2**). If a sufficient fluorine mole balance was not obtained, nontarget screening of intermediates was performed using high resolution mass spectrometry as well as quantification of suspected organic degradation products for which standards were available at the time. In addition, loss over time (rates) was characterized in batch reactors and degradation pathways were explored. For technologies involving bimetal reductants, the ability of the technology to retain reactivity was explored in batch reactors with a subset of delivery mechanisms including 2:1 clays and activated carbon (**Task 3**). The effects of a subset of constituents that may be present in solution or associated with aquifer material were evaluated in batch reactors for some of the technologies (**Task 4**). For the most promising bimetal technology, PFOS and PFAA mixture degradation was evaluated in constant saturated flow 1-D column studies, which were considered a type of bench scale permeable reactive barrier (PRB) (**Task 5**). Effluent pH, ORP, PFAS concentrations and fluoride concentrations were monitored followed by column sectioning and extraction of column sections for PFAS and fluoride. We also evaluated in batch reactors claims that a permanganate-persulfate oxidative/reductive system degraded PFOS (**Task 6**) because apparent lab-based observations were inconsistent with theory regarding PFOS transformation. We suspected other mechanisms and artifacts were leading to such results. Additional method details can be found in the results and discussion and in the associated journal articles (Modiri Gharehveran et al., 2021; Park et al., 2020, 2018, 2017; Zenobio et al., 2021, 2020).

Results and Discussion

Vitamin B12 (VB12) Systems. Our initial work focused on seeing if Vitamin B12 systems could be optimized to degrade both linear and branched PFOS under conditions amenable for in situ use. The effectiveness of VB12 in the systems evaluated by Ochoa-Herrera et al. (2008) required high concentrations of Ti(III)-citrate and only transformed br-PFOS. Therefore, we explored alternate reductants for use in VB12 systems with a primary focus on nano-sized zero valent zinc (nZn⁰), which has a higher reduction potential than Ti(III) (Bratsch, 1989), and to a lesser extent

(one temperature and time), $n\text{Fe}^0$ and $n\text{Pd}^0\text{Fe}^0$. As expected, $n\text{Zn}^0$ performed the best of the three metal catalysts tested. Transformation over time with VB12- $n\text{Zn}^0$ was investigated at 22, 70 and 90°C for PFOS and at 70°C for PFHxS, with F^- generation and isomer-specific PFSA removal rates quantified (Figure ES-1). Only br-PFOS degraded with 95% of the br-PFOS isomers transformed at 90 °C within 5 d. Isomer-specific removal rates were positively correlated to the br- CF_3 's proximity to the terminal CF_3 . Br-PFHxS transformation was approximately two times slower with less defluorination than br-PFOS. C8/C7 and C6/C5 polyfluorinated sulfonates from br-PFOS and br-PFHxS, respectively, were identified as both intermediates and apparent dead-end products. Pathways included 4 F replaced by 2 H and a C=C bond, and serial F replacement by H with up to 12 F atoms removed from br-PFOS.

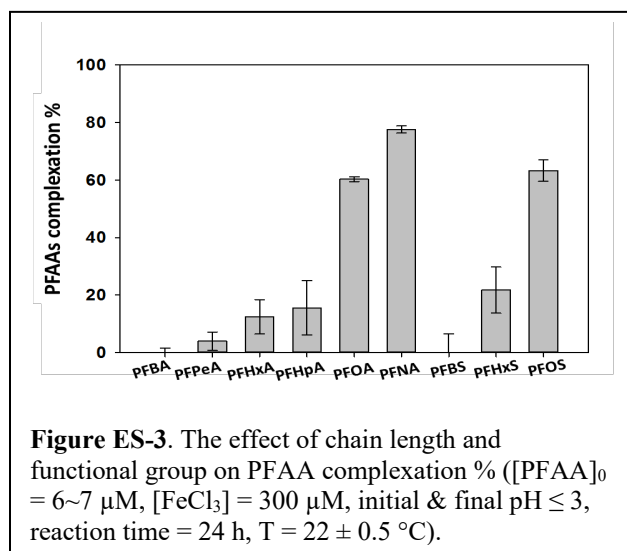
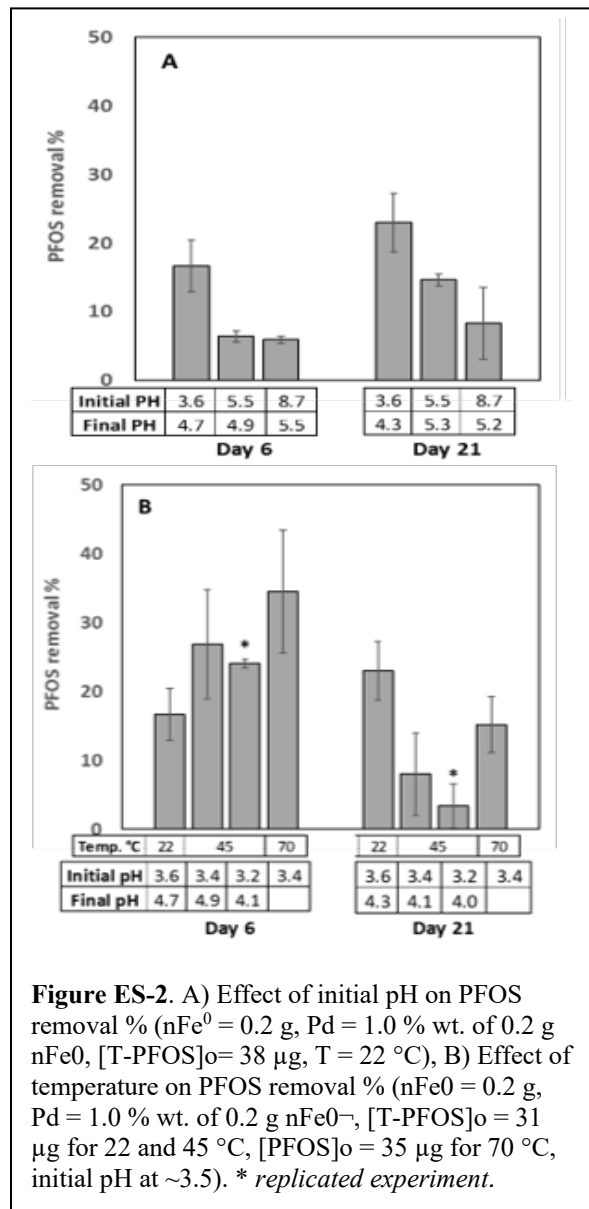
L-PFOS was not degraded with VB12 regardless of addition of $n\text{Zn}^0$, $n\text{Fe}^0$, and $\text{Pd}/n\text{Fe}^0$ as catalysts. The absence of L-PFOS transformation by VB12 appeared to be due to the inability of L-PFSAs to complex with VB12 and not an activation energy issue, thus not something that can be overcome by stronger reductants/catalysts. Additional details can be found in (Park et al., 2017).



$n\text{PdFe}^0$ Systems. The use of $n\text{PdFe}^0$ did not enhance L-PFOS destruction in Vitamin B12 systems because the process was limited by VB12's ability to complex L-PFOS and not activation energy. However, we wanted to evaluate if it could independently defluorinate PFOS. Palladizing $n\text{Fe}^0$ is known to reduce the activation energy for defluorination of organochlorine molecules due to the electron filling potential of the unfilled orbitals in Pd (Wang et al., 2008; Zhang et al., 1998), increase the reactive surface area, and increase the reactive sites on the Fe^0 surface for conversion of H^+ or/and H_2 to hydrogen radicals ($\text{H}^\bullet$) (Elliott and Zhang, 2001; Shao-ping et al., 2005). PFOS removal using $\text{Pd}^0/n\text{Fe}^0$ NPs was evaluated as a function of initial pH (3.6, 5.5 and 8.7) and

temperature (22, 45 and 70 °C) after a 6-d and 21-d reaction time. PFOS was measured in aqueous phases and exhaustive extracts of the NPs. PFOS loss based on the remaining PFOS quantified by liquid chromatography tandem mass spectrometry (LC-MS/MS) appeared to be the greatest at the lowest pH (Figure ES-2A); however, generation of expected inorganic byproducts F^- or SO_4^{2-} (from cleavage of the SO_3^{2-}) was not observed. In addition, at higher temperatures, PFOS loss

decreased (more recovered) at the longer reaction times further supporting the absence of transformation (Figure ES-2B). Using x-ray diffraction (XRD) and x-ray photoelectron spectroscopic techniques, it was determined that changes in Fe-oxides from $\gamma\text{-Fe}_2\text{O}_3$ (at 6 d) to $\text{FeO}(\text{OH})$ (at 21 d) led to a concomitant release of previously unrecovered PFOS. PFOS-complexed with Fe released during corrosion was found to reduce quantifiable PFOS levels in LC-MS/MS. Elevating solution pH to > 10 released PFOS from the complex allowing it to be quantified using LC-MS/MS. Complexation increased with Fe concentration and valence (III $>$ II) and was greater for longer chain PFAAs with no significant differences between PFCAs and PFSAAs (Figure ES-3). Additional details can be found in (Park et al., 2018).



Metal/bimetal Nanoparticle Activated Carbon (AC) Supported Systems. Preliminary studies included evaluating in batch reactors a combination of metals and supports including nNi⁰Fe⁰-AC, nFe⁰-AC, nPdNiFe⁰-AC, nCuNiFe⁰-AC, and nMgNiFe⁰-AC. Particles were all prepared using solutions of chloride salts for the targeted metals and reducing the metals with sodium borohydride with a 1-h synthesis stirring time followed by addition of subsequent metal salts for bi/trimetals

(Zenobio, 2019; Zenobio et al., 2020). In addition $\text{nNiFe}^0\text{-AC-Fe}_3\text{O}_4$ and $\text{nFe}^0\text{-AC-Fe}_3\text{O}_4$ were evaluated. Of these materials, $\text{nNiFe}^0\text{-AC}$ was the best and the only one where generation of sulfite and fluoride from PFOS destruction were clearly evident, thus the remainder of our work with bimetals focused on evaluating the $\text{nNiFe}^0\text{-AC}$ nanocomposite. Work included optimizing the synthesis process for improved $\text{nNiFe}^0\text{-AC}$ reactivity followed by evaluating transformation of representative PFCAs, PFSAs, and a subset of other PFAS. Optimal $\text{nNiFe}^0\text{-AC}$ reactivity towards PFOS occurred with a 3-h synthesis stirring time. The resulting $\text{nNiFe}^0\text{-AC}$ nanocomposites ranged from 25 to 60 nm with a mean size of 42.3 nm. XPS and XRD characterization of the $\text{nNiFe}^0\text{-AC}$ nanocomposites confirmed both Ni and Fe were zerovalent and converted to oxides during reactions with PFOS. H_2 -generating corrosion of Fe^0 was greater in reactions with PFOS. PFOS was only degraded with nNi^0 or $\text{nNi}^0\text{-AC}$ under H_2 -bubbling conditions. However, overall PFOS transformation was much less than observed in the $\text{nNiFe}^0\text{-AC}$ system. PFOS transformation kinetics with $\text{nNiFe}^0\text{-AC}$ over 120 h period at 60 °C showed degradation of linear (L) and branched (br) PFOS, which was demonstrated for the first time (Zenobio et al., 2020) and included several lines of evidence (Figure ES-4A). At 60 °C, PFOS degradation rates were estimated at $0.028 \pm 0.003 \text{ h}^{-1}$ and fluoride and sulfite generation rates at $0.70 \pm 0.165 \text{ h}^{-1}$ and $0.62 \pm 0.157 \text{ h}^{-1}$, respectively, with no differences between L-PFOS and total br-PFOS (Figure ES-4b). Although most unrecovered PFOS was completely defluorinated, some organic products were identified in the particle extracts using QToF/MS. Products included single-bonded C8 polyfluoroalkyl sulfonates (F_{16} to F_7) and alkyl acids (PFCAs, C4-C8) and one perfluorinated C8 desulfonated product supporting both defluorination and desulfonation pathways. Most of the organic products were gone within 25 h. While PFOS degradation plateaued at $50 \pm 6\%$, at 60 °C, PFOS degradation at 50 °C increased to $94 \pm 4.1\%$ (Figure ES-5). Lower PFOS

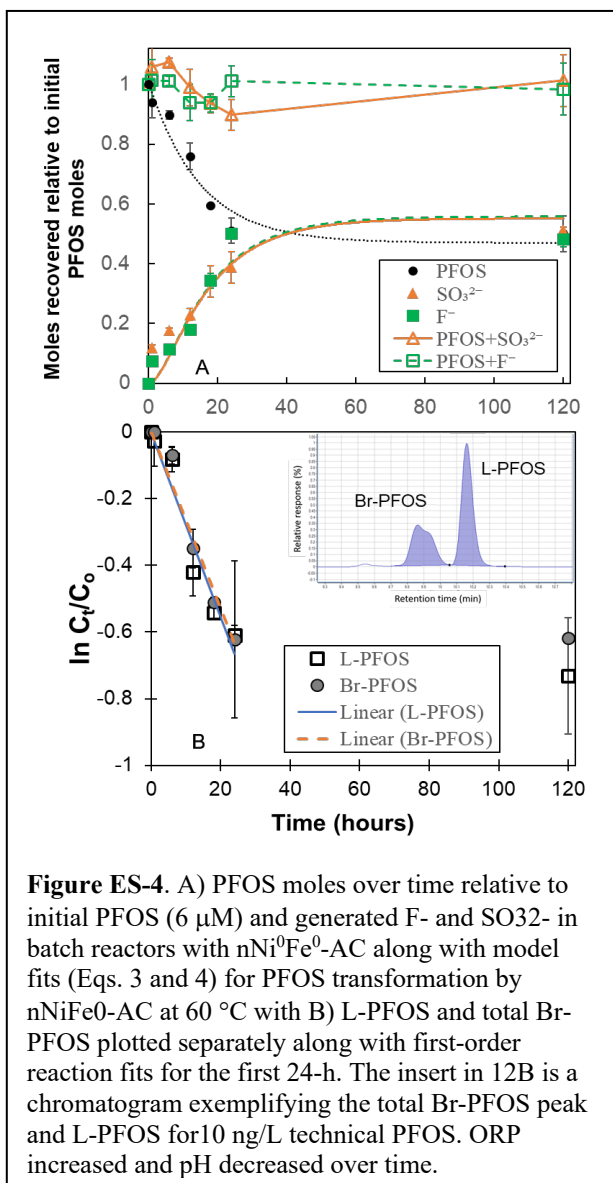


Figure ES-4. A) PFOS moles over time relative to initial PFOS (6 μM) and generated F^- and SO_3^{2-} in batch reactors with $\text{nNiFe}^0\text{-AC}$ along with model fits (Eqs. 3 and 4) for PFOS transformation by $\text{nNiFe}^0\text{-AC}$ at 60 °C with B) L-PFOS and total Br-PFOS plotted separately along with first-order reaction fits for the first 24-h. The insert in 12B is a chromatogram exemplifying the total Br-PFOS peak and L-PFOS for 10 ng/L technical PFOS. ORP increased and pH decreased over time.

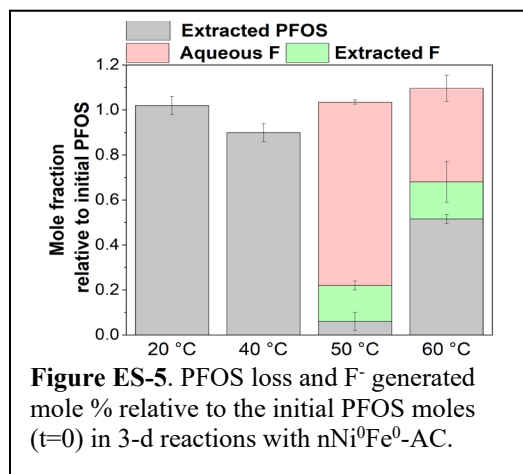


Figure ES-5. PFOS loss and F^- generated mole % relative to the initial PFOS moles ($t=0$) in 3-d reactions with $\text{nNiFe}^0\text{-AC}$.

transformation at 60 °C was attributed to an accelerated iron corrosion passivating the particles. At both temperatures, the moles of fluoride generated accounted for ~ 97% of the PFOS transformed.

For C4, C6 and C8 PFSA and PFCAs in 1-d and 5-d reactions, transformation occurred faster for the longer chain PFAAs with fluorine mole balance lower for the C4 PFAAs. Higher or similar PFAA transformation was observed at 50 °C relative to 60 °C (Figure ES-6A). The % fluoride generated relative to moles of parent transformed increased with perfluorocarbon chain length and was greater increases for the PFSA (Figure ES-6B). For nNi⁰Fe⁰-AC in 5-d reactions with a PFAA

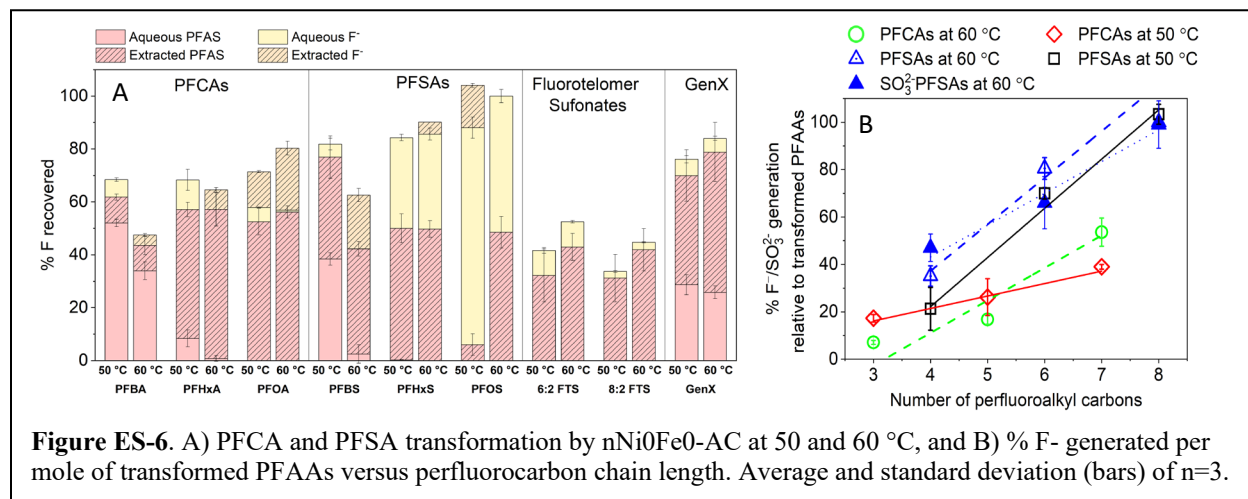


Figure ES-6. A) PFCAs and PFSA transformation by nNi⁰Fe⁰-AC at 50 and 60 °C, and B) % F- generated per mole of transformed PFAAs versus perfluorocarbon chain length. Average and standard deviation (bars) of n=3.

mixture, PFAA transformation was similar or lower than with single PFAA systems. In some cases, PFCAs were generated as intermediates in the transformation process; therefore, limiting a direct comparison. In single solute systems, low levels of PFCAs as well as some polyfluoroalkyl sulfonates and/or carboxylates were generated from all PFAAs. Fluorine mole balance in all PFAA mixture reactions (50 and 60 °C) was > 95%.

Three other non-PFAA PFAS were also evaluated. At 50 and 60 °C, transformation of 6:2 fluorotelomer (FTS) and 8:2 FTS was in the 55-70% range whereas < 30% of GenX was transformed. Fluoride generation was low for all three of these PFAS. Increasing the reaction time for GenX to 12 d did not change the % transformed but did increase the % defluorination by about almost a factor of 3.

We also performed a 5-d reaction at 60 °C with AFFF-contaminated groundwater from Cape Cod with nNi⁰Fe⁰-AC NPs for 5 days (Figure ES-7). Results were somewhat similar but not identical to what we observed in single solute and PFAA mixtures in deionized water systems. Undetermined

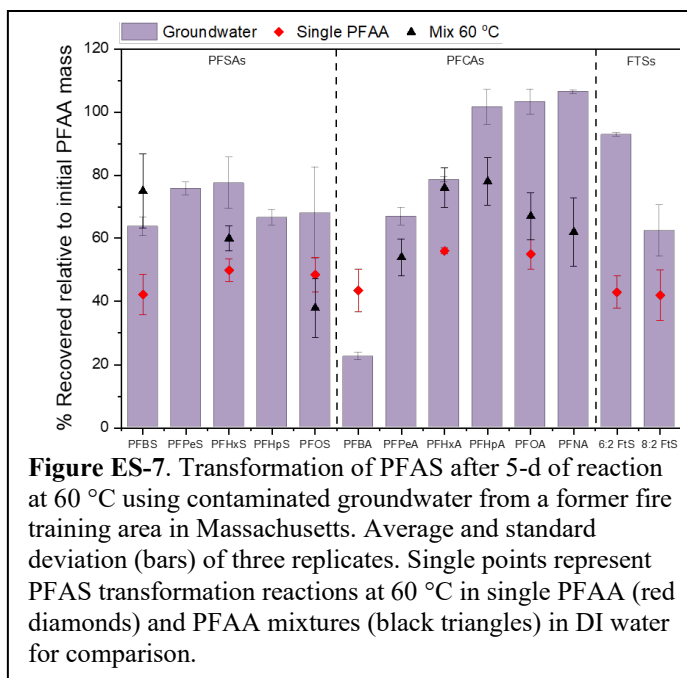


Figure ES-7. Transformation of PFAS after 5-d of reaction at 60 °C using contaminated groundwater from a former fire training area in Massachusetts. Average and standard deviation (bars) of three replicates. Single points represent PFAS transformation reactions at 60 °C in single PFAA (red diamonds) and PFAA mixtures (black triangles) in DI water for comparison.

precursors present in the groundwater sample were likely partially transformed to some PFAAs, which made a direct comparison difficult. Additional work is needed with AFFF-impacted groundwater.

In 1-D saturated flow columns with PFAA mixtures, PFAA breakthrough was consistent with chain length effects on both mobility and reactivity (Figure ES-8). Shorter chain PFAAs had shorter residence times thus shorter reaction times. In extracting column sections, longer chain PFAAs were recovered near the inlet whereas shorter chain PFAAs near the outlet. For PFAA transformation in 1-D column systems followed similar patterns as observed in the batch reactors for a given

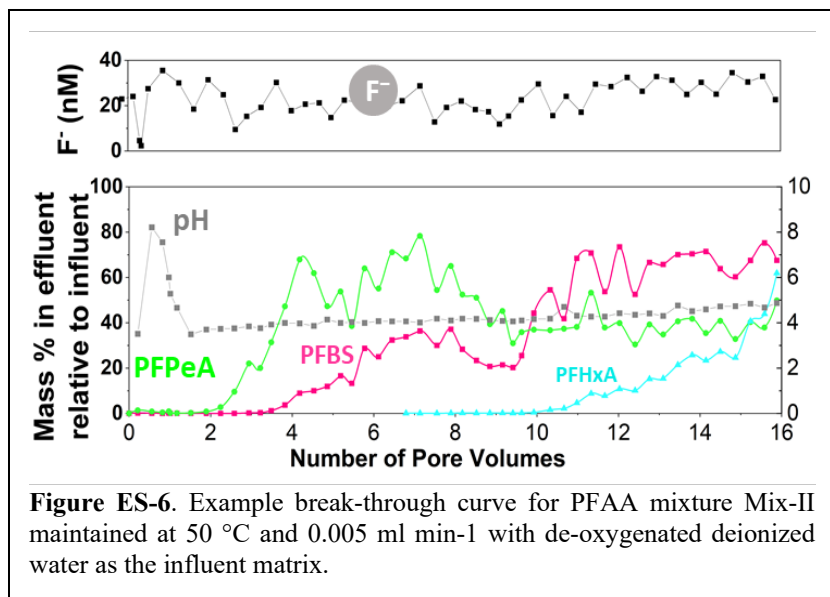


Figure ES-6. Example break-through curve for PFAA mixture Mix-II maintained at 50 °C and 0.005 ml min⁻¹ with de-oxygenated deionized water as the influent matrix.

residence time with higher % total transformation with increasing residence times (Figure ES-8). Transformation was higher in Mix-II (~53%) compared to Mix-I (~36%), but Mix-I had a higher % fluoride generated per mole of transformed PFAA (~23%) compared to Mix-II (Figure ES-9). The difference is most likely due to the latter column being terminated after only 16 pore volumes (PVs) versus 138 PVs for Mix-I. However, % fluoride generated per mole of transformed PFAA was higher (23%). One toxicity concern in regard to using these nanocomposites in situ may be causing Ni concentrations in groundwater to exceed levels of concern. However, < 2 % of the total Ni present was detected in 138 pore volumes of the effluent. Additional discussion for the batch and column results for the single solute and mixed PFAA systems can be found in (Modiri Gharehveran et al., 2021; Zenobio et al., 2021).

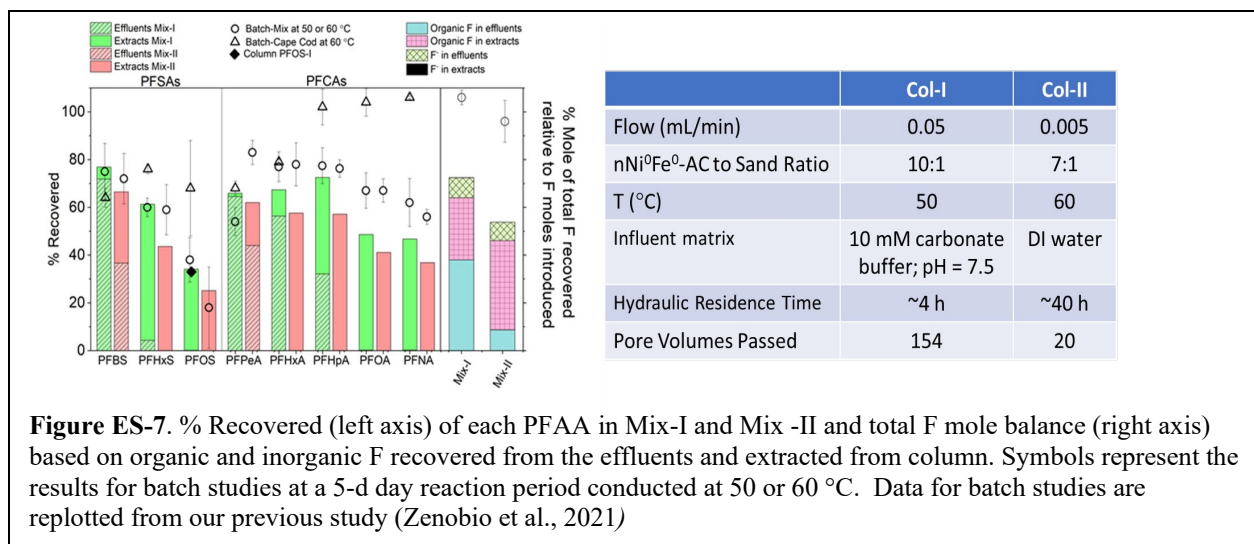
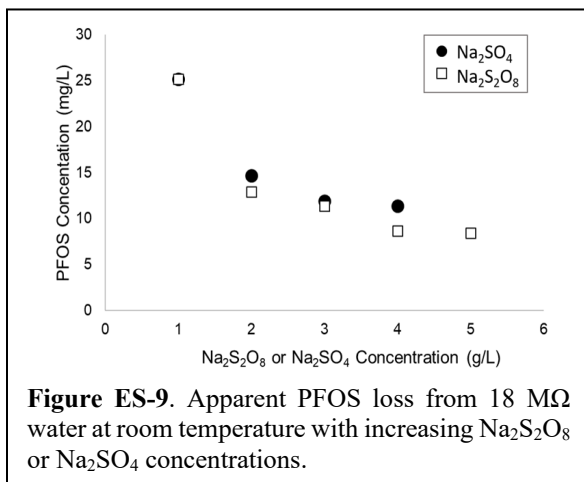
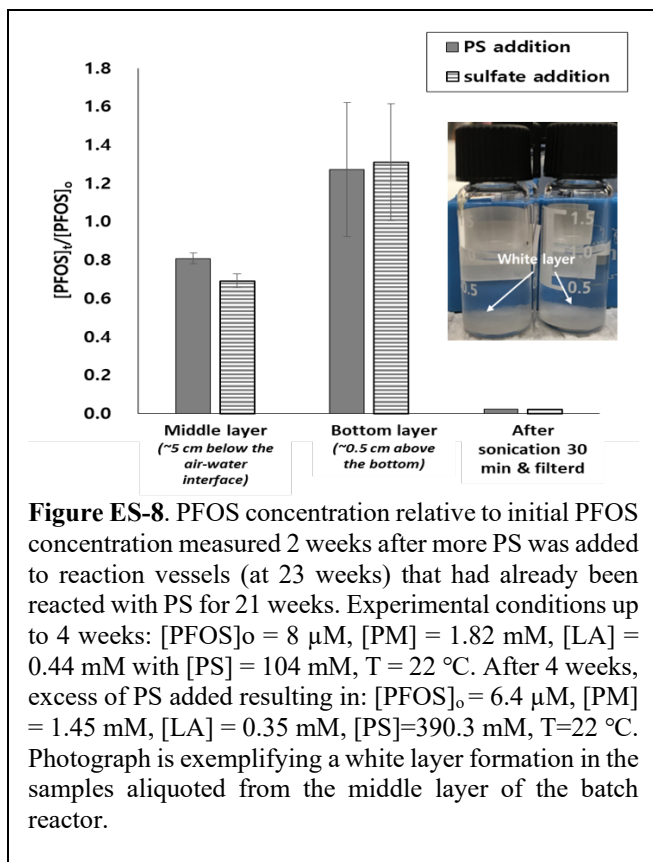


Figure ES-7. % Recovered (left axis) of each PFAA in Mix-I and Mix -II and total F mole balance (right axis) based on organic and inorganic F recovered from the effluents and extracted from column. Symbols represent the results for batch studies at a 5-d day reaction period conducted at 50 or 60 °C. Data for batch studies are replotted from our previous study (Zenobio et al., 2021)

Permanganate-based Systems. Of the AOTs explored at the start of ER-2426, some publications and advertising had indicated that permanganate (PM) was able to oxidize PFOS; however, several scientists questioned the mechanisms of PFOS removal by PM. To provide clarity to what may be happening to PFOS in PM systems, we evaluated the ability of PM to degrade PFOS by conducting studies similar to previous studies that reported PFOS destruction which included PM solutions and PM combined with persulfate (PS) with the latter known as ScisoR Technology® (Ross, 2012; Yao et al., 2016). We also evaluated if addition of various soluble catalysts could enhance PM's potential to breakdown PFOS. We observed no PFOS destruction by PM regardless of buffer concentration or type used to control pH or with the addition of selected catalysts ($[\text{RuCl}_3] = 5 \mu\text{M}$, $[\text{NaHSO}_3] = 150 \mu\text{M}$, $[\text{FeCl}_2] = 20 \mu\text{M}$, and $[\text{ABTS}] = 5 \mu\text{M}$). We investigated if the type (Na^+ or K^+) or concentrations of phosphate salt solutions (0–200 mM) affected the occurrence or stabilization of water-soluble MnO_2 colloids, which were hypothesized by previous work to enhance the PFOS transformation process by permanganate. We measured zeta potential and the size of MnO_2 colloids and found that increasing phosphate ions up to 50 mM resulted in increasingly larger MnO_2 colloids to a similar degree for both salt forms. Differences in quenching techniques also did not appear to alter results. We also showed that the F^- and SO_4^{2-} generation reported in a published study (Liu et al., 2012) as evidence that PM was breaking PFOS bonds were below or not significantly higher than reported limits of quantitation. In our duplication of the work, we noticed the presence of an unknown peak that interfered with fluoride quantitation. For SO_4^{2-} , impurities were found in technical PM bringing into question the reported SO_4^{2-} levels in the published work by (Liu et al., 2012). For PM-PS systems (ScisoR Technology®), PFOS was not found to be degraded but rather PFOS distribution became heterogeneous as confirmed when subsampling reaction vessels at different depths (Figure ES-10) and visual evidence of PFOS 'salting-out' (Figure 10 insert). The decreasing changes in PFOS concentrations observed with both increasing persulfate concentrations or the salt products that form as persulfate is degraded (controls) further support the PFOS 'salting out' phenomena (Figure ES-



11). In addition, subsequent sonication and filtering of the samples led to the apparent disappearance of most of the PFOS, which was an artifact arising from the behavior of PFOS aggregates or potential hemi-micelle formation. Given these findings, it is clear that neither permanganate or the ScisoR Technology® destroy PFOS, but the addition of salts may have application for collecting or concentrating PFOS and other PFAAs in a remediation or water treatment strategy. Additional details can be found in (Park et al., 2020)

Implications for Future Research and Benefits

At the start of this ER-2426 project, the primary approach to mitigate PFAS transport and contamination of drinking water was sorbents, which came with challenges to effectively capture shorter chain PFAAs. Also the sorbent still had to be disposed of as a hazardous waste or regenerated in a way that brought back its sorbent abilities and destroyed the sorbed PFAS. Very little was known about potential technologies that could destroy PFAS, in particular PFOS, which had been identified as the most recalcitrant PFAS for even abiotic technologies. What we did know at the time was that microbial degradation of PFAS would lead to terminal PFAAs. Also, the abiotic technologies that had been evaluated at some level for destruction of PFOS and PFOA were either unsuccessful, had questionable results or were simply not amenable for use in situ remediation of groundwater. The large PFAS-contaminated plumes being generated from military bases due to the frequent use of AFFFs called for the need to identify in situ destructive remediation technologies to mitigate PFAS transport offsite.

Key Findings:

- Vitamin B12 systems are not effective at degrading L-PFOS, which appears to be due to steric hindrances that limit L-PFOS complexation with VB12.
- Neither PM, persulfate or a combination of the two (ScisoR Technology®) can transform PFOS. Apparent PFOS loss appeared to be due to clustering and ‘salting out’, which leads to sampling artifacts, thus underestimates of PFOS concentrations. We also determined that fluoride impurities in reagents used as well as peaks that interfere with proper fluoride quantitation led to wrong conclusions that fluoride was being generated.
- The initial promise that $n\text{PdFe}^0$ was able to degrade PFOS was proven to be an artifact of changes in sorption affinity during iron corrosion. Some of the iron released during corrosion precipitated as Fe-oxides causing PFOS to be strongly sorbed (not methanol extractable), and thus, appear transformed. As the oxides changed forms over longer reaction times, PFOS was released revealing it had not been transformed.
- PFOS was found to complex with Fe released to solution during corrosion, which reduced quantifiable PFOS levels by LC-MS/MS. Elevating solution pH to > 10 released PFOS for quantification. Complexation increased with Fe concentration and valence state ($\text{III} > \text{II}$). Complexation was greater for longer chain PFAAs.
- Of the metals (single, bi and tri) evaluated, $n\text{Ni}^0\text{Fe}^0$ -AC nanocomposites synthesized with a 3-h synthesis stirring time using sodium borohydride to reduce and precipitate the metals to zero valence were the most effective at degrading L-PFOS with $> 97\%$ of unrecovered PFOS accounted for by the fluoride and sulfite generated. PFOS transformation and defluorination was $\sim 94\%$ at 50°C .
- $n\text{Ni}^0\text{Fe}^0$ -AC nanocomposites also transformed other PFAS, which transformed and defluorinated to varying degrees. For the PFAAs, transformation rates and % fluoride generated relative to moles of parent transformed decreased with a decreasing number of

perfluorocarbons. Overall, F- generation was greatest for the PFSAs. For fluorotelomer sulfonates (6:2 and 8:2 FTS), more than half of the substances were transformed with C-S cleavage, but % defluorination was low indicating that once the C-S bond was cleaved, propensity to defluorinate was low. GenX was the least transformed PFAS evaluated.

- In bench-scale PRBs (saturated columns systems), sorption and transformation limited PFAS breakthrough according to chain length with the longer chain PFASs remaining near the inlet.

Implications and Benefits:

- Our studies showed that there are many artifacts that can lead to wrong conclusions regarding PFAS removal, thus it is imperative that multiple lines of evidence be required when assessing PFAS remediation technology potential.
- The salting out phenomena that was observed as an artifact leading to wrong conclusions of PFOS removal indicates that exploiting the ‘salting out’ may have potential for treating PFAS-contaminated water – forcing PFAS to precipitate with addition of salts. Precipitates could be filtered out and the salty water processed to remove salts using standard technologies.
- AC serves to immobilize or reduce PFAS mobility through sorptive processes, thus increasing proximity to the nNi^0Fe^0 nanocomposites facilitating reductive transformation. To date, these are the first such nanocomposites that have shown to transform and defluorinate PFAS.
- Application of nNi^0Fe^0 -AC nanocomposites in PRBs for use in PFAS capture and transformation in groundwater plumes especially where groundwater is already fairly reduced has potential and warrants further investigation.
- The use of nNi^0Fe^0 -AC nanocomposites can also be used in column reactors above ground in place of just AC, which is what is currently used the most.
- In situ injection of nNi^0Fe^0 -AC nanocomposites is also plausible. The main concern with regards to toxicity for any in situ use of these nanocomposites would likely be nickel concentrations in groundwater. However, < 2% Ni in total was observed in column effluent after more than 138 pore volumes, thus the use of these nanocomposites will likely not lead to Ni levels of concern in groundwater.
- Lastly, while it is evident that nNi^0Fe^0 -AC technology may be very successful at rapidly defluorinating the longer chain PFSAs like PFOS, it is unlikely to be sufficient on its own for degrading the range of co-occurring PFAS, thus would be best considered as part of a treatment train coupled with other treatment technologies. For example, once the sulfonate group is cleaved, attack by oxidative technologies may be more effective.

Future work:

- Additional studies at longer reaction times (> 5 d) are needed to evaluate if transformation and defluorination of some of the less-transformed PFAS will increase.
- Additional column studies using AFFF-impacted groundwater are needed and are underway.
- Studies to evaluate regeneration potential of the nNi^0Fe^0 -AC nanocomposites are needed and are underway, which would improve chances of adoptability in PRBs and above ground column reactors.
- nNi^0Fe^0 -AC technology in a field-scale pilot study at an AFFF-impacted site are warranted and may be funded through an ESTCP-type project. We currently have companies interested in our nNi^0Fe^0 -AC technology pending patent.

SECTION 1: INTRODUCTION

At the time of the ER-2426 project, capture with activated carbon was the only technology being used for removal of PFAA contaminated groundwater (NRC Report, 2012). However, this approach commonly results in only limited remediation and typically requires decades of operation. Because of this, the U.S. Air Force, which had the most PFAS-contaminated sites among DOD-associated sites, had endeavored to apply in situ destructive technologies whenever possible. However, no such treatment methods were available for the entire range of PFAS. Advanced oxidative technologies have been demonstrated with some success for PFOA and other PFAAs, but not for PFOS (both in literature review and our own research). Similarly, to the best of our knowledge, biological treatment had not been demonstrated effective for either perfluorooctanoic acid (PFOA) or PFOS. Methods that have been demonstrated as effective for both PFOA and PFOS required conditions that were not applicable for use in situ, including high temperature, pressure, the presence of UV light, or the lack of dispersed treatment (such as in the case of an electrode treatment). Therefore, the overarching goal of this research was to identify an in situ chemical reductive defluorination (ISCRD) technology that could destroy PFAAs in AFFF-impacted groundwater with an initial focus on PFOS.

To address our overarching goal, we posted the following questions:

- *What degree of defluorination (especially for L- PFOS) can be achieved with the various reductive techniques that are amenable for in situ use?*
- *What are the reaction mechanisms and pathways (intermediates) for PFOS defluorination using the proposed reductive techniques?*
- *For techniques where fluoride generation is the greatest, do perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonic acids (PFSA) defluorinate to a similar extent and through a similar pathway?*
- *For techniques where fluoride generation is the greatest, how is defluorination potential affected by various solution parameters (pH, electrolyte composition, redox potential) and co-contaminants likely to be associated with AFFF-contaminated groundwater?*
- *For the techniques where fluoride generation is the greatest, how does the presence of porous media affect defluorination potential and reductant reactivity?*
- *How can the overall effectiveness and remediation success be increased by a treatment train approach; how amenable are intermediates to other remediation processes?*

To address these questions, we had defined the following technical objectives (tasks):

1. Quantify the degree of PFOS defluorination that can be achieved with selected abiotic reductive techniques
2. Characterize rates, intermediates, and pathways
3. Evaluate enhanced delivery techniques of bimetal reductants
4. Quantify key solution and porous media effects on defluorination
5. Assess permeable bimetal reactive barrier potential
6. Probe degradation potential of intermediates by other remediation processes in support of treatment train strategies.

SECTION 2: BACKGROUND

Per- and poly-fluoroalkyl substances (PFAS) are a large group of highly fluorinated aliphatic chemicals that have been synthesized for over 60 years (Wang et al., 2017). PFAS have a fluorinated hydrophobic carbon chain (tail) attached to a hydrophilic functional group (head), which makes them hydro- and oleophobic, tensioactive, and chemically stable (Buck et al., 2011; Xiang et al., 2019). The unique structure and characteristics of PFAS have made them suitable compounds for a wide range of industrial and military uses (Baran, 2001; Barzen-Hanson et al., 2017; D'Agostino and Mabury, 2014; Gebbink et al., 2017; Song et al., 2018). The same characteristics that give them versatility also resulted in their recalcitrant nature and persistence in the environment, thus frequent occurrence (Hu et al., 2016). Perfluorooctane sulfonate (PFOS) has received much attention due to its widespread distribution in the environment, environmental persistence, biological and chemical recalcitrance, potential toxicity, and bioaccumulative property (CDC, 2015, 2009; Conder et al., 2008; Lau et al., 2007). Recently, other perfluoroalkyl acids (PFAAs) including perfluorohexane sulfonate (PFHxS) have been added to U.S. EPA Unregulated Contaminant Monitoring Regulation (UCMR3) (USEPA, 2015).

Most military facilities that routinely service aircraft maintain fire-fighting training areas during which training with AFFFs for more than 30 years has resulted in repeated short-term releases of AFFFs. According to the report from the Knowledge-Based Corporate Reporting System of the Department of Defense, nearly 600 military sites are exposed to AFFFs with a majority of sites located at Air Force facilities (Rak and Vogel, 2009). Among the sites surveyed at the time of the proposed work, fire training areas at Wurtsmith Air Force Base (AFB), Tyndall AFB, and Naval Air Station Fallon had reported PFOA concentrations in groundwater as high as 105 µg/L, 116 µg/L and 6,570 µg/L, respectively (Moody et al., 2003; Moody and Field, 2000, 1999) and PFOS concentrations as high as 110 µg/L, 2,300 µg/L and 380 µg/L, respectively (Schultz et al., 2004). Since that time, groundwater at many military facilities have been found to contain PFAS being detected in the low ppb to low ppm range (D'Agostino and Mabury, 2017; Kärman et al., 2011; Place and Field, 2012). These values are well above the US EPA announced Provisional Health Advisory value for drinking water of 70 ng/L for combined perfluorooctanoic acid (PFOA) and PFOS (USEPA, 2015). PFOS is typically the PFAA found at the most elevated concentrations in groundwater at AFFFs-impacted sites (Backe et al., 2013) thus a main driver in risk assessment. The frequent occurrence of PFOS as well as other PFAAs above regulatory limits in groundwater at AFFF-impacted sites and their persistence against microbial degradation (Liu and Mejia Avendano, 2013; Zhang et al., 2017), remediation technologies to address PFAS mitigation were and continue to be needed.

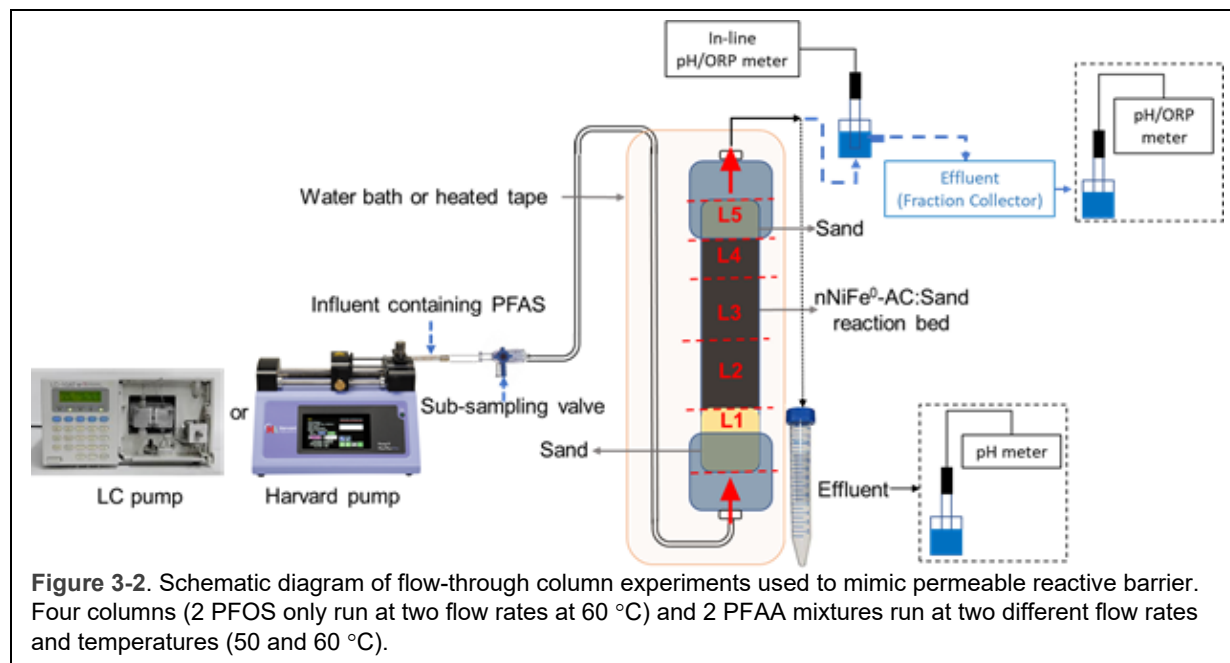
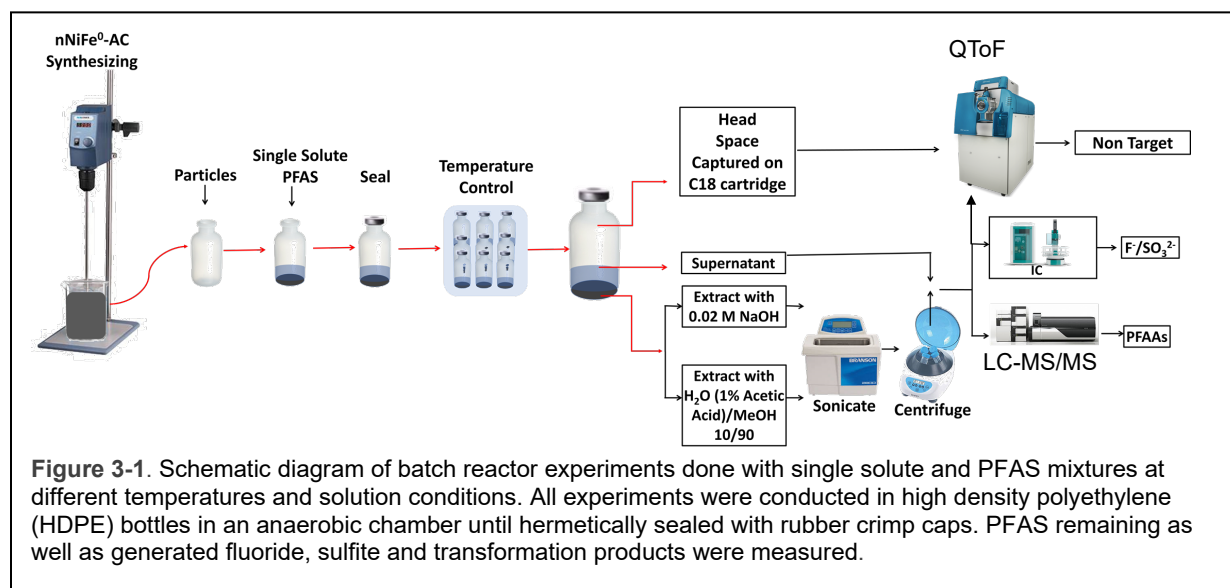
This project was in response to SON ERSON-14-02, which was seeking applied research to develop cost effective in situ remedial alternatives for perfluoroalkyl contaminated groundwater. Prior to this work, the peer-reviewed literature has just begun to address the potential for abiotic degradation of PFAAs; however, most studies to date only showed success for PFOA even under extreme conditions (high heat, high pressure, etc.). Some success in partial transformation of PFOS or perfluorohexane sulfonate (PFHxS) had been shown using sonolysis (Moriwaki et al., 2005; Vecitis et al., 2008a), Fe⁰ in subcritical water (Hori et al., 2006), boron-doped electrodes (Carter and Farrell, 2008) and permanganate oxidation at 95 °C (Liu et al., 2012). These advanced oxidation technologies (AOTs) require substantial amounts of energy or extreme reaction conditions (e.g., highly acidic conditions, high pressures, etc.), thus likely impractical for in situ

soil and groundwater remediation. In situ chemical oxidation (ISCO) methods that have been tested for degradation of PFOA or PFOS at the lab-scale include peroxide, Fenton's reagent, permanganate, and persulfate (Liu et al., 2012; Vecitis et al., 2009). Of these oxidants, the persulfate ion ($\text{S}_2\text{O}_8^{2-}$) is the strongest oxidant and when activated, produces free sulfate radicals. Persulfate activation used in lab-scale PFOA degradation studies include UV photolysis (Chen and Zhang, 2006; Hori et al., 2004), microwave (Lee et al., 2009), and heat (25-80 °C) (Lee et al., 2012). Some of these approaches can also be highly energy intensive and all were assessed only at high initial PFOA concentrations ($\geq 100,000 \mu\text{g/L}$). With funding through the AFCEC BAA program in conjunction with the Army ERDC, we further explored persulfate oxidation potential for several representative PFAS using heat (30-60 °C range) and base activation, which are both amenable to in situ use. Although PFOA and 2:6 FTS were degraded, PFOS was not even at higher temperatures and higher persulfate concentrations (Park et al., 2016). Others had reported some loss of PFOS from solution with heat-activated (70 °C) and H_2O_2 -activated persulfate, Fenton and Super-Fenton reagents and/or permanganate (Kingshott, 2008; Liu et al., 2012; Ross, 2012); however, we suspected PFAS loss was not due to degradation but other processes. (Vecitis et al., 2008a) in their detailed review paper determined that advanced oxidation methods relying on the hydroxyl radical (such as Fenton's chemistry, ozonation, and peroxone approaches) would likely be ineffective for PFAAs especially PFASs.

The average oxidation state of the C atoms in PFOS is 2.125 and higher than that of tetrachloroethene (2.0) and trichloroethene (1.5) for which reduction is commonly used as a treatment method, thus supporting the potential for PFOS to be transformed reductively. Park et al. (2009) was able to transform PFOS and PFOA using aquated electrons generated from UV photolysis of aqueous iodide solutions. For reduction using a vitamin B12 system, some success has been reported for reductive dehalogenation of branched PFOS isomers (54 μM ; $\sim 100,000$ ppb) using 260 μM vitamin B12 as the catalyst and 36 mM Ti(III) citrate as the reducing agent and at 70°C and pH=9 (Ochoa-Herrera et al., 2008; Ochoa-Herrera, 2008), but not L-PFOS, which is present at > 65% of most formulations. Previous work with PCBs in aqueous solutions showed that addition of ethanol could enhance the effectiveness of the vitamin B12-Ti(III)-citrate system (Xu, 2005). A preliminary 3-d experiment in our lab with 30 vol% ethanol (30 vol%) appeared to enhance PFOA and PFOS with fluoride production in the vitamin B12-Ti(III)-citrate system. Therefore, we targeted our investigation on reductive approaches with a focus on technologies that would be amenable for in situ remediation (e.g., in situ injection and permeable reactive barriers) given that management of diffuse PFAA groundwater plumes above EPA recommended drinking water guidance levels at a large number of military bases continues to challenge PFAS management at these sites. We also focused most of our work on bimetal technology that include zero valent iron (Fe^0). Fe^0 has been extensively studied and accepted as an attractive approach for remediation of persistent organic compounds given it is inexpensive, readily available, and has minimal environmental risk (Cho and Park, 2006; He et al., 2010; Keum and Li, 2005; Lutze et al., 2011; NRC Report, 2012). Reducing particles to the nanoscale increases specific surface area to 30 - 40 m^2g^{-1} , which is about 40 times greater than conventional microscale particles, thus yielding higher reactivity (Jia et al., 2011). Moreover, depositing a second metal onto the iron surface as a catalyst like Ni, Cu, Pt or Pd will enhance the defluorination reaction. We specifically proposed to investigate the use of various zero valent metals/bimetals combinations combined with a subset of delivery methods that would decrease agglomeration tendency and reactivity as well as cosolvent and metal assisted Vitamin B12 defluorination. We also wanted to validate and explore mechanisms responsible for observed PFOS losses observed in permanganate systems.

SECTION 3: MATERIALS AND METHODS

General Method Overview. A multiple lines-of-evidence approach was taken with each technology explored (exemplified in Figure 3-1). First, we quantified the loss of the target PFOS for several different reductive approaches in batch reactors. The reductive approaches investigated included vitamin B12 systems with nano-Fe⁰ and micro-Zn⁰ catalysts; Pd/micro-Mg⁰, Pd/nFe⁰ and Ni⁰/nFe⁰ bimetals of which in some cases, the bimetals were synthesized within a 2:1 clay support; nano Ni⁰Fe⁰, PdNiFe⁰, CuNiFe⁰, MgNiFe⁰ particles synthesized onto an activated carbon (AC) support; nNi⁰Fe⁰ and Fe⁰ on an AC-magnetite (Fe₃O₄) platform; and reductive/oxidative permanganate-based systems. Almost all work was done in high-density polyethylene (HDPE) or glass batch reactors except for the nNi⁰Fe⁰-AC work, which included 1-D column studies (Figure 3-2).



Each technology suite being explored required some associated method development such that we could accurately quantify target parent PFAS and main PFAS isomers (exemplified for PFOS in Figure 3-3) where possible/appropriate (Figure 3-4 and Table 3-1), accurately quantify fluoride and sulfite metabolites where applicable, and identify organic metabolites with quantitation when possible, and ensure an exhaustive extraction of PFAAs towards achieving a fluorine mole balance. If PFOS mass recovered was less than the initial PFOS mass introduced, then generation of fluoride and in some cases sulfite (after oxidative conversion to sulfate) was quantified using ion chromatography with electrochemical detection (**Task 1**). We optimized the inorganic anion analyses to ensure separation of early eluting fluoride from other early eluting byproducts (e.g., acetate and formate) (Figure 3-5). For technologies that showed fluoride generation, additional analysis was done (**Task 2**). If a sufficient fluorine mole balance was not obtained, nontarget screening of intermediates was performed using

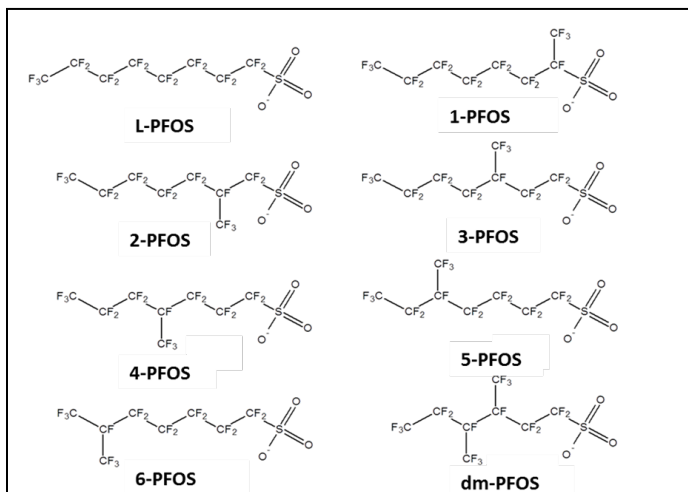


Figure 3-3. A) Chromatographs of PFOS isomers in PFOS standard (obtained from Sigma-Aldrich), B) Chromatographs of PFHxS isomers in PFHxS standard (obtained from Sigma-Aldrich).

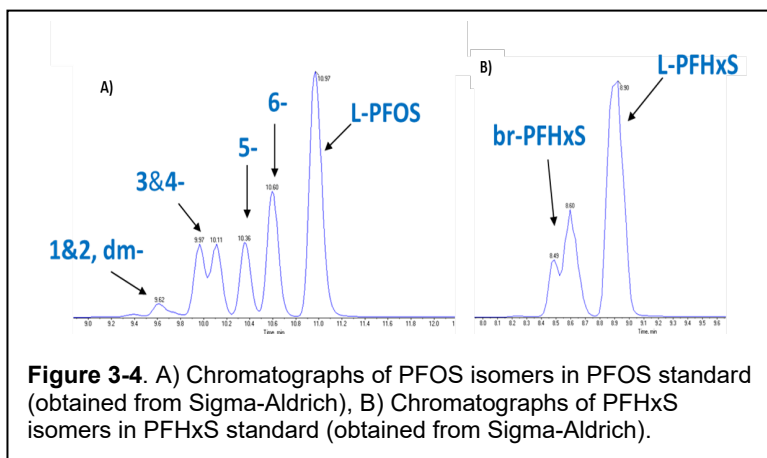


Figure 3-4. A) Chromatographs of PFOS isomers in PFOS standard (obtained from Sigma-Aldrich), B) Chromatographs of PFHxS isomers in PFHxS standard (obtained from Sigma-Aldrich).

Table 3-1. % composition quantified for individual isomers in technical PFOS and PFHxS obtained Sigma-Aldrich using characterized standards obtained from Wellington. LOD (limits of detection), LOQ (limits of quantitation).

	Sigma-Aldrich PFOS (%)	LOD (µg/L)	LOQ (µg/L)		Sigma-Aldrich PFHxS (%)	LOD (µg/L)	LOQ (µg/L)
L-PFOS	68.1 ± 1.6	1.3	4.1	L-PFHxS	78.2 ± 1.6	1.4	4.4
6-PFOS	10.0 ± 0.3	1.9	5.9	br-PFHxS	21.8 ± 1.6	1.1	3.1
5-PFOS	5.6 ± 0.1	1.2	3.8				
3 & 4-PFOS	8.2 ± 0.8	1.7	5.1				
Other isomers	8.1 ± 0.9	--	--				
SUM	100.0				100.0		

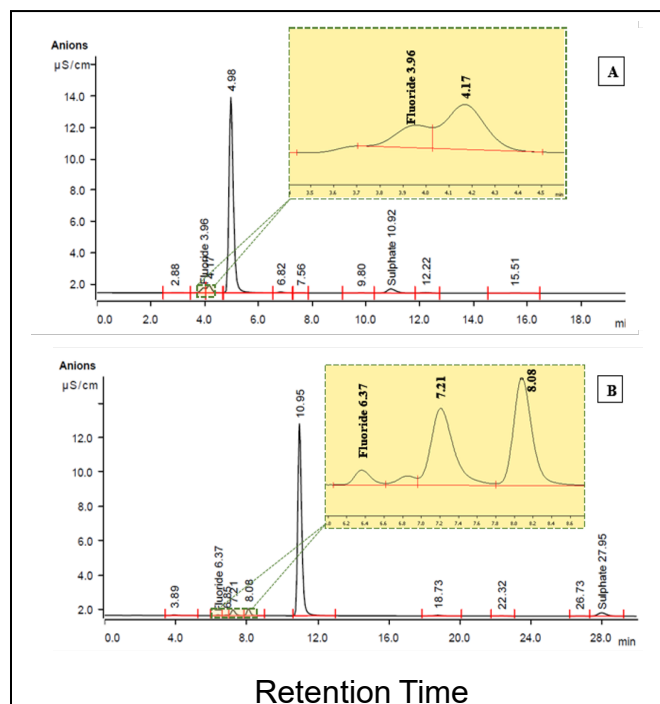


Figure 3-5. The IC chromatograms associated with F/SO_3^{2-} extract from nNi^0Fe^0 -AC for 3-d PFOS reactions at 50 °C. A) Exemplifying peaks interfering with fluoride using the Metrosep A Supp 5 (150 mm × 4 mm) with 1 mM $HNaCO_3$ and 3.2 mmol/L Na_2CO_3 eluant at 0.7 mL/min. B) Chromatogram for the same sample with a Metrosep A Supp 7 (150 mm × 4 mm) with a 3.6 mM Na_2CO_3 eluant at 0.7 mL/min. Retention times at 7.21, 8.08 and 10.95 mins in the lower chromatogram were confirmed to be formate, acetate, and chloride. Chloride is from the Fe and Ni chloride reagents used in the nanocomposite synthesis.

PFAA mixture degradation was evaluated in 1-D column studies, which were considered a type of bench scale permeable reactive barrier (PRB) (**Task 5**) (Figure 3-2). We also evaluated claims that a permanganate-persulfate oxidative-reductive system degraded PFOS (**Task 6**) based on some literature reports were inconsistent with PFOS transformation theories, thus other mechanism and artifacts were suspected and investigated.

high resolution mass spectrometry as well as quantification of suspected organic degradation products for which standards were available at the time (Figure 3-6). In addition, measurement of loss over time (rates) were characterized in batch and degradation pathways were explored. For technologies involving bimetal reductants, nanocomposite synthesis was optimized for reactivity and the ability of the technology to retain reactivity was explored in batch reactors with a subset of delivery mechanisms (**Task 3**) (Figure 3-7). The effects of a subset of constituents that may be present in solution or associated with aquifer material were evaluated in batch reactors for some of the technologies (**Task 4**). For the most promising bimetal technology ($n-Ni^0Fe^0$ -AC), PFOS and

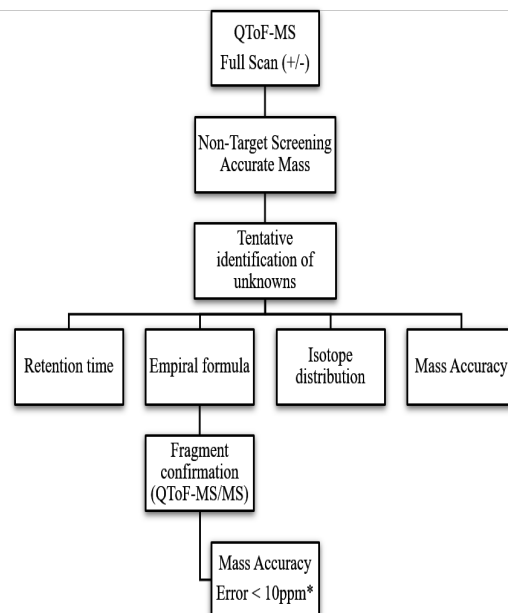
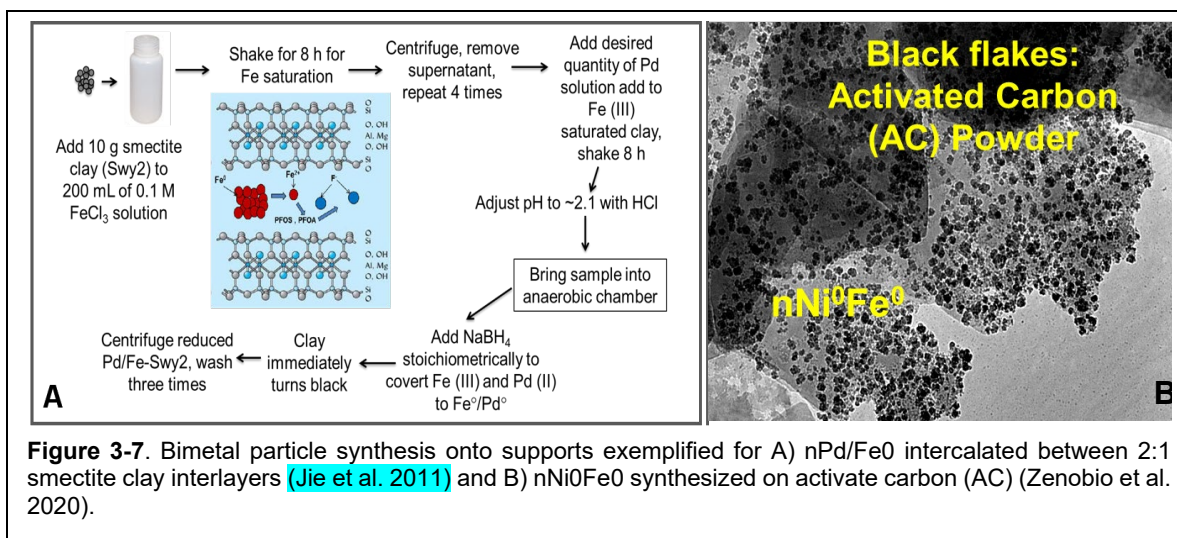


Figure 3-6. Identification process for PFOS transformation products using QToF-MS. *Except for $m/z < 100$ Da.



Chemicals. Isotopically mass-labelled and native PFCA/PFSA mixtures (MPFAC-MXA and PFAC-MXC), perfluoro-¹³C₈octanesulfonate (M8PFOS), and perfluoro-n-¹³C₈octanoic acid (M8PFOA) were acquired from Wellington Laboratories (Overland Park, KS or Ontario, Canada). Iron (II) chloride tetrahydrate (FeCl₂·4H₂O, 98%), sodium borohydride (NaBH₄, 99%), nickel chloride hexahydrate (NiCl₂·6H₂O, 98%), sodium fluoride (NaF, 99%), sodium sulfate (Na₂SO₄, 99%), potassium perfluorobutanesulfonate (PFBSK, C₄F₉SO₃K, 98%), potassium perfluorohexanesulfonate (PFHxSK, C₆F₁₃SO₃K, ≥98%), potassium perfluorooctanesulfonate (PFOSK, C₈F₁₇SO₃K, 98%), perfluorobutyric acid (PFBA, C₃F₇COOH, 98%), perfluorohexanoic acid (PFHxA, C₅F₁₁COOH, 98%), perfluorooctanoic acid (PFOA, C₇F₁₅COOH, 98%), and hexafluoropropylene oxide dimer acid (HFPO-DA aka GenX, 99%) were obtained from Sigma-Aldrich (St. Louis, MO). Fluorotelomer sulfonates (6:2 FTS, C₈H₄F₁₃SO₃, 98% and 8:2 FTS, C₁₀H₄F₁₇SO₃, 97%) were purchased from SynQuest Laboratories, Inc. Powder activated carbon (surface area 1300 – 1400 m²/g) was provided by Strem Chemicals (Newburyport, MA). LC-MS grade solvents, such as formic acid, ammonium acetate, acetic acid, sodium hydroxide, and methanol were purchased from Fisher Scientific (Pittsburgh, PA). Nanopure (Thermo Scientific) water purification system was used to provide reagent grade water (≥18.2 MΩ cm). An aliquot of contaminated groundwater samples was obtained from a study conducted on western Cape Cod, Massachusetts at the U.S. Geological Survey Toxic Substances Hydrology Program Cape Cod Research site. Groundwater samples were collected from a former fire-training area and near to a wastewater treatment plant located on Joint Base Cape Cod (Barber et al., 2017; Weber et al., 2017). DI water and groundwater were deoxygenated by bubbling N₂ gas for 2 h or autoclaving for 30 min before each experiment.

Vitamin B12 (VB12, Cyanocobalamin, C₆₃H₈₈CoN₁₄O₁₄P, ≥ 98%) was purchased from Sigma-Aldrich (St. Louis, MO, USA). Palladium acetate (Pd(C₂H₃O₂)₂, 99.98% metal basis) was obtained from Alfa Aesar (Ward Hill, MA). Mass-labelled sodium perfluoro-1-¹³C₈ octane sulfonate (M8PFOS, ¹³C₈F₁₇SO₃Na, > 99%) and sodium perfluoro-1-[1,2,3-¹³C₃] hexane sulfonate (M3PFHxS, ¹³C₃¹²C₃SO₃Na, ≥ 99%) were obtained from Wellington Laboratories (Ontario, Canada) for use as internal standards (IS). For isomer identification and composition quantification in technical PFOS and technical PFHxS, potassium perfluoro-1-octanesulfonate (L-PFOS), sodium perfluoro-1-hexanesulfonate (L-PFHxS), potassium perfluorooctane sulfonate (Technical grade), sodium perfluoro-1-methylheptane sulfonate (P1MHpS; 1-PFOS), sodium perfluoro-3-

methylheptane sulfonate (P3MHpS; 3–PFOS), sodium perfluoro-4-methylheptane sulfonate (P4MHpS, 4–PFOS), sodium perfluoro-5-methylheptane sulfonate (P5MHpS; 5–PFOS), and sodium perfluoro-6-methylheptane sulfonate (P6MHpS; 6–PFOS) were obtained from Wellington Laboratories (Ontario, Canada). $n\text{Zn}^0$ (99.7%, 40 ~ 60 nm) and $n\text{Fe}^0$ (99.9%, ~25 nm) were obtained from SkySpring Nanomaterials, Inc. (Houston, TX). Potassium permanganate (KMnO_4 , ACS reagent $\geq 99.0\%$, $\text{Cl}^- \leq 0.005\%$, $\text{SO}_4^{2-} \leq 0.02\%$) and potassium phosphate, monobasic (KH_2PO_4 , $\geq 99.0\%$) were obtained from J.T. Baker. Ruthenium(III) chloride (RuCl_3 , anhydrous, 99%), sodium bisulfite (NaHSO_3 , ACS grade) and iron(II) chloride (FeCl_2 , anhydrous, 99%) were obtained from ACROS Organics™. 2,2'-Azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS, $\geq 98\%$), hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$, $\geq 99.99\%$), L-ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$, 99%), sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$, 98%), sodium sulfate (Na_2SO_4 , anhydrous, $\geq 99\%$), and sodium hydroxide (NaOH , $\geq 97\%$), and sodium phosphate monobasic (NaH_2PO_4 , $\geq 99\%$) were purchased from Sigma-Aldrich. Lactic acid (LA, 85 ~ 90%, aq. soln.) was obtained from Alfa-Aesar. Solvents methanol (MeOH , ACS grade, 99.9%), acetonitrile (ACN , $\text{C}_2\text{H}_3\text{N}$, $> 99.8\%$), hydrochloric acid (HCl , 33 ~ 40%), glacial acetic acid (CH_3COOH , $> 99\%$), and sulfuric acid (H_2SO_4 , 95 ~ 98%) were obtained from Mallinckrodt Baker (Phillipsburg, NJ).

LC/MS/MS. Two different LC/MS/MS including Agilent 6460 LC-3Q-MS/MS and Shimadzu LC-3Q-MS/MS 8040 were used for routine PFAS quantification. For Agilent 6460 LC-3Q-MS/MS at Harvard, an online SPE using a 300 μL injection was used where the elution onto the analytical column from performed with water (0.1% formic acid) and methanol (more details about online SPE are described previously (Barber et al., 2017; Weber et al., 2017)). The column was reversed phase poroshell 120 EC-C18 (3.0 mm x 50 mm) at 55 °C with mobile phases including 2 mM ammonium acetate in water (solvent A) and 2 mM ammonium acetate in methanol (solvent B) at 0.5 mL/min following a gradient program/ PFAS concentrations were typically quantified with internal standard calibration curves in the 0.5 to 100 $\mu\text{g/L}$ range with correlation coefficients (r^2) > 0.995 with [$^{13}\text{C}_8$] PFOS (M8PFOS) as internal standard. For Shimadzu LC-3Q-MS/MS 8040 at Purdue, the column was a Phenomenex Kinetex 5 μM EVO C18 100Å (100 $\times$ 2.1 mm $\times$ 5 μm) in connection with a Phenomenex column pre-filter (#AF0-8497) at 40 °C. The eluents included 20 mM ammonium acetate in water (solution A) and methanol (solution B) with a flow of was 0.4 mL/min in gradient mode. The desolvation line (DL) and heat block temperatures were maintained at 250 and 400 °C at all time, respectively. The nebulizing and drying gas flow rates were maintained at 1.5 and 6.0 mL/min, respectively. Details on gradient programs, source parameters and MRM transitions are the SI of Zenobio et al. (2020).

PFSA and isomer specific analysis. Aqueous phase samples were diluted with MeOH (1:1 v/v) and solvent extracts were diluted with water so all samples prior to injection were 1:1 v/v MeOH /water to reduce adsorption to high-performance liquid chromatography (HPLC) vials, minimize matrix effects, and optimize sensitivity. All samples were analyzed using a Shimadzu (Nexera x2) ultra-HPLC (uPLC) with an AB Sciex Quadrupole Time of Flight (QTOF) 5600 mass spectrometer (MS). Immediately prior to analysis, 30 μL of IS was added to each HPLC vial and used for quantification. PFSA isomer analysis was done using an Ascentis Express F5 PFP column (2.1 $\times$ 100 mm, 2.7 μm , 90 Å, Sigma-Aldrich) with a Phenomenex column pre-filter. Retention times of the PFSA isomers were confirmed and quantified using commercially-available individual PFSA isomer standards. See the supplementary information (SI) of Park et al. (2017). Percent

isomer compositions were calculated by the ratio of each isomer-specific concentration to total PFOS concentration, which was determined by integration of all isomer peaks. The 3- and 4-PFOS isomers were quantified together due to co-elution (Figure 3-4). Although we had a 1-PFOS standard, the 1-PFOS peak was not well resolved from the dm-PFOS and 2-PFOS isomers with peaks being of low intensity and broad. Therefore, the difference between total isomers in technical PFOS minus the isomers that were quantified independently provided estimates for the sum of the other unspecified isomers. For PFHxS isomer analysis, only br- versus L- was quantified in technical PFHxS using L-PFHxS standard calibration curves with M3PFHxS IS correction (linear, $r^2 > 0.99$). The difference between total PFHxS concentration and L-PFHxS quantified independently was used as an estimated of the total br-PFHxS isomers. Estimated percent isomeric compositions of technical PFOS and PFHxS, isomer-specific limits of detection (LOD) and limits of quantification (LOQ) are reported in Table 3-1.

Non-target analysis with Quadrupole Time-of-Flight (QToF) MS. Nontarget screening for unknown byproducts was performed using a Sciex 5600 Triple Quadrupole Time-of-Flight (QToF) MS following procedures described previously (Zenobio et al., 2020). A Shimadzu uPLC system coupled to a QToF MS was used for non-target analysis using gradient elution (details provided in SI of Zenobio et al. (2020) through a Kinetex EVO C18 (2.1 x 100 mm, 5 μ m, 100 Å) column with a Phenomenex AF0-8497 filter maintained at 40 °C. The eluents included 0.15% acetic acid in water (A) and 20 mM ammonium acetate in MeOH (B). The injection volume was 50 μ L and total runtime was 47 min. Samples were ionized in negative mode using DualSpray source allowing either electrospray ionization (ESI) or atmospheric pressure ionization (APCI). The QToF was calibrated with appropriate calibration solutions using an automated calibration device system every 5 samples. PeakView 2.2 and Analyst 1.7 were used for processing the acquired data. Details regarding chromatography separation and source parameters are summarized the SI of Zenobio et al. (2020). Samples were ionized using two ionization techniques both in negative mode including electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI) over an acquisition range of 50 - 1250 m/z. MS/MS spectra were also screened for fragmentation of ions using a mass defect filtering approach for a mass defect of ~ 0.9 which is common for fluorinated compounds (Myers et al., 2014). PFAAs and FTSS extracts were concentrated 3 and 10 times before non-target screening in order to better detect products with low intensities. The overall process to identify organic products is detailed by our previous study on PFOS degradation with $n\text{Ni}^0\text{Fe}^0\text{-AC}$ where a few organic products were successfully identified and confirmed for PFOS transformation (Zenobio et al., 2020).

Inorganics Analysis. The collected supernatants and extracts were all analyzed for fluoride (F^-) and sulfite (measured as SO_4^{2-}) (Zenobio et al., 2020) using ion chromatography (IC) with conductivity detection. Two different IC systems with different mobile phases and columns were used. The limits of detection (LOD) was 10 $\mu\text{g/L}$ and fluoride limits of quantitation (LOQ) was 20 $\mu\text{g/L}$ or 30 $\mu\text{g/L}$ depending on the analytical system used. LOD and LOQ for sulfate (for quantitation of sulfite) were 5 $\mu\text{g/L}$ and 20 $\mu\text{g/L}$, respectively.

Two different ion chromatography (IC) systems (one at Harvard University and one at Purdue University) both with conductivity detectors but different column and mobile phase conditions were used for quantifying fluoride and sulfite (as sulfate). The IC used at Purdue University is a 940 Professional IC System from Metrohm with MSM II (Metrohm Suppressor Module)

suppressor, conductometric detector and 50- μ L injection volume which was operated with a Metrosep A Supp 7 (250 mm $\times$ 4 mm) from Metrohm with mobile phase of 3.6 mmol/L Na_2CO_3 at 0.7 mL/min. Prior to injection, the column was equilibrated for 30 min to reach base conductivity noise signal < 2 nS. The LOQ was 20 $\mu\text{g/L}$ for both sulfate and fluoride. The IC used at Harvard was a Dionex ICS-3000 system equipped with a Dionex IonPac AS25 main column (4.0 $\times$ 250 mm), Dionex IonPac AS25 guard column (4.0 $\times$ 50 mm) and used sodium hydroxide (NaOH) as the mobile phase (gradient for F^- detailed in SI of Zenobio et al. (2020)). The background conductivity was suppressed with a Dionex ERS 500 system operating in recycle mode. Before each injection, the column equilibrated for 30 min until the conductivity baseline noise signal decreased to < 10 nS. The flow rate was 1.5 mL/min with an injection volume of 50 μL and a column temperature of 30 $^\circ\text{C}$. SO_3^{2-} analysis was performed with separate injections under isocratic conditions with 6 mM NaOH and a suppressor current of 15 mA. F^- and SO_3^{2-} standards were injected first to confirm their retention times. For F^- measurements, the suppressor current was set to 52 mA and the eluent concentration started at 1.8 mM NaOH for the first 11 min and then increase to 21 mM NaOH to remove the excess of chloride ions for 20 min. Finally, the eluent concentration returned to initial conditions of 1.8 mM NaOH for another 10 min for re-equilibration. Before injection extracted samples were diluted to 2-fold dilution in 50:50 NaOH/water to avoid matrix interferences. Using reference standards, the limits of detection (LOD) and quantification (LOQ) for fluoride were 10 $\mu\text{g/L}$ and 30 $\mu\text{g/L}$, respectively. LOD and LOQ for sulfite (quantified as sulfate) were 5 $\mu\text{g/L}$ and 20 $\mu\text{g/L}$, respectively.

Headspace Sampling. In an effort to evaluate if there were measurable volatile organic products during transformation of individual PFAS, in a set of replicate 5-d batch reactors, headspace samples were collected as described previously (Dasu et al., 2012). Briefly, ~ 20 mL of gas in headspace was taken by a gas-tight syringe, passed through C18 cartridge, and eluted twice with 5 mL of ACN. Eluants were concentrated 10 times and non-target screening performed using the QToF, as previously described.

Batch Experiments for Vitamin B12. Batch experiments were conducted to assess if 0.2 g nZn^0 in 10-mL 0.4 mM VB12 can transform technical PFOS (8 μM) at 22, 70, and 90 $^\circ\text{C}$ and at 70 $^\circ\text{C}$ using 0.2 g nFe^0 and Pd^0nFe^0 (1.0% of Pd weight basis to 0.2 g nFe^0) at an initial pH (pH_i) = 10.4 in unbuffered solutions. Synthesis of Pd^0nFe^0 particles was described in Park et al. (2017). L–PFOS transformation in the absence of br-PFOS isomers and transformation of technical PFHxS (8 μM) were also evaluated in VB12- nZn^0 systems (pH_i = 10.4) but only at 70 $^\circ\text{C}$. We chose an initial high pH condition to assess the role of alternate reductants based on previous work by Ochoa-Herrera et al. (2008) for PFOS (pH 6.4 to 8.9) using Ti(III) as the reductant and Amir and Lee (2011) for tetrachloroethene (pH 5 to 9) using nZn^0 as a reductant that showed removal in VB12 systems increases with increasing pH. We did not want to use buffers; therefore, pH_i was set at 10.4 by adjusting with 0.001 M NaOH such that the pH would hopefully stay in the alkaline range during the reaction to maintain VB12 reactivity.

All sample preparation and treatments were conducted in an anaerobic chamber ($> 95\%$ N_2 , $< 5\%$ H_2). High density 120-mL polyethylene (HDPE) crimp serum bottles were used; HDPE was previously shown to have negligible adsorption of PFOS and PFHxS (Zhi, 2019). To each bottle, nZn^0 or other alternate reductants (0.2 g) was added followed by 5 mL each of VB12 (0.8 mM) and PFSA (16 μM) solutions. Bottles were capped with rubber stoppers sealed with aluminum crimp caps and wrapped with aluminum foil to prevent light exposure. Samples were placed in a

preheated oven (70 & 90°C) or kept at room temperature ($22 \pm 0.5^\circ\text{C}$) under static conditions. Final pH (pH_f) was measured in one sample at the last sampling time. The pH measured at the end of each sampling time (1, 2, 3, 5, 7, 11, and 21 d for 22 and 70°C for VB12- nZn^0 ; 1, 2, 3, and 5 d for 90°C for VB12- nZn^0 ; and 5-d for nFe^0 and Pd^0/nFe^0) is referred to as pH_f (final pH for that sample time). Heated samples were quickly cooled to room temperature ($22 \pm 0.5^\circ\text{C}$) by placing them in ice followed by centrifugation (1 h at 3,300 rpm; 2,042 g). The aqueous phase was transferred to a 50-mL polypropylene (PP) tube and the remaining solid particles were extracted 5 times successively with 15-mL of acidified methanol (10:90, v/v, 1% acetic acid/MeOH). No residual PFSA was detected in the 5th extraction. When discussing PFSA removal in this study, PFSA removal is defined as PFSA not recovered after exhaustive extraction of the solid reductants (nZn^0 , nFe^0 , or Pd^0/nFe^0). Therefore, % PFSA was quantified by comparing the combined PFSA mass in the aqueous phase and extracts of the solid particles to the initial PFSA mass measured in the applied PFSA solution $\times 100$.

Pd/Fe Particle Synthesis and Batch Reactions. Batch experiments were conducted Pd^0/nFe^0 NP synthesis as well as subsequent reactions with PFOS were conducted in an anaerobic chamber under 95 % of N_2 and < 5 % of H_2 atmosphere. nFe^0 particles were coated with 1% Pd by adding 20-mL of $[\text{Pd}(\text{C}_2\text{H}_3\text{O}_2)_2]_3$ (Pd-acetate) dissolved in acetone to 50-mL polypropylene (PP) centrifuge round bottom tubes followed by addition of the proper amount of nFe^0 to achieve the 1 % Pd. Mixtures were sonicated for 40 min to coat the surface of nFe^0 with Pd through the following reaction: $\text{Pd}^{2+} + \text{Fe}^0 \rightarrow \text{Pd}^0 + \text{Fe}^{2+}$ (Grittini et al., 1995), which was confirmed by a color change of the Pd solution from yellow-reddish to colorless. After equilibration, solid and liquid phases were separated by centrifugation (30 min at 3,300 rpm = 2042 g) followed by washing the Pd^0/nFe^0 NPs three times with deoxygenated 18 M Ω water with centrifugation between each wash. All samples were capped tightly and wrapped with parafilm to minimize oxygen entry. 2,4,6-trichlorophenol was used as a positive control to confirm the reactivity of the synthesized Pd^0/nFe^0 NPs.

PFOS removal using Pd^0/nFe^0 NPs was evaluated as a function of initial pH and temperature after a 6-d and 21-d reaction time. PFOS (7 ~8 μM) was added through an aqueous solution to freshly prepared Pd^0/nFe^0 NPs in 50-mL PP centrifuge round bottom tubes (PP was previously shown to be the least sorptive of PFAAs by Higgins and Luthy (2006), and mixed (110 rpm) on a temperature-controlled horizontal mixer. When a specific initial pH was desired (initial pH= 3.5 to 8.7), pH was adjusted using 0.5 M HCl or 0.5 M NaOH solutions. Hereafter, pH values reported as initial (pH_i) will refer to aqueous PFOS solution pH prior to exposure to Pd^0/nFe^0 NPs and pH measured after a reaction will refer to the final pH (pH_f).

Samples were sacrificed for analysis at designated times and centrifuged (1 h at 3,300 rpm = 2,042 g) followed by removal of the aqueous solution analysis. The remaining metal particles were extracted five times with 10-mL of acidified methanol (10/90, v/v, 1 % acetic acid/MeOH). Minimal PFOS was measured in 4th and 5th extracts, thus all PFOS was assumed to have been extracted. After the 5th extract, a subset of samples were extracted with 25/75 v/v 200 mM KOH/acetonitrile (ACN) and sonicated (30 min) at 45 °C to confirm no additional PFOS was extractable.

Fe(II/III) complexation experiments. PFOS-Fe(II/III) complexation was quantified as a

function of the Fe valence state (II and III) including 89.6 μM and 200 μM Fe(II) and 8 μM to 540 μM Fe(III), initial solution pH (3.3 to 8.8), and of competing ligand additions (OH^- , EDTA) towards breaking complexes prior to analysis. The effect of chain length and polar functional group (carboxylate versus sulfonate) on PFAA-Fe complexation was also assessed. The effect of different PFAAs on complexation was assessed at 500 μM Fe(III) using C4 to C9 PFCA and perfluorobutane sulfonate (PFBS), PFHxS and PFOS at PFAAs concentrations of 6 to 7 μM at pH 3~4, which was found to be the most susceptible pH range for complexation. Assuming PFOS-Fe(II/III) complexation was the reason for differences in PFOS quantitation between solutions with and without dissolved Fe ions and that the release mechanism would be controlled by ligand exchange selectivity and mass action, we explored addition of a few amendments that we hypothesized could release PFOS from the complex. These amendments included pH adjustment by adding 0.5 M NaOH to pH ~10.5, 6 mM EDTA with no pH adjustment, and pH adjusted 6 mM EDTA 6 mM to pH ~10.1. Experimental and analysis details can be found in Park et al. (2018).

Batch Reactions in Permanganate (PM) Systems. Batch reactions were conducted to bring clarity to whether or not PM can degrade PFOS. Initially, studies similar to those detailed by Liu et al. (2012) and Yao et al. (2016) were conducted followed by investigating diverse catalysts. Catalysts included Ru(III)Cl₃, NaHSO₃, FeCl₂ and 2,2'-Azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) which may serve to catalyze PM for PFOS transformation or enhance degradation rates. Ru(III)Cl₃ and FeCl₂ are expected to form complexes with substrates catalyzing rapid electron transfer (Fawzy et al., 2016; Park et al., 2017) and NaHSO₃ and ABTS are expected to enhance production of more powerful oxidants and/or radicals (Song et al., 2015; Sun et al., 2016) leading to PFOS destruction. To evaluate PFOS destruction, PFOS concentrations were measured over time in addition to F^- and SO_4^{2-} , which are expected with defluorination or cleavage of the C-S bond. To elucidate apparent PFOS loss when there was no evidence of destruction, additional time-dependent data were collected for a subset of samples or experiments. These data included pH, ORP, electrical conductivity (EC), Mn oxidation states, solution color changes and the size of MnO₂ colloids formed along with the associated zeta potential. Additional experimental details including the specific rationale for catalysts chosen are in the SI of Park et al. (2020).

nNi⁰Fe⁰-AC Synthesis and Batch Reactions. nNi⁰Fe⁰-AC particle preparation was performed under nitrogen atmosphere following the same procedure previously described by Zenobio et al. (Zenobio et al., 2020). Briefly, FeCl₂·4H₂O and AC were mixed for 10 min under N₂ purging atmosphere followed by slowly adding NaBH₄ to precipitate nFe⁰ on AC following by washing the particles three times with DI water. The washed nFe⁰-AC was then mixed with an aqueous solution containing NiCl₂·6H₂O while stirring at 600 rpm for 3 h during which Ni was deposited onto the nFe⁰-AC surface. Finally, particles were sonicated for 30 min and the final nanocomposite nNi⁰Fe⁰-AC washed three times to remove residual impurities. Final particle composition consisted of 1.7 wt% Ni, 85.5 wt% Fe, and 12.8 wt% AC. Additional particle characterization has been previously described (Zenobio et al., 2020) showing the formation of spherical nanoparticles with sizes ranging from 20 to 70-nm. The deposition of Fe and Ni particles on AC was previously confirmed by TEM-EDX. To gain some insight into mechanisms, nNi⁰, AC, nNi⁰Fe⁰ and nNi⁰-AC particles for use in reactions with PFOS were synthesized or treated (AC) in a similar manner as nNi⁰Fe⁰-AC with an oxygen-free environment and NaBH₄ as the reductant but with the appropriate ingredient variations.

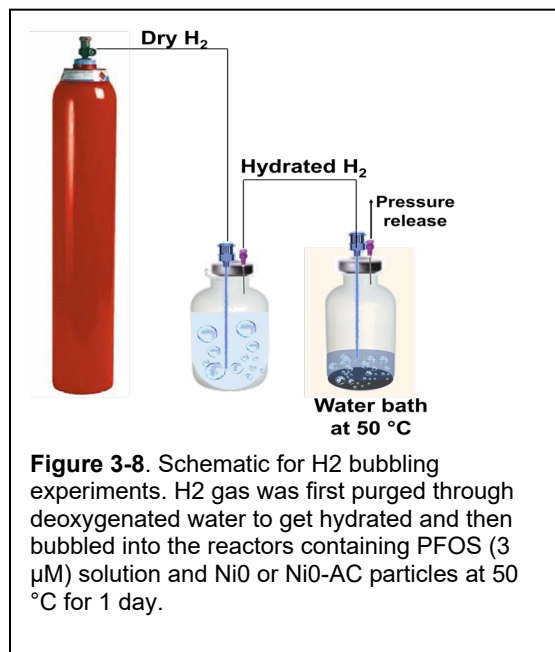
All single solute PFAS, PFAA mixtures, or contaminated groundwater were reacted with $n\text{Ni}^0\text{Fe}^0\text{-AC}$ particles in unbuffered deoxygenated DI or groundwater under a N_2 atmosphere in an anaerobic chamber. The PFAS evaluated included three PFASs (PFBS, PFHxS and PFOS), three PFCAs (PFBA, PFHxA and PFOA), two FTSs (6:2 and 8:2) and GenX (a polyfluoroalkyl ether). For PFOS, results from our previous study conducted under the same conditions are used for comparison purposes (Zenobio et al., 2020). Reactions were initiated by adding freshly synthesized 0.2 g of $n\text{Ni}^0\text{Fe}^0\text{-AC}$ and 10 mL of DI water containing individual PFAAs ($\sim 6 \mu\text{M}$ at 60°C), PFBS ($\sim 1.5 \mu\text{M}$ at 50°C), PFHxS, ($\sim 1 \mu\text{M}$ at 50°C), PFBA ($\sim 0.84 \mu\text{M}$ at 50°C), PFHxA ($\sim 1.4 \mu\text{M}$ at 50°C), PFOA ($\sim 1.2 \mu\text{M}$ at 50°C), 6:2 FTS ($\sim 0.95 \mu\text{M}$ at 50 and 60°C), 8:2 FTS ($\sim 0.9 \mu\text{M}$ at 50 and 60°C), and GenX ($\sim 1.9 \mu\text{M}$ at 50 and 60°C). PFAA mixtures in DI water at 50°C (1-d, 3-d and 5-d reactions) and 60°C (5-d reaction) were also assessed as well as an AFFF-contaminated groundwater from Cape Cod reacted at 60°C . Reactions took place in 60-mL high-density polyethylene (HDPE) bottles hermetically sealed with rubber crimp caps. The 1-d and 5-d reactions with single PFAAs and an AFFF-contaminated groundwater at 60°C were conducted at Harvard University where vials were shaken (150 rpm) in a temperature-controlled chamber. All other reactions were performed at Purdue University including FTSs, GenX, and mixtures at 60°C and all reactions at 50°C using a temperature-controlled water bath or rotating oven. For all experiments, two types of control reactors were included: PFAS solution with no particles and DI water with particles but no PFAS at the corresponding temperatures as well as an additional set of controls kept at room temperature in some cases. Recoveries in room temperature controls were in the 92 to 102% range (Table 3-2).

Table 3-2. % Recoveries of PFAS from room temperature controls (particles and PFAS solution) from three replicates ($n = 3$) unless noted otherwise.

PFAS	% Recovery
PFBS	95 ± 10
PFHxS	100 ± 7
PFOS	102 ± 3.9
PFBA	98 ± 7
PFHxA	92 ± 14
PFOA	103 ± 7
8:2 FTS	$92.1 (n=1)$
GenX	102 ± 3.9

$n\text{Ni}^0\text{Fe}^0\text{-AC}$ Mechanistic Insight Experiments. To achieve better mechanistic insights in the reductive system of $n\text{Ni}^0\text{Fe}^0\text{-AC}$, in particular to evaluate the role of activated carbon, Ni, and Fe, the chemical state and surface composition of metals and carbon in nanocomposites before and after reaction with PFOS were characterized by a Thermo Scientific K-Alpha XPS instrument with a monochromatic Al $K\alpha$ X-ray source. After or prior to reaction, particles were dried overnight at 60°C . A survey (0-1350 eV) and individual element scans were completed for Fe 2p (700-740 eV), Ni 2p (845-885 eV), C (275-295 eV), and O (520-540).

To further aid in elucidating the role of the different $\text{nNi}^0\text{Fe}^0\text{-AC}$ components in PFAS transformation and defluorination, additional batch experiments were conducted at 50 °C with nNi^0 , nNi^0Fe^0 , $\text{nNi}^0\text{-AC}$. To assess the role of AC, batch experiments were done with *i*) ~0.2 g AC-only or AC- NaBH_4 treated and 10 mL DI water containing 10 μM PFOS in reaction bottles, or *ii*) ~0.2 g freshly synthesized nNi^0Fe^0 particles without AC and 10 mL DI water containing ~3 μM of PFOS. To independently assess if the role of Fe was limited to generating H_2 , 1-d batch reactions were conducted in which H_2 was introduced in the absence of Fe. In this case, ~0.8 g of freshly synthesized nNi^0 or $\text{nNi}^0\text{-AC}$ particles and 40 mL of PFOS were placed in 120-mL high-density polyethylene (HDPE) bottles and hermetically sealed with rubber crimp caps. Reactors were then moved from the anaerobic chamber to a 50 °C water bath and outfitted to purge hydrated H_2 gas through the reactor (Figure 3-8) by first bubbling high purity H_2 through oxygen-free DI water before bubbling into the reactors containing 3 μM PFOS and Ni or Ni-AC particles at 50 °C for 1 d.



Column Studies. Four column experiments (PFOS- I, PFOS- II, Mix- I and Mix- II) were conducted with differences in $\text{nNi}^0\text{Fe}^0\text{-AC}$:sand ratios, solution matrix, flow rate and temperature. A Kontes Chromaflex glass column (2.5 cm x 10.5 cm) with a total inner volume of 51.5 cm^3 was packed and capped inside the anaerobic chamber before taking out to initiate flow experiments. For all columns, the influent end was packed with 3 cm of sand, followed by 6 cm of the $\text{nNi}^0\text{Fe}^0\text{-AC}$:sand mix (reactive zone), and topped off with 1.5 cm of sand followed by a mesh to prevent particles from exiting the column. Bulk densities and saturated water content for all four columns were approximately 1.6 g/cm^3 and 0.4 mL/cm^3 , respectively. The $\text{nNi}^0\text{Fe}^0\text{-AC}$:sand mix reaction zone for PFOS- I, PFOS-II, and Mix-I was 1:10 whereas higher ratio of 1:7 was used for Mix-II. Autoclaved de-oxygenated nanopore water was used for the influent matrix in all columns except Mix-I for which autoclaved de-oxygenated carbonate buffer (10 mM; pH = 7.5) was used. Influent solutions were prepared in the anaerobic chamber by adding an aliquot of aqueous PFOS or PFAA stock solution to autoclaved matrix solutions to achieve the target concentrations. Packed columns were taken out of the anaerobic chamber followed by attaching appropriate polyethylene tubing and placing columns in a water bath or covered with a heated tape at 60 °C for PFOS-I, PFOS-II, Mix-I or 50 °C for Mix-II, respectively. The PFAA-containing influents were pumped through the columns in upward vertical flow using a Shimadzu LC pump for the higher flow rate and an 11-ELITE infusion syringe pump (Harvard Apparatus, Holliston, MA, USA) for the lower flow rates (Figure ES-2). Column parameters are summarized in Table 3-3. For PFOS-I and PFOS-II, the initial influent was sufficient for the entire experimental period. For Mix-I, PFAA mix solution was renewed every ~20 days (total number of 3 times for 2-month period of experiment), and for Mix-II, every ~4 days (total number of ~15 times for 2-month period of experiment). Influent was sub-sampled and prepared for analysis prior to use and prior to each renewal or at the end of the experiment.

Table 3-3. Differentiating details in the PFOS and PFAA mixture (Mix) column experiments

Column ID	°C	Flow (mL min⁻¹)	nNi⁰Fe⁰- AC to sand ratio	Influent	Pump Type	Effluent pH	Effluent ORP	Total Effluent (PVs)
PFOS-I	60	0.05	1:10	DI water	LC	Subsample ^a	In-line ^b	59
PFOS-II	60	0.15	1:10	DI water	LC	In-line ^c	Sub-sample	105
Mix-I	60	0.05	1:10	pH 7.5 carbonate buffer	LC	Subsample	NA ^d	138
Mix-II	50	0.005	1:7	DI water	Harvard	Subsample	NA	16

^aMeasurements made in each effluent collection; ^bORP measured every 10 mins for 1 day, 20 mins for 8 days, and 60 mins for the remaining experimental period; ^cpH measured every 10 mins for 1 day, and 180 mins for rest of experimental period; ^dnot applicable (not measured).

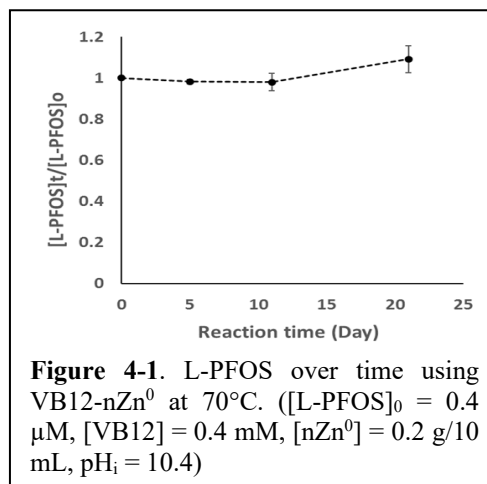
SECTION 4: RESULTS AND DISCUSSION

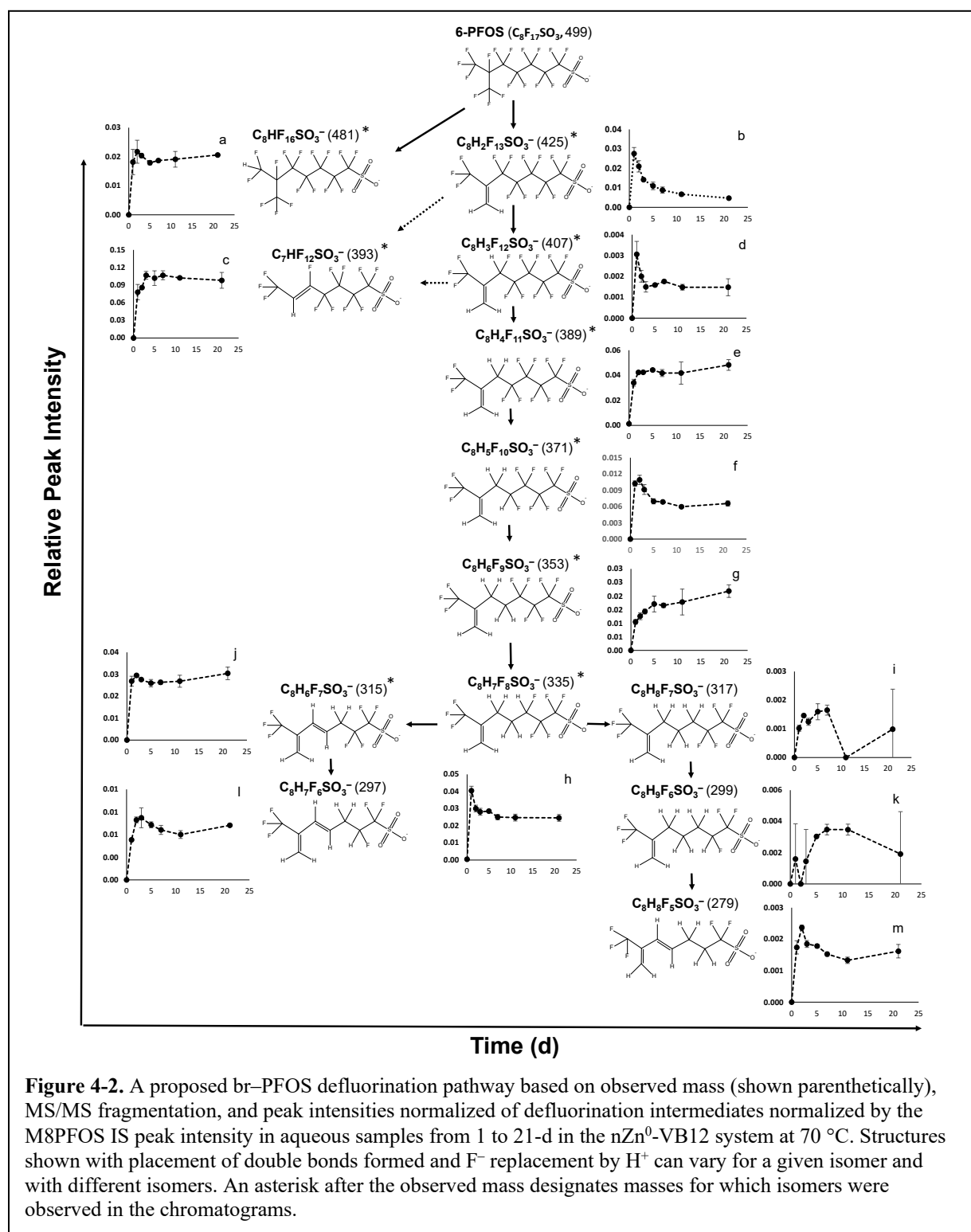
Vitamin B12 Systems. Our initial work focused on seeing if Vitamin B12 systems could be optimized to degrade both linear and branched PFOS under conditions amenable for in situ use. The effectiveness of VB12 in the systems evaluated by Ochoa-Herrera et al. (2008) required high concentrations of Ti(III)-citrate and only transformed br-PFOS. Therefore, we explored alternate reductants for use in VB12 systems with a primary focus on nano-sized zero valent zinc (nZn^0), which has a higher reduction potential than Ti(III) (Bratsch, 1989). Transformation over time with VB12- nZn^0 was investigated at 22, 70 and 90°C for PFOS and at 70°C for PFHxS, with F⁻ generation and isomer-specific PFSA removal rates quantified. Only br-PFOS isomers were removed and transformed by VB12- nZn^0 similar to what was found with VB12 and Ti-citrate (Figure ES-1). Data not shown here can be found in the SI of (Park et al., 2017) (Park et al., 2018).

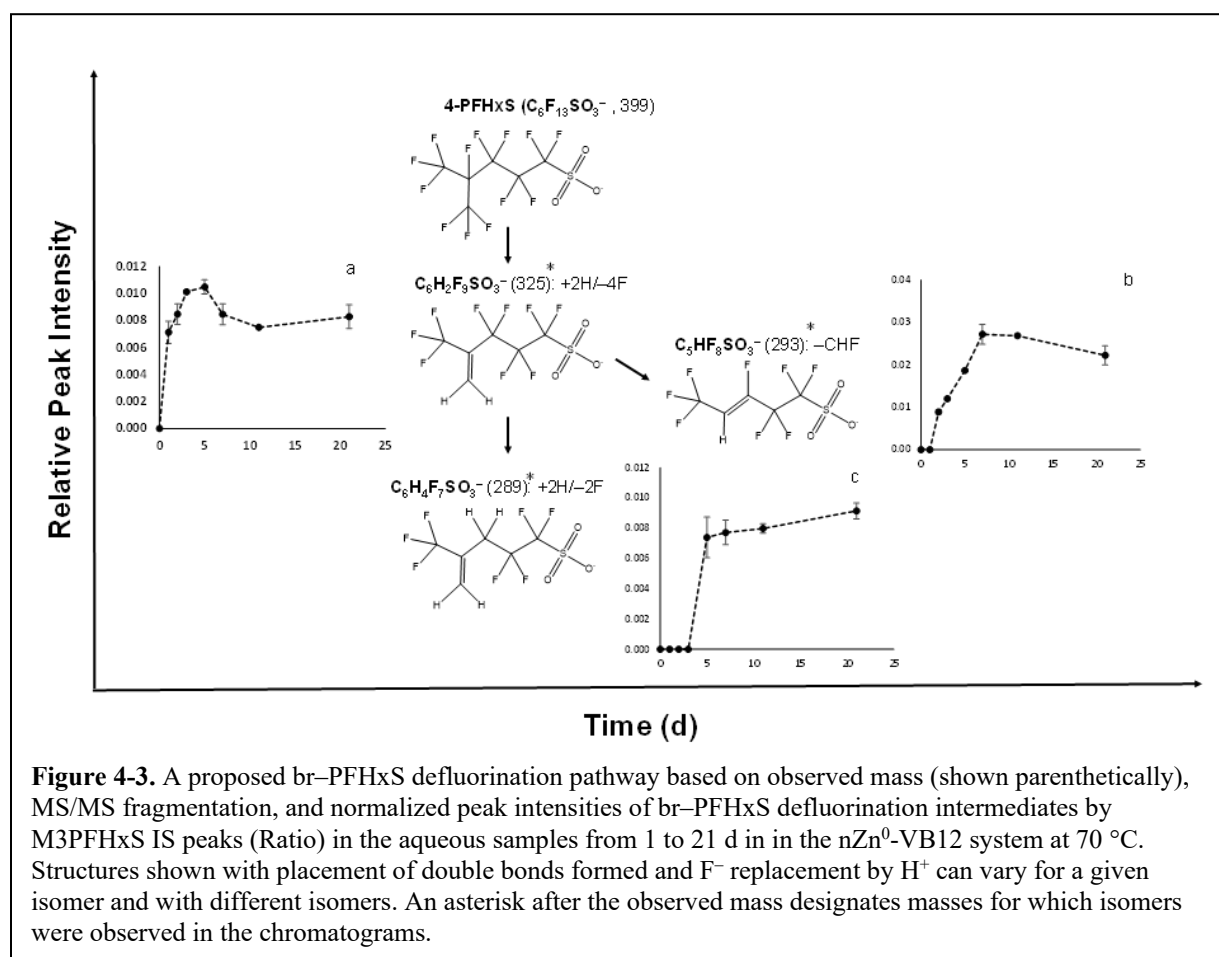
Fluoride generation accompanied br-PFOS removal, but no sulfate generation was observed. The samples from the VB12- nZn^0 reactions at 90°C where degradation was the highest were used to explore isomer-specific removal rates. Rates were estimated using specific isomer concentration relative to initial isomer-specific concentration for the time periods where concentrations were above LOQ: 0-5 d for 3&4-PFOS, 0-3 d for 5-PFOS and 0-2 d for 6-PFOS isomers. 6-PFOS removal was the fastest followed by 5-PFOS and 3&4-PFOS with estimated rates (d^{-1}) of -3.35 ± 0.25 , -1.39 ± 0.10 , and -0.37 ± 0.03 , respectively, and no removal of L-PFOS was already noted. The coeluting and three broad peaks, which contributed to the remaining unquantified br-isomers decreased over time as well but to different extents

L-PFOS did not degrade with any of the catalysis tested with vitamin B12. Even when only the L-PFOS isomer was present, no removal was observed ($101 \pm 7\%$ recovered, $p = 0.2318$, Figure 4-1); therefore, lack of L-PFOS removal is not due to a competitive effect in the multiple isomer system (technical PFOS). The absence of L-PFOS transformation by VB12 appeared to be due to the inability of L-PFSAs to complex with VB12 and not an activation energy issue, thus not something that can be overcome by stronger reductants/catalysts. At 90°C, 95% of br-PFOS isomers were transformed within 5 d.

For br-isomers, organic intermediates were identified at each sampling time in the 70°C experiments, and feasible reaction pathways were proposed (Figures 4-2 and 4-3). Isomer-specific removal rates were positively correlated to the br- CF_3 's proximity to the terminal CF_3 . Br-PFHxS transformation was approximately two times slower with less defluorination than br-PFOS. C8/C7 and C6/C5 polyfluorinated sulfonates from br-PFOS and br-PFHxS, respectively, were identified as both intermediates and apparent dead-end products. Pathways included 4 F replaced by 2 H and a C=C bond, and serial F replacement by H with up to 12 F atoms removed from br-PFOS. Additional details can be found in Park et al. (2017).

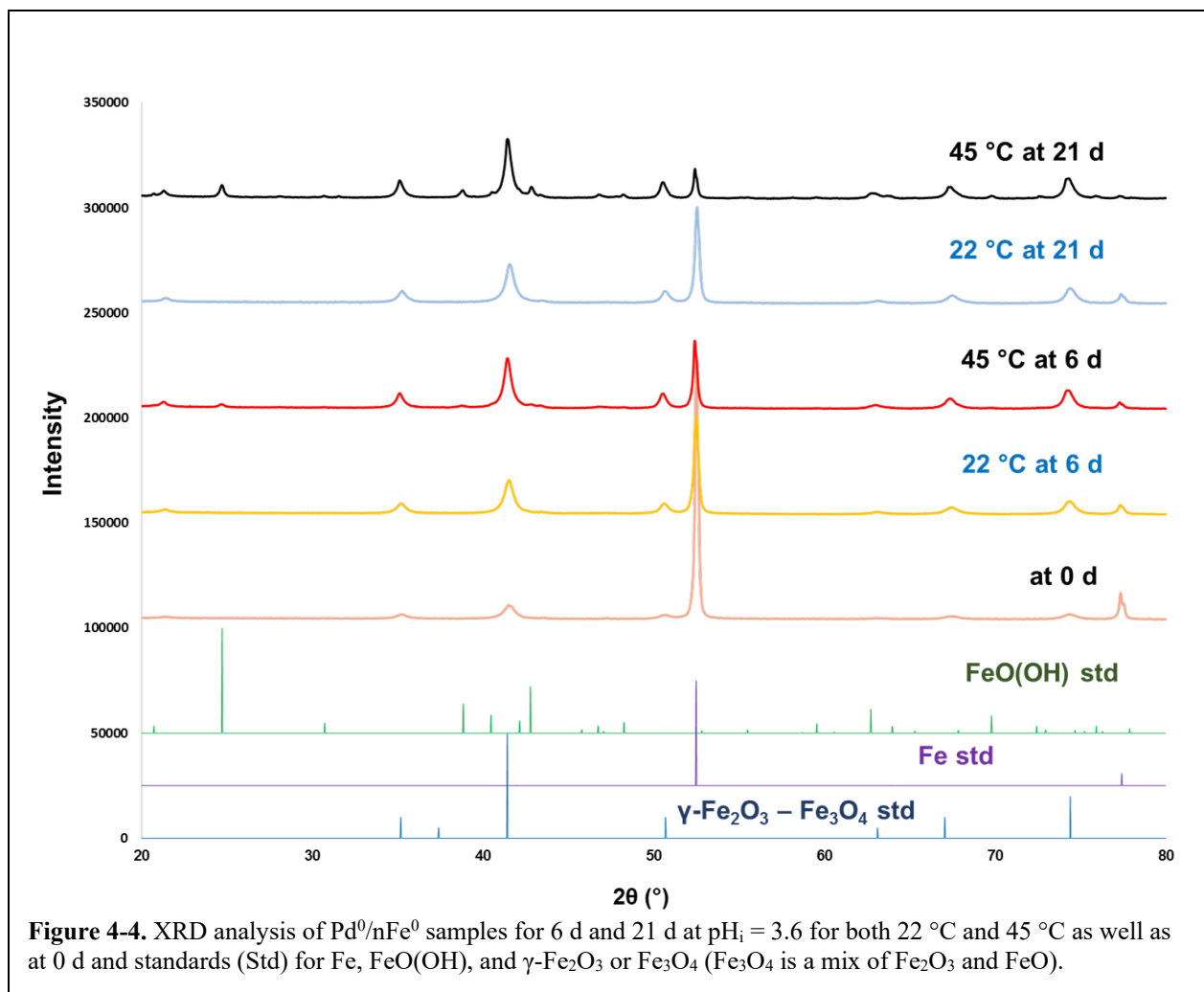






nPdFe⁰ Systems. Although nPdFe⁰ did not enhance L-PFOS destruction in Vitamin B12 systems because it could not change the steric hindrances that limited Vitamin B12's ability to complex L-PFOS, it was still plausible that it could independently defluorinate PFOS. Palladized nFe⁰ is known to reduce the activation energy for defluorination organochlorine molecules due to the electron filling potential of the unfilled orbitals in Pd (Wang et al., 2008; Zhang et al., 1998), increases the reactive surface area, and increases the reactive sites on the Fe⁰ surface for conversion of H⁺ or/and H₂ to hydrogen radicals (H[•]) (Elliott and Zhang, 2001; Shao-ping et al., 2005). PFOS removal using Pd⁰/nFe⁰ NPs was evaluated as a function of initial pH (3.6, 5.5 and 8.7) and temperature (22, 45 and 70 °C) after a 6-d and 21-d reaction time. PFOS was measured in aqueous phases and exhaustive extracts of the NPs. PFOS loss (unrecovered by liquid chromatography mass spectrometry) at the lowest pH (Figure ES-2A); however, generation of expected inorganic byproducts F⁻ or SO₄²⁻ (from cleavage of the SO₃²⁻) was not observed. In addition, at higher temperatures, measured PFOS loss decreased (more recovered) at the longer reaction time further supporting the absence of transformation (Figure ES2-B). Spectroscopically, it was determined that changes in the Fe-oxides from γ-Fe₂O₃ (at 6 d) to FeO(OH) (at 21 d) (Figure 4-4) led to a concomitant release of previously unrecovered PFOS (Figure 4-4). PFOS-complexed with Fe released during corrosion was found to reduce quantifiable PFOS levels (Figure 4-5). The pH effected complexation with increasing pH reducing complexation (Figure 4-6). Therefore,

elevating solution pH to > 10 released PFOS for quantification (Figure 4-7). Complexation increased with Fe concentration and valence (III $>$ II) and was greater for longer chain PFAAs with no significant differences between PFCAs and PFSAAs (Figure ES-3). Additional details and figures can be found in Park et al. (2018).



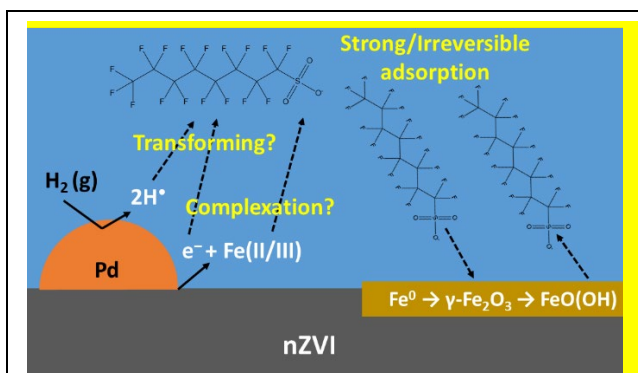


Figure 4-5. Schematic of dynamics in PFOS reactions with a nPdFe⁰. PFOS is not transformed but apparent loss is due to strong sorption to γ-Fe₂O₃ which in conversion to FeO(OH) releases PFOS.

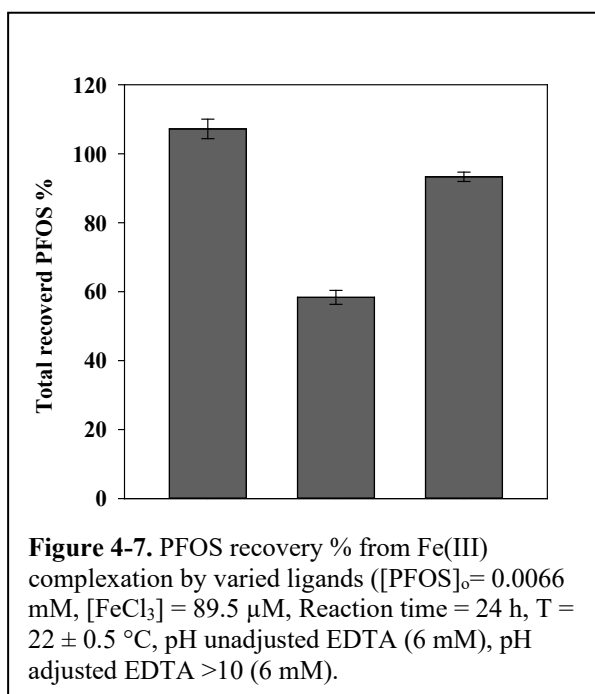


Figure 4-7. PFOS recovery % from Fe(III) complexation by varied ligands ([PFOS]₀ = 0.0066 mM, [FeCl₃] = 89.5 μM, Reaction time = 24 h, T = 22 ± 0.5 °C, pH unadjusted EDTA (6 mM), pH adjusted EDTA >10 (6 mM)).

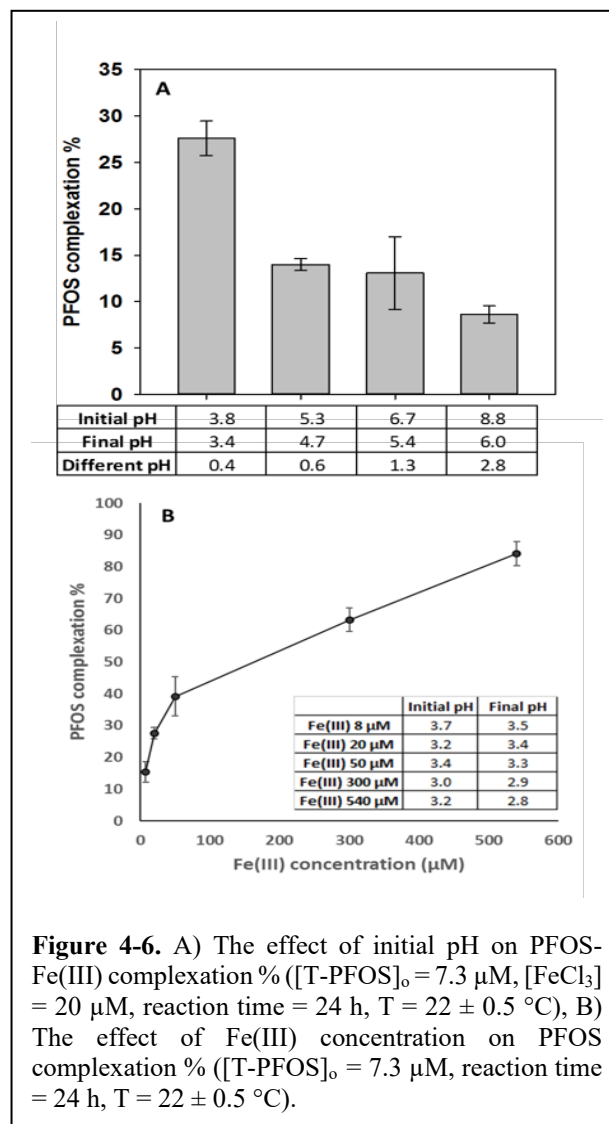


Figure 4-6. A) The effect of initial pH on PFOS-Fe(III) complexation % ([T-PFOS]₀ = 7.3 μM, [FeCl₃] = 20 μM, reaction time = 24 h, T = 22 ± 0.5 °C), B) The effect of Fe(III) concentration on PFOS complexation % ([T-PFOS]₀ = 7.3 μM, reaction time = 24 h, T = 22 ± 0.5 °C).

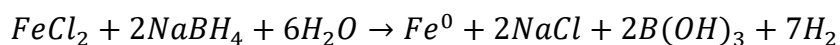
Metal/bimetal Nanoparticle Systems.

PFOA and PFOS removal using Pd/nFe⁰ saturated Swy2. No removal of PFOA and PFOS were observed using the Pd/nFe⁰ supported in the interlayers of Swy2 clay with almost all PFOA and PFOS observed in the aqueous phase (~ 95% and 100% the aqueous phase, respectively) after the 48-h reaction period (data not shown). Therefore, even sorption to the material was negligible, which is likely due to the size, shape and charge of PFOA and PFOS, which limited their ability to enter into the Swy2 clay interlayer (0.1 ~ 1.8 nm; (Schoonheydt, 2002)) and interaction with Pd/nFe⁰.

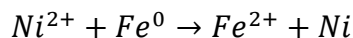
PFOA and PFOS removal using Pd/nFe⁰ saturated CTAB-Swy2. Modification of the Swy2 interlayer with the CTAB surfactant was expected to enhance PFOA and PFOS sorption into the interlayer, thus increasing the probability of interaction with the bimetal, which did occur with 95 ± 0.3 % and 94 ± 0.2 % of PFOA and PFOS removed from solution, respectively. Upon extraction of the solid particles, essentially all PFOA and PFOS were recovered (data not shown), thus again removal was completely due to sorption and not decomposition.

Synthesis of Ni⁰/C-Fe⁰ catalyst. Carbonyl iron (C-Fe⁰) was included for evaluation as a substitute for nFe⁰ because particles prepared with C-Fe⁰ can be done in an aerobic environment. Individual replicates of Ni/C-Fe⁰ and C-Fe⁰ (no catalyst control) were performed adding 0.2 g of the commercial carbonyl iron powder and 0.015 g of NiCl₂·6H₂O. Then, the Ni/C-Fe⁰ particles were mixed for 1 hour under mechanical stirring at 600 rpm. After mixing, particles were washed three times with deionized water (18.2 MΩ cm), centrifuged at 3,000 rpm and supernatant removed.

Synthesis of Fe⁰, Fe⁰-AC, Ni/Fe⁰ and NiFe⁰-AC nanoparticles (NPs). Nanoparticles preparation was performed under anaerobic conditions. First, 1.26 g FeCl₂·4H₂O and 0.34 g of NaBH₄ were added dropwise under mechanical stirring (600 rpm) for 10 min to form Fe⁰ following the reaction:



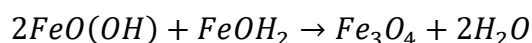
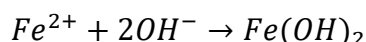
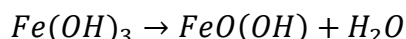
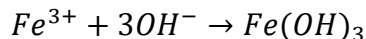
After Fe⁰ precipitated (visible black particles), samples were washed with deionized water and supernatant was removed. Lastly, 0.03 g of NiCl₂·6H₂O aqueous solution was added to the wet Fe⁰ with strong stirring (600 rpm) for 1 hour and then sonicated for 30 min. Again, the resulting nanocomposite was washed and the supernatant was removed. Ni content over Fe⁰ was ~2 wt%. A total of ~1 g of Ni/Fe⁰ NPs were synthesized according to the following reaction:



For the NiFe⁰-AC NPs, activated carbon (AC) was mixed with FeCl₂·4H₂O before the addition of NaBH₄. All deionized water used to make the nanocomposites was deoxygenated by bubbling nitrogen gas for 1 h. Only mechanical stirring was used to mix the solutions (magnetic stirring was avoided to reduce magnetically induced aggregation of the resultant iron particles). The resulting Fe⁰, Fe⁰-AC, NiFe⁰ and NiFe⁰-AC NPs were synthesized immediately before use.

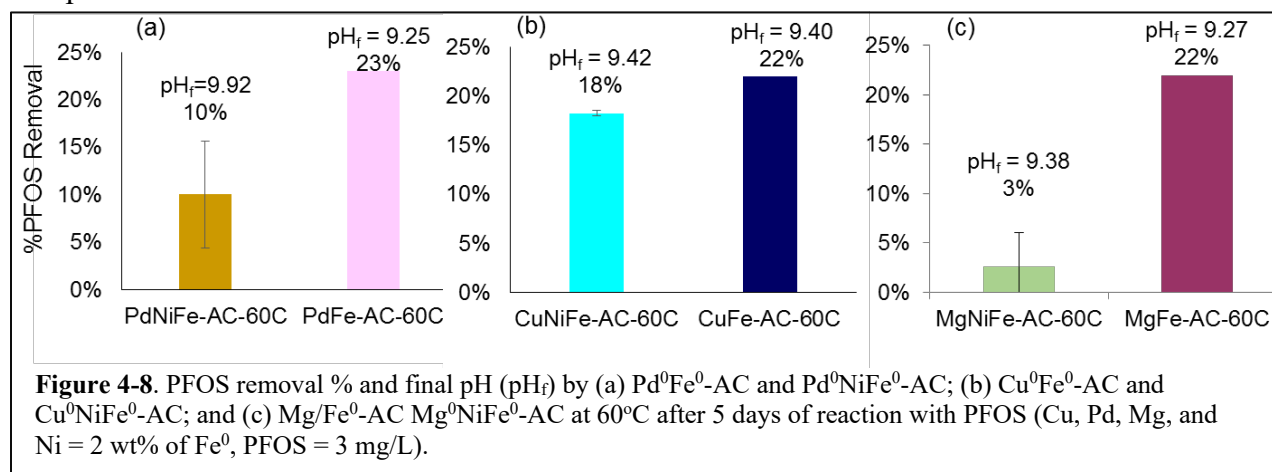
Synthesis of bi/trimetal-AC containing Pd, Cu, Mg nanoparticles (NPs). Bimetals were prepared as describe for Ni⁰Fe⁰-AC. For the trimetals, after the NiFe⁰-AC particles were prepared as described above, they were mixed with Pd, Cu or Mg for 10 min at 600 rpm and the resulting nanocomposite was washed, centrifuged at 3000 rpm, and supernatant removed.

Synthesis of nFe₃O₄-Ni/Fe⁰ NPs. nFe₃O₄ NPs were synthesized in a separate container and then mixed with the NiFe⁰-AC particles. Briefly, 0.583 g of FeCl₃.6H₂O and 0.214 g of FeCl₂.4H₂O (molar ratio 2:1) were added to 50 mL of deionized water and sonicated for 10 min. Then, 0.692 mL of NH₃.H₂O was added slowly to precipitate nFe₃O₄ according to the following reaction steps:



After nFe₃O₄ precipitated, samples were washed three times with deionized water and supernatant removed. NiFe⁰ NPs were made following the procedure described before. Then, the nFe₃O₄ and NiFe⁰ NPs were mixed for 10 min.

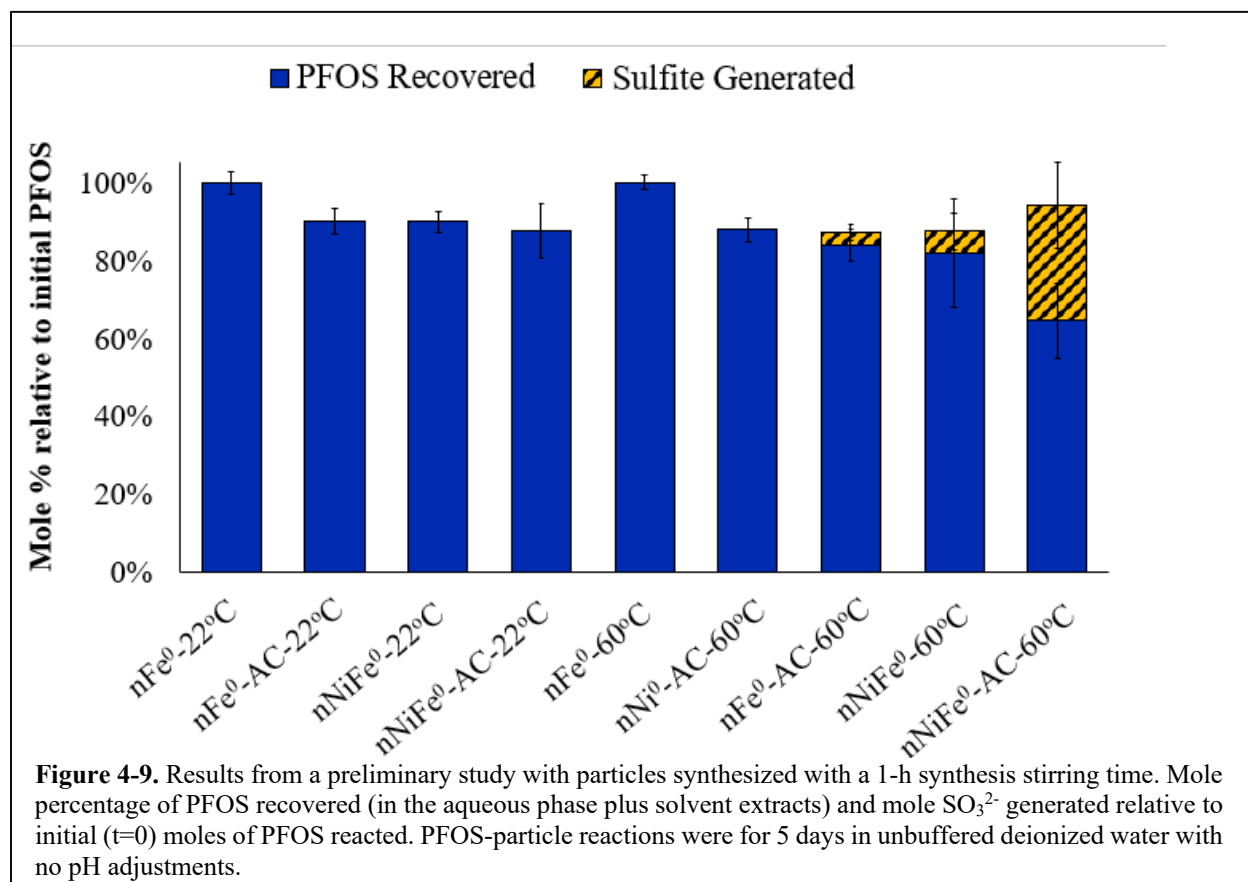
Effect of the oxidation-reduction potential of catalyst on PFOS removal. Three catalysts of varying reductive potential were selected: high (Pd, E° = +0.987 V), low (Cu, E° = +0.337 V), and very low (Mg, E° = -2.37 V) to evaluate their potential to enhance PFOS removal in Ni⁰Fe⁰-AC systems at 60 °C. All catalysts were plated at ~2 wt% Ni⁰/Fe⁰-AC. The addition of the third catalyst decreased PFOS removal (Figure 4-8) for all the three added metals. The decrease was higher with MgNi⁰Fe⁰-AC (3%) compared to PdNi⁰Fe⁰-AC (10%), and CuNi⁰Fe⁰-AC (18%). Final solution pH values were > 9 for Cu, but remained acidic with the addition of Pd and Mg. Note XPS analysis of the NPs containing Cu, Pd, or Mg were not characterized, thus final NP composition has not been verified.



Addition of magnetite (nFe₃O₄). Effects of nFe₃O₄, as a heterogeneous catalyst, in the NiFe⁰-AC system for the decomposition of PFOS was evaluated. XPS was used to evaluate the nFe₃O₄-Ni⁰Fe⁰-AC particles. XPS showed the presence of both Ni and Fe⁰, but Ni content appeared lower

than observed on $\text{NiFe}^0\text{-AC}$. The presence of Fe_3O_4 was also confirmed and peaks at energies that correspond to C-O binds were present, which was not observed in $\text{Ni}^0\text{Fe}^0\text{-AC}$. The addition of Fe_3O_4 to $\text{Ni}^0\text{Fe}^0\text{-AC}$ or $\text{Fe}^0\text{-AC}$ did not increase PFOS removal; however, the final solution pH values were acidic. Inhibitory effects of Fe_3O_4 have been observed for 1,1,1-TCA decomposition when Fe_3O_4 was in excess (Bae and Lee, 2010). According to Bae and Lee (2010), the decrease of Fe^0 reactivity was attributed to the competitive reduction of Fe_3O_4 to Fe(III) by Fe^0 , thus reducing the transfer of electrons to the target contaminant.

nNi⁰Fe⁰-AC Nanocomposites. Of the metal particles investigated, $\text{nNi}^0\text{Fe}^0\text{-AC}$ was the best and the only one where generation of sulfite and fluoride from PFOS destruction was clearly evident (Figure 4-9), thus the remainder of our work with bimetals focused on evaluating the $\text{nNi}^0\text{Fe}^0\text{-AC}$. Work included optimizing the synthesis process for improved $\text{nNi}^0\text{Fe}^0\text{-AC}$ reactivity, which occurred with a 3-h synthesis stirring time. We found a longer synthesis stirring time improved nanoparticle dispersion and reactivity. Therefore, all subsequent data was obtained with $\text{nNi}^0\text{Fe}^0\text{-AC}$ particles synthesized with a 3-h synthesis stirring time.



nNi⁰Fe⁰-AC Nanocomposite Characterization. The nNiFe⁰ particles are spherical (amorphous) particles distributed onto large gray sheets of AC (Figure 4-10a and 4-10b) with sizes ranging from 20 to 70 nm (Figure 4-10c). The TEM-EDX analysis confirmed Ni and AC at ~2 wt% and ~13 wt%, respectively.

To achieve better mechanistic insights in the reductive system of nNi⁰Fe⁰-AC, in particular to evaluate the role of activated carbon, Ni, and Fe, the chemical state and surface composition of metals and carbon in nanocomposites before and after reaction with PFOS were characterized by a Thermo Scientific K-Alpha XPS instrument with a monochromatic Al K α X-ray source. After or prior to reaction, particles were dried overnight at 60 °C. A survey (0-1350 eV) and individual element scans were completed for Fe 2p (700-740 eV), Ni 2p (845-885 eV), C (275-295 eV), and O (520-540).

The overall XPS spectrum before and after reaction is illustrated in Figure 4-11. The main elements on the particle surface are Fe2p, Ni2p, O1s, and C1s. Analyses of the Fe, Ni, O, and C regions were performed by fitting the raw data to individual Gaussian curves (dashed lines). The sum of these individual curves is indicated by a black solid line. A high-resolution spectrum of Ni before and after reacting with PFAS is shown in Figure 4-11a and b, respectively. The peaks at 852.7 and 869.8 eV correspond to the Ni 2p_{3/2} and Ni 2p_{1/2} main peaks, while 858 and 875.9 eV to their corresponding satellites (Grosvenor et al., 2006). The position of the Ni 2p_{3/2} peak (red dashed line) at 852.7 eV is indicative of Ni⁰. The presence of other peaks (light blue dashed lines) at 856, 861.7, 864, 865.3, 873.3, 874, 878.6 eV confirm the presence of nickel oxides (Grosvenor et al., 2006), which may be present as Ni²⁺ or Ni³⁺. Using XPS is difficult to differentiate between these Ni²⁺ and Ni³⁺ containing species. After contact with PFAS, the Ni⁰ peak intensity decreased, and the Ni oxide peak increased significantly. The results indicate that Ni was reduced by Fe⁰ during particle synthesis and Ni²⁺ and Ni³⁺ formation is accelerated during the reaction with PFAS.

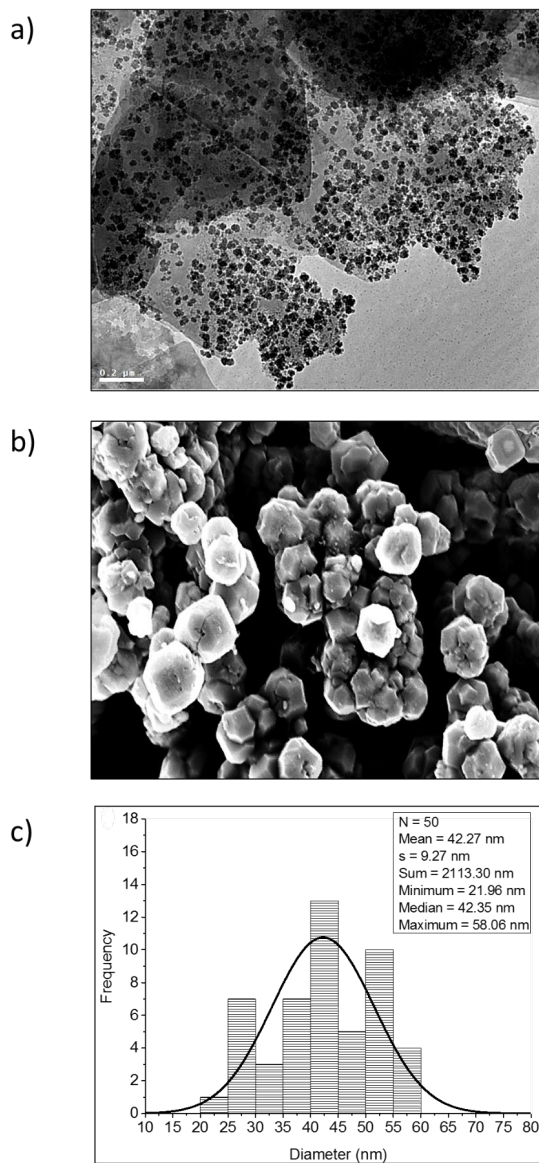


Figure 4-10. a) TEM and b) SEM images of the morphology of AC-supported nNiFe⁰ particles and c) associated size distribution histograms.

Figure 4-11c and d show the high-resolution spectra of Fe2p before and after reaction, respectively. The purple dashed lines with peaks at 709, 715.3, 723.5, and 730.1 eV correspond

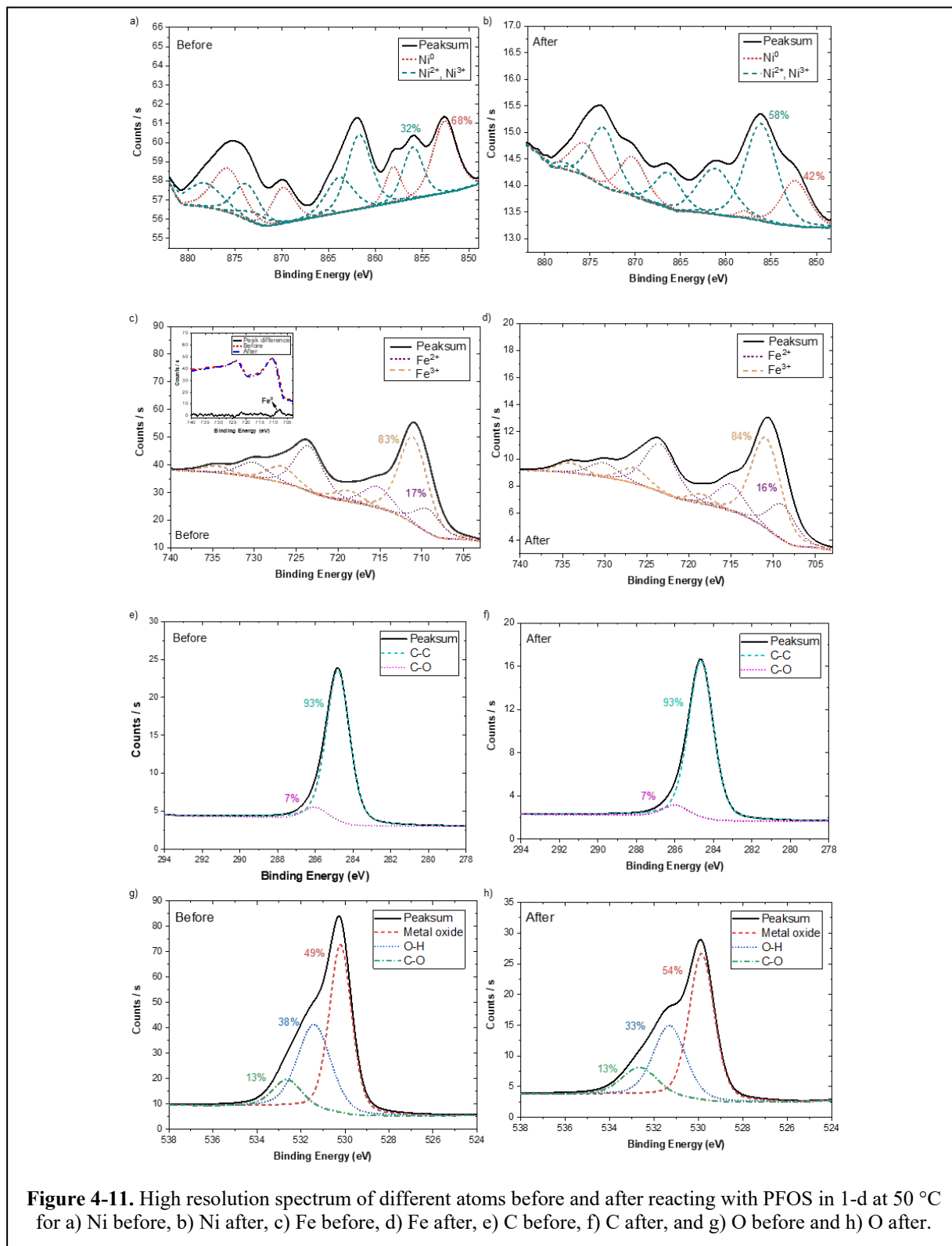


Figure 4-11. High resolution spectrum of different atoms before and after reacting with PFOS in 1-d at 50 °C for a) Ni before, b) Ni after, c) Fe before, d) Fe after, e) C before, f) C after, and g) O before and h) O after.

to Fe^{2+} , while the orange dashed lines with peaks at 710.9, 718.5, 726.8, and 734.4 V correspond to Fe^{3+} species (Yu et al., 2019). Only a small decrease and increase of the Fe^{2+} and Fe^{3+} atomic %, respectively, were noticed after reaction. However, after subtracting the Fe spectra before and after reaction, a small peak at 706.9 eV was observed confirming the presence of Fe^0 in the composite surface only before reacting with PFOS (Figure 4-11c). High-resolution XPS spectra of C1s before and after reaction are shown in Figure 4-11e and f, respectively. Two peaks were observed at 284.8 and 286 eV corresponding to C-C and C-O (Burke et al., 1992), respectively. The atomic % composing the particle surface was 93% for C-C and 7% for C-O. However, no differences in the carbon functional states were observed before and after reaction. The high-resolution O1s spectra (Figure 4-11g and h) before and after reaction was deconvoluted into three peaks with binding energy at 530, 531.4, and 532.6 eV. The first peak at 530 eV is characteristic of metal oxides, while the second peak at 531.4 eV is attributed to O-H (Zhang et al., 2019). The presence of hydroxyl oxygen groups in the composite surface indicates that iron/nickel oxides exist in the form of $\text{FeOOH}/\text{NiOOH}$. The peak at 532.6 eV corresponds to C-O confirmed previously with the C1s high-resolution spectra. After reaction, the atomic % increase for metal oxides from 49% to 54%, but the hydroxylation of the composite surface decrease from 38% to 33%. Again, no difference was observed for C-O atomic %.

nNi⁰Fe⁰-AC Reaction Kinetics with PFOS. The percentage of PFOS that was defluorinated (Eq 1) or desulfonation (Eq 2) were calculated as follows:

$$\% \text{ defluorination} = (n_{\text{produced}}^{\text{F}^-}) / (n_{\text{initial}}^{\text{PFOS}} \times 17) \times 100 \quad \text{Eq. (1)}$$

$$\% \text{ desulfonation} = (n_{\text{produced}}^{\text{SO}_3^{2-}}) / (n_{\text{initial}}^{\text{PFOS}} \times 1) \times 100 \quad \text{Eq. (2)}$$

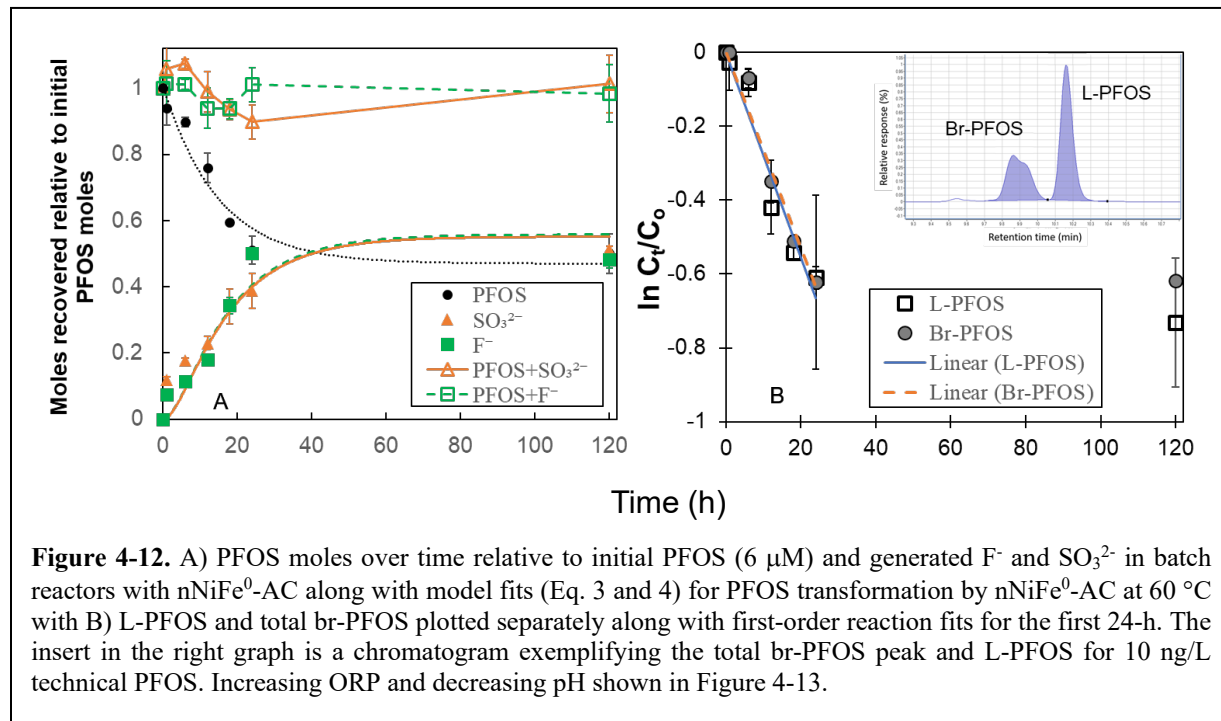
where $n_{\text{produced}}^{\text{F}^-}$ and $n_{\text{produced}}^{\text{SO}_3^{2-}}$ are the moles of fluoride and sulfite ions, respectively, and $n_{\text{initial}}^{\text{PFOS}}$ is the initial moles of PFOS; 17 mole of fluorine and one mole of sulfite corresponds to one mole of PFOS. Total PFOS loss and F^- and SO_3^{2-} generation were fitted by the following exponential decay model (Eq. 3) and exponential growth model (Eq. 4), respectively, as proposed by Vecitis et al. (2008):

$$\text{PFOS}_t / \text{PFOS}_{\text{initial}} = \exp(-k_1^{-\text{PFOS}} t) \quad \text{Eq. (3)}$$

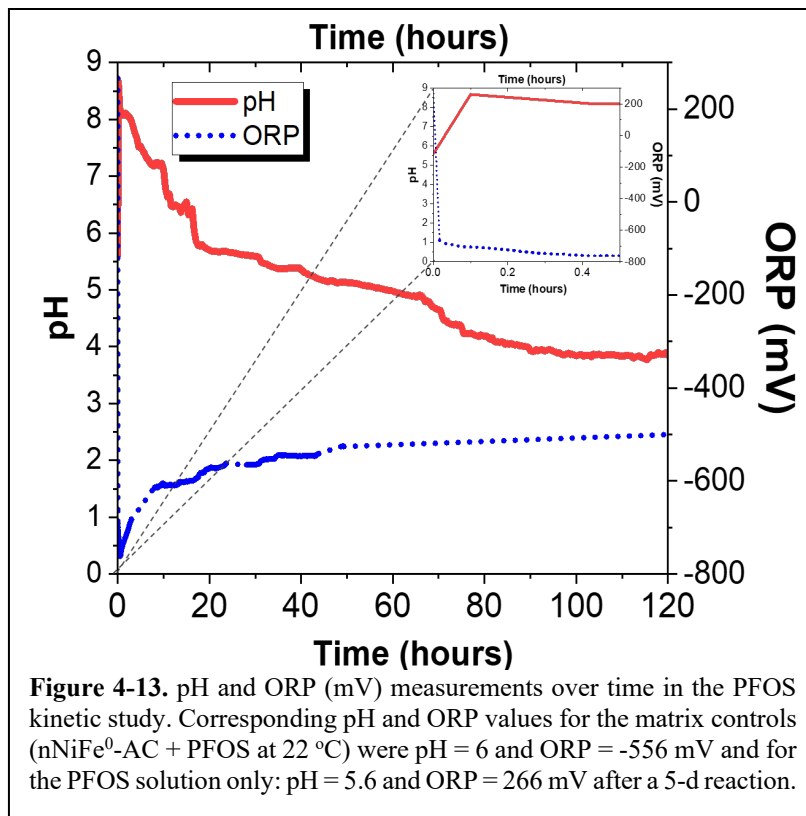
$$\frac{\{\text{moles } (\text{F}^-, \text{SO}_3^{2-}) t\}}{\{\text{moles } \text{F}^-, \text{SO}_3^{2-}\} \text{PFOS}_i} = \frac{1}{k_1^{-\text{PFOS}} + k_2^{(\text{F}^-, \text{SO}_3^{2-})}} [k_2^{(\text{F}^-, \text{SO}_3^{2-})} (1 - \exp(-k_1^{-\text{PFOS}} t)) - k_1^{-\text{PFOS}} (1 - \exp(-k_2^{(\text{F}^-, \text{SO}_3^{2-})} t))] \quad \text{Eq. (4)}$$

where $k_1^{-\text{PFOS}}$ is the PFOS decay rate constant and $k_2^{(\text{F}^-, \text{SO}_3^{2-})}$ is the generation rate constant for F^- or SO_3^{2-} . Eq. (4) is a double exponential growth model that defines F^- and SO_3^{2-} generation rates using $k_1^{-\text{PFOS}}$ estimated from Eq (1) and assuming an undefined intermediate decay (e.g. $\text{PFOS} \rightarrow \text{“X” Intermediate} \rightarrow \text{F}^- \text{ or } \text{SO}_3^{2-}$).

PFOS transformation kinetics with $\text{nNiFe}^0\text{-AC}$ over 120 h period at 60 °C showed degradation of linear (L) and branched (Br) PFOS, which was demonstrated for the first time (Zenobio et al., 2020) and included several lines of evidence (Figure 4-12). PFOS degradation plateaued at $50 \pm 6\%$ at 60 °C. At 60 °C, PFOS degradation rates were estimated at $0.028 \pm 0.003 \text{ h}^{-1}$ and fluoride



and sulfite generation rates at $0.70 \pm 0.165 \text{ h}^{-1}$ and $0.62 \pm 0.157 \text{ h}^{-1}$, respectively, with no differences between L-PFOS and total br-PFOS. Decreasing pH and increasing ORP values after addition of PFOS correlated to PFOS degradation over time (Figure 4-13). In the first 25 minutes, pH increased rapidly from 5.6 to 8.21 due to the anaerobic corrosion of Fe^0 followed by slower decreases to 3.85 over the remaining reaction time. Under anaerobic conditions, water serves as the main oxidant forming hydroxide ions and generating hydrogen gas ($\text{Fe}^0 + 2\text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + \text{H}_2 + 2\text{OH}^-$). The subsequent decrease in pH (Figure 4-13)



is caused by the consumption of hydroxyl ions through the precipitation of metal hydroxides. ORP and pH are inversely correlated with ORP rapidly decreasing from +266 mV to -762 mV in the first 25 min followed by increases to -500 mV at 120 h.

Most unrecovered PFOS was accounted for by the fluoride and sulfite generated; however, some organic products were identified in the particle extracts using QToF/MS throughout reaction period at 60 °C. No products were observed in the aqueous phase of the PFOS reacted with $n\text{Ni}^0\text{Fe}^0\text{-AC}$. The latter suggests that the reactions are occurring with sorbed molecules consistent with previous Fe-mediated reductive reactions (Matheson and Tratnyek, 1994); however, the possibility of sorption subsequent to aqueous-phase reactions cannot be ruled out. Products detected in ESI⁻ mode included several C8 polyfluoroalkyl sulfonates (MS and MS/MS fragmentation and chromatograms are detailed in Tables 4-1 and 4-2). At early reaction times, $\text{C}_8\text{HF}_{16}\text{SO}_3^-$ was identified as the dominant reduction product. The additional polyfluoroalkyl intermediates detected support continued F/H exchange of up to 10 out of the 17 fluorine atoms (1st grouping in Table 4-1).

Sulfite⁻ generation provided evidence of C-S bond cleavage, which is further supported by the generation of several PFCAs and a fluorinated alkane. PFOA, PFHpA, PFHxA, PFPeA, and PFBA were observed and quantified at low concentrations. Bentel et al. (2019) also observed chain shortening of PFCAs with UV-generated hydrated electrons. All the quantified PFCA products were < 0.9 µg/L, which corresponded to no more than 0.1% of the transformed PFOS. Desulfonated products were scanned by APCI⁻ (considering perfluoroalkanes do not ionize by ESI). During the method development stage for the desulfonated products, an artifact of perfluoroalkane analysis using APCI ionization was observed (detailed in SI). Perfluorooctane (C_8F_{18}) and 1-bromo-perfluorooctane ($\text{C}_8\text{F}_{17}\text{Br}$) were injected into the QToF-APCI⁻ to observe the MS/MS fragmentation and optimize detector response. The highest peak detected in APCI⁻ mode with the standards was 434.9707 for which the exact mass (434.9683, 5.5 ppm error) and MS/MS fragmentation correspond to $\text{C}_8\text{F}_{17}\text{O}^-$. The halogen attached to the terminal carbon (CF_3 - or CF_2Br -) swaps out with an oxygen in the APCI source, *i.e.*, O for F and O for Br, respectively, as observed by others for perfluoroalkanes (Marotta et al., 2004; Schütz et al., 2015). In samples, $\text{C}_8\text{F}_{17}\text{O}^-$ (434.9707, Table 4-1) was detected which could be the product of the hydroxylation of the $\text{C}_8\text{F}_{17}^\bullet$ radical or $\text{C}_8\text{F}_{17}\text{H}$ after the H/O swap in the APCI source (C-H bond has lower energy than the C-F bond). The fluorinated alkane detected was not quantified due to the lack of commercial standards. Additional details and figures can be found in Zenobio et al. (2020).

Table 4-1. Products detected in concentrated samples at four or more sampling times after 6 μM PFOS solution react with $\text{nNi}^0\text{Fe}^0\text{-AC}$ at 60 $^\circ\text{C}$. Degradation products were detected using QToF electrospray ionization (ESI⁻) except for the desulfonation products which were detected with atmospheric pressure chemical ionization (APCI). Both ESI and APCI were in negative mode. For reference, PFOS: $\text{C}_8\text{F}_{17}\text{SO}_3^-$, m/z 498.9297, t_r = 11.34 min.

Formula	Theoretical m/z	Observed m/z	Error ^a (ppm)	Error ^b (mDa)	t_r ^c (min)
Defluorination F/H exchange products					
C-C Single bond C_8 products					
$\text{C}_8\text{HF}_{16}\text{SO}_3^-$	480.9391	480.9355	7.49	3.6	10.56
$\text{C}_8\text{H}_2\text{F}_{15}\text{SO}_3^-$	462.9485	462.9477	1.73	0.8	10.2
$\text{C}_8\text{H}_3\text{F}_{14}\text{SO}_3^-$	444.9579	444.9547	7.27	3.23	10.13
$\text{C}_8\text{H}_4\text{F}_{13}\text{SO}_3^-$	426.9674	426.9644	7.03	3	9.63
$\text{C}_8\text{H}_5\text{F}_{12}\text{SO}_3^-$	408.9768	408.9757	2.64	1.08	9.56
$\text{C}_8\text{H}_6\text{F}_{11}\text{SO}_3^-$	390.9862	390.9844	4.6	1.8	9.43
$\text{C}_8\text{H}_7\text{F}_{10}\text{SO}_3^-$	372.9956	372.9948	2.2	0.82	9.19
$\text{C}_8\text{H}_8\text{F}_9\text{SO}_3^-$	355.0050	355.003	5.76	2.04	9.08
$\text{C}_8\text{H}_9\text{F}_8\text{SO}_3^-$	337.0145	337.0142	0.79	0.26	9.05
$\text{C}_8\text{H}_{10}\text{F}_7\text{SO}_3^-$	319.0239	319.0224	4.7	1.5	8.56
Products after desulfonation: Perfluorocarboxylic acids					
$\text{C}_8\text{F}_{15}\text{O}_2^-$	412.9659	412.9681	5.39	2.23	10.32
$\text{C}_7\text{F}_{13}\text{O}_2^-$	362.9691	362.9684	1.84	0.67	9.37
$\text{C}_6\text{F}_{11}\text{O}_2^-$	312.9723	312.9705	5.63	1.76	8.49
$\text{C}_4\text{F}_7\text{O}_2^-$	212.9787	212.9795	3.99	0.85	6.46
Desulfonation product					
$\text{C}_8\text{F}_{17}\text{O}^-$ ^d	434.9678	434.9671	1.61	0.7	--

Error = mass error, ^a(Difference between theoretical mass and experimentally measured mass/theoretical mass) $\times 10^6$; ^b(Theoretical mass/(1/error PPM*1000)); ^cRetention time; ^d $\text{C}_8\text{F}_{17}\text{O}^-$ or $\text{C}_8\text{F}_{17}\text{H}$, but in the APCI source an H/O swap.

Table 4-2. A summary of % F and % SO_3^{2-} generated relative to SO_3^{2-} and F content in initial PFOS (1 SO_3^{2-} /PFOS and 17 F/PFOS) along with total F⁻ and SO_3^{2-} mole balance based on generated F⁻ and SO_3^{2-} and remaining PFOS quantified. The total quantified PFCA products were < 0.9 $\mu\text{g/L}$ with a F contribution of < 0.03% (not shown).

Reaction time (h)	Remaining PFOS	F ⁻	SO_3^{2-} **	Total F content (%)	Total SO_3^{2-} content (%)
0	100.0%	0.0%	0.0%	100.0%	100.0%
1	94.0%	7.3%	11.9%	101.3%	105.9%
6	89.7%	11.4%	17.7%	101.1%	107.4%
12	76.0%	17.9%	23.0%	93.9%	99.0%
18	59.5%	34.3%	34.1%	93.8%	93.6%
24	51.0%	50.1%	38.8%	101.1%	89.8%
120	50.1%	48.3%	51.2%	98.4%	101.3%
Average over the reaction period				98.5%	99.6%
Standard Deviation over the reaction period				3.3%	6.3%

*F⁻ yield = [(moles of F⁻ formed)/(moles of fluorine in initial PFOS x17)] x 100.

** SO_3^{2-} yield = [(moles of SO_3^{2-} formed)/(moles of sulfite in initial PFOS)] x 100.

Shorter chain (C_7 - C_4) single bond and the C_8 double bond ($\text{C}=\text{C}$) polyfluoroalkane sulfonates were also detected and identified in the reacted samples (See SI of Zenobio et al. (2020)) ; however, we believe these were produced from PFSA impurities in the technical PFOS used. Consistent with impurities in a commercial PFOS reagent recently reported by Bentel et al. (2019), we detected PFHpS (6750 ng/L, 0.23% relative to PFOS stock), PFHxS (295 ng/L, 0.010% relative to PFOS stock), PFPeS (45 ng/L, 0.002% relative to PFOS stock), and PFBS (34 ng/L, 0.001% relative to PFOS stock), which we believe led to the $\text{C}_7\text{HF}_{14}\text{SO}_3^-$, $\text{C}_6\text{HF}_{12}\text{SO}_3^-$, and $\text{C}_5\text{HF}_{10}\text{SO}_3^-$ degradation products, respectively. We also identified $\text{C}_8\text{F}_{15}\text{SO}_3^-$ in the PFOS technical stock, which we believe led to the reductive formation of $\text{C}_8\text{H}_n\text{F}_{15-n}\text{SO}_3^-$ products and not from PFOS. This impurity was not detected in the reactions using the high purity L-PFOS standard. Liu et al. (2018) also identified $\text{C}_8\text{F}_{15}\text{SO}_3^-$ among several other unknown PFAS in a commercial PFOS reagent.

Time-dependent changes in the intensities of the identified intermediates are presented in Figures 4-14 and 4-15. Some intermediates not show a consistent trend over time other than appearing after the reactions were initiated, but some general trends are apparent. Products conserving the sulfonate group and PFCAs increased in the first 6 to 12 h and then disappeared almost completely after 24 h with a few exceptions. The peak intensities of the defluorinated polyfluoroalkyl sulfonate intermediates ($\text{C}_8\text{H}_8\text{F}_9\text{SO}_3^-$, $\text{C}_8\text{H}_9\text{F}_8\text{SO}_3^-$, $\text{C}_8\text{H}_{10}\text{F}_7\text{SO}_3^-$) appeared to increase between the 24-h and 120-h sampling time (Figure 4-14). PFCAs generally reached a maximum peak value at 12-h except for PFBA, which was variable with some replicates being highest at 120-h (Figure. 4-15). Using PFOS standard curves to semi-quantify detected organic products, the total contribution of these transformation products only accounted for 0.3% to 1.1% of the total fluorine in the system relative to the moles of PFOS at t=0.

Defluorinated products (F/H)

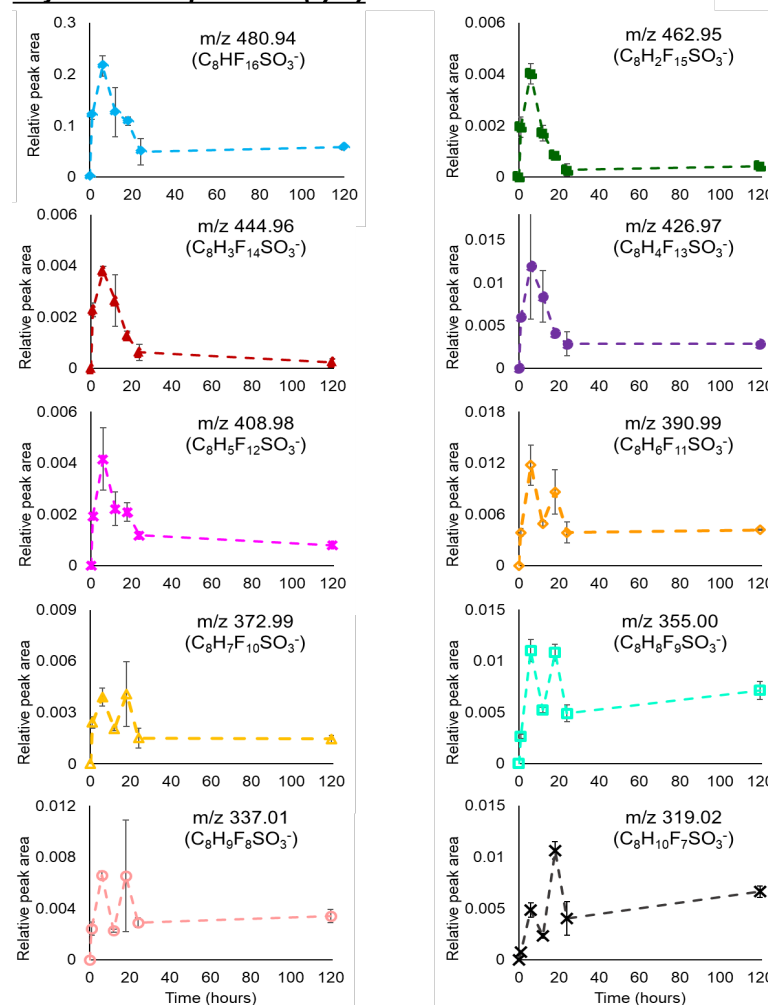


Figure 4-14. Generation of polyfluoroalkyl sulfonates over time from sequential F/H exchanges from PFOS reduction. Peak areas of individual products were normalized by M8PFOS IS (188 $\mu g/L$) peak area. All products shown were detected using electrospray ionization in negative mode (ESI-).

Desulfonated products: Perfluorocarboxylic acid

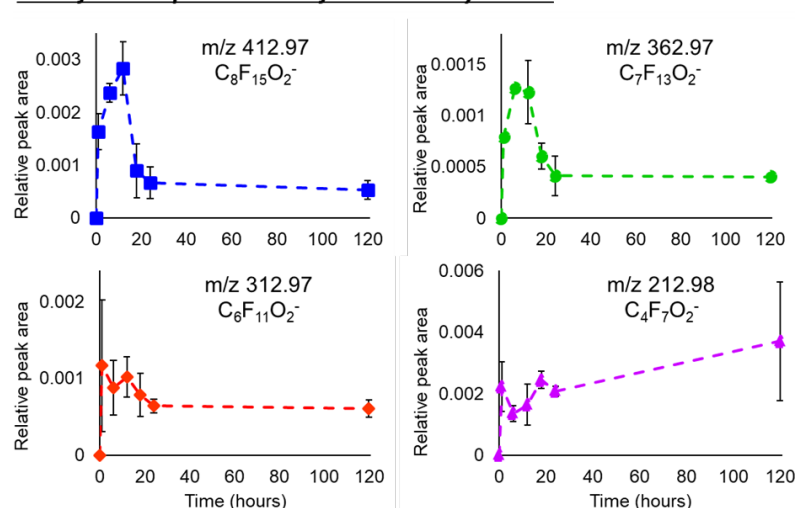
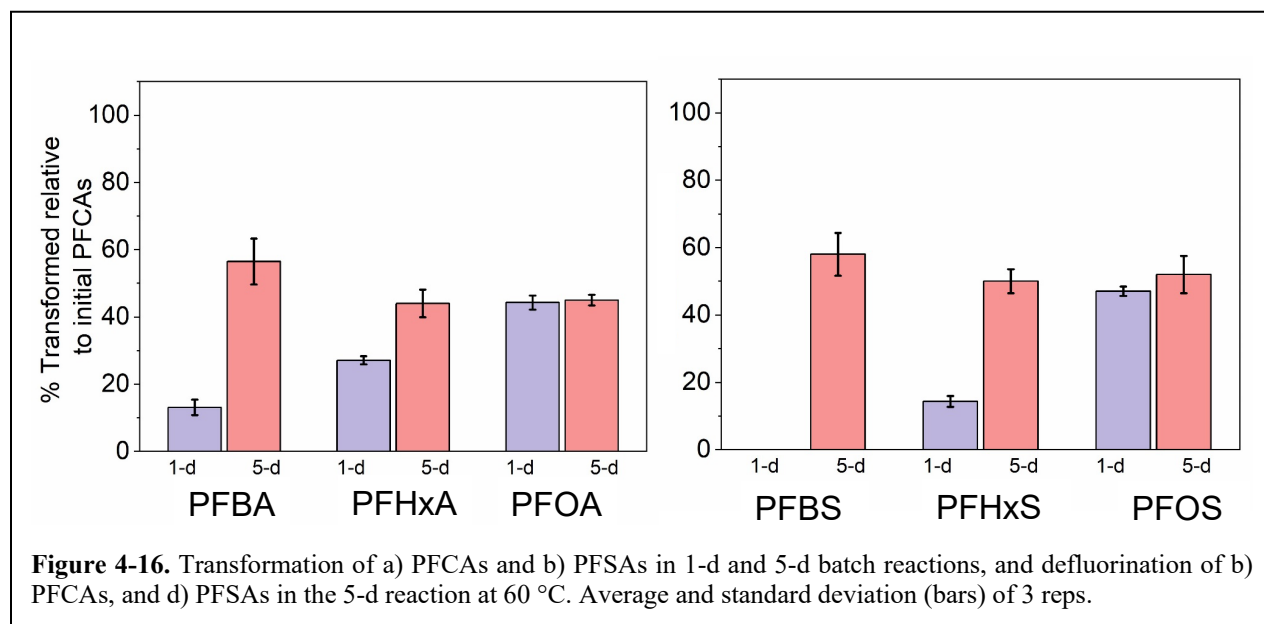


Figure 4-15. Generation and changes in relative PFCA intensities detected in concentrated ($\times 3$) samples during PFOS reduction. Peak areas were normalized by $[^{13}C_4]$ PFOA for PFOA and PFHpA, $[^{13}C_2]$ PFHxA for PFHxA, and $[^{13}C_4]$ PFBA for PFBA with IS at 100 $\mu g/L$.

Exploring Temperature Effects on PFOS transformation. PFOS loss and F^- generated in 3-d reactions with increasing temperature from 40 °C to 60 °C did not follow a positive correlation. Transformation was highest at 50 °C with $94 \pm 4.1\%$ PFOS transformed (Figure ES-5). Results at 60 °C were statistically consistent with the plateau observed in the 120-h kinetic study with about half ($49 \pm 2.5\%$) of the PFOS not recovered being matched by approximately equal moles of F^- generated. Based on the F^- generated, most PFOS not recovered was mineralized at the higher temperatures: $97\% \pm 4.4\%$ at 60 °C and $104\% \pm 6.4\%$ at 50 °C. At 40 °C, $84.7 \pm 4.5\%$ PFOS was recovered and no F^- was detected indicating no transformation occurred within the 3-d reaction time similar to what was observed at room temperature (22 °C) (Figure ES-5). Also, at both 22 °C and 40 °C, gas production was very low and the color of the MeOH extracts for PFOS were much lighter compared to the higher temperatures (light brownish vs nearly black).

Additional PFAS Transformation with nNi^0Fe^0 -AC. Additional PFAS that were evaluated included C4 and C-5 PFSAAs and C4, C6, and C8 PFCAs, two fluorotelomer sulfonates (6:2 and 8:2 FTS) and GenX. All PFAAs experienced some transformation by nNi^0Fe^0 -AC at 60 °C in 5-d reactions. Increases in % transformation and % defluorination between 1-d and 5-d reactions varied with carbon chain length and headgroup (Figure 4-16, Table 4-3).



For both PFCAs and PFSAAs, the transformation of shorter chains between 1-d and 5-d reactions increased significantly (PFBS, $p = 0.008$; PFHxS, $p = 0.004$; PFBA, $p = 0.013$; and PFHxA, $p = 0.05$), whereas transformation of the longer chains was not different (PFOS and PFOA, $p > 0.8$). Also, % transformation in 1-d reactions increased with increasing alkyl chain length for both PFCAs and PFSAAs, but this was not statistically evident in the 5-d reactions for any of the PFAAs. Conversely, for % defluorination relative to the initial PFAS (Eq. 1), little defluorination ($< 2\%$) was observed in 1-d reactions with the exception of PFOS ($53 \pm 1\%$); however, in 5-d reactions, % defluorination statistically increased with chain length and between PFCAs and PFSAAs. For a similar alkyl chain length, statistically higher % defluorination was generally observed for the PFSAAs. These results with nNi^0Fe^0 -AC are somewhat different than what was observed by Bentel et al. (2019) with UV-generated hydrated electrons in which % defluorination increased only for

the PFASs. For all PFCAs, they observed ~55% defluorination (2 to 10 perfluoroalkyl carbons) (Bentel et al., 2019) whereas with nNiFe⁰-AC 4.0, 7.4 and 24.1 % defluorination was observed for C4, C6, and C8 PFCAs and 20.3, 40.4, and 57.6 % for C4, C6, and C8 PFASs. It remains unclear as to why the -SO₃⁻ versus -COOH headgroups affected PFAA defluorination differently for nNiFe⁰-AC compared to the hydrated electron system.

Table 4-3. F and SO₃²⁻ mass balance from 5-d single solute batch reactions with PFCAs (PFBA, PFHxA, and PFOA) and PFASs (PFBS and PFHxS), 6:2 FTS, 8:2 FTS, and GenX at 60 °C. All reactions were performed in DI water.

PFAS	%Transformed relative to initial PFAS	% PFCAs generated relative to transformed PFAS	% Defluorination relative to initial PFAS (Eq. 1)	% F ⁻ generation relative to transformed PFAS (Eq. 2)	Total F content (%)
PFBA	56.5 ± 6.8%	< LOQ	4.0 ± 0.5%	7.1 ± 0.84%	7.7 ± 6.9%
PFHxA	44.0 ± 1.0%	< LOQ	7.4 ± 0.9%	16.8 ± 2.04%	3.2 ± 1.3%
PFOA	45 ± 4.6 %	< LOQ	24.1 ± 2.7%	53.6 ± 5.95 %	9.1 ± 5.3%
PFBS	57.7 ± 6.3%	< LOQ	20.3 ± 2.4%	35.1 ± 4.27%	2.3 ± 6.7%
PFHxS	50.1 ± 3.6%	< LOQ	40.4 ± 2.3%	80.51 ± 4.6%	0.4 ± 4.2%
PFOS	51.6 ± 5.5%	< LOQ	57.6 ± 3.2%	100 ± 0.57%	0.0 ± 6.3 %
6:2 FTS	57 ± 5.1%	1.7 ± 0.15%	9.5 ± 0.5%	17 ± 0.01%	3.4 ± 5.1%
8:2 FTS	58 ± 8 %	2.15 ± 0.3%	2.8 ± 0.26*	4.8 ± 0.45*	5.9 ± 8.1%
GenX	21 ± 11 %	ND	5.2 ± 0.8*	24.8 ± 3.8 %*	1.1 ± 11.2%

Measured pH values between the 1-d and 5-d 60 °C reactions (Table 4-4) decreased for the shorter chain PFAAs whereas there was no statistical difference for the longer chains (PFOA and PFOS). Interestingly, there was also a strong positive correlation between the 5-d pH values and % defluorination for the PFCAs that followed increasing chain length ($R^2 = 0.995$). However, for all PFAS 5-d 60 °C reactions, pH decreased from the pH in the particle only controls consistent with what was observed in our previous work evaluating PFOS transformation kinetics with nNiFe⁰-AC nanocomposites at 60 °C (Zenobio et al., 2020). In the latter study, pH increased from 5.6 to 8.21 in the first 25 minutes, which was attributed to anaerobic corrosion of Fe⁰, followed by a slower decrease to 3.85 over the 5-d reaction, which was attributed to consumption of hydroxyl ions through metal hydroxide precipitation. In room temperature controls, pH at 5-d was near neutral reflecting little iron corrosion. In 50 °C reactions at 5 d, all samples and particle controls were in the pH 3.71-4.14 range. For some PFAAs, in particular the shorter chain PFCAs at 60 °C, the 5-d pH was considerably below what was observed for PFOS at 5 d. It is unclear what competing reactions are occurring that result in varying pH effects; however, as pH drops, there is an increasing probability of losing some F⁻ through HF volatilization (HF has a $pK_a = 3.2$ (Burgher et al., 2011)). For example, for PFBA and PFHxA at the final 5-d pH values, > 50% of any F⁻ that may have been present in the aqueous phase would have been as HF and thus had potential to volatilize.

Table 4-4. Final solution pH measured after 1-d or 5-d reactions with nNiFe⁰-AC at 50 and 60 °C.

	60 °C		50 °C	20-22 °C
	1-d	5-d	5-d	5-d
Particles only (control)	5.8	5.6	3.81	---
PFAS only (control)	6.7	6.5	5.89 ± 0.18	---
PFBA	3.54 ± 0.14	3.03 ± 0.23	3.07 ± 0.1	---
PFHxA	3.77 ± 0.16	3.17 ± 0.18	3.16 ± 0.14	---
PFOA	4.47 ± 0.38	4.48 ± 0.59	4.14 ± 0.21	---
PFBS	3.96 ± 0.56	3.80 ± 0.47	3.71 ± 0.34	---
PFHxS	4.28 ± 0.21	3.32 ± 0.28	3.37 ± 0.46	---
PFOS	3.48 ± 0.49	3.78 ± 0.53	3.68 ± 0.15	---
6:2 FTS	---	3.93 ± 0.12	3.72 ± 0.23	---
8:2 FTS	---	4.03 ± 0.12	3.91 ± 0.08	6.95
GenX	---	4.46 ± 0.09	3.97 ± 0.13	6.9

For 6:2 FTS and 8:2 FTS, $57 \pm 5.1\%$ and $58 \pm 8\%$ were transformed (Table 4-3) in a 5-d reaction at 60 °C, respectively, which are similar to the % transformation for PFAAs with identical perfluoroalkyl chain lengths: PFHxS ($50.1 \pm 3.6\%$) and PFOS ($51.6 \pm 5.5\%$), respectively. However, only 17% and 4.8% fluoride generation (Eq. 2) were observed for 6:2 FTS and 8:2 FTS, respectively, in contrast to ~81% and 100% fluoride generation observed for PFHxS and PFOS, respectively (Table 4-3). This indicates that 6:2 FTS and 8:2 FTS % transformation in the 5-d reaction period was primarily by C-S cleavage. Unfortunately, SO_3^{2-} generation could not be evaluated due to background sulfate levels originating from a new batch of GAC (received from the same vendor, but new stock #). However, desulfonation is supported by detection of PFCAs generation in particle extracts from reactions with FTS. The most dominant PFCAs were PFHpA and PFHxA from 6:2 FTS and PFOA from 8:2 FTS, albeit low yields with only $\sim 1.7 \pm 0.15\%$ generated PFHxA and PFHpA from transformed 6:2 FTS and $\sim 2.15 \pm 0.3\%$ PFOA from transformed 8:2 FTS, respectively (Tables 4-3).

The overall fluorine mole balance calculated based on measured 6:2 FTS and 8:2 FTS, generated PFCAs, and F^- was only 53.4% and 45.9% for 6:2 FTS and 8:2 FTS, respectively (Table 4-3). Other sources of the fluorine shortfall in the fluorine mole balance is due to the difficulty in identifying and quantifying low levels of unknown fluorinated products without standards for optimizing MS and MS/MS sensitivity.

For GenX, $21 \pm 11\%$ was transformed with $24.8 \pm 3.8\%$ fluoride generation from the transformed PFAS (Table 4-3). Fluorine mole balance was calculated for GenX at 60 °C as recovered GenX and generated F^- , where F mass balance was not closed (Table 4-3). Additional studies at reaction times of 12 d were done to evaluate if additional transformation and defluorination will occur at

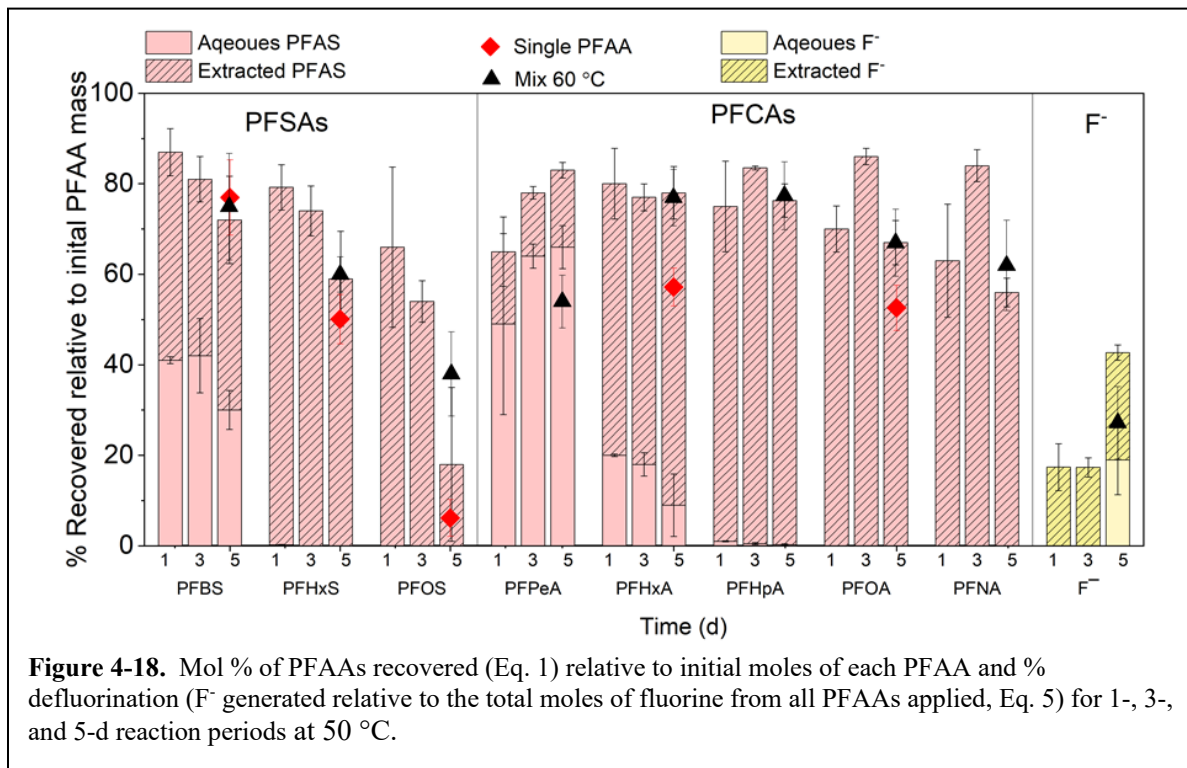
longer reaction times. However, % transformation did not change statistically from 5 d ($30.1\% \pm 9.7\%$ at 5-d vs $26.83\% \pm 3.2\%$ at 12-d). But, the defluorination rate relative to the initial (Eq. 2) increased from $6.2\% \pm 1.4\%$ at 5 d to $16.7\% \pm 2.5$ at 12-d. Nevertheless, results exemplify that inserting an oxygen atom in the perfluoroalkyl chain did not improve its degradation or defluorination by $n\text{Ni}^0\text{Fe}^0\text{-AC}$.

The solution pH during PFAS reactions with $n\text{Ni}^0\text{Fe}^0\text{-AC}$ decrease by $\sim 1.9 \pm 0.5$ pH units compared to particle no PFAS controls (pH $\sim 5.6\text{-}5.8$) (Table 4-4). Under anaerobic conditions, water serves as the main oxidant forming hydroxide ions and generating hydrogen gas ($\text{Fe}^0 + 2\text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + \text{H}_2 + 2\text{OH}^-$). The subsequent consumption of hydroxyl ions through metal hydroxides precipitation causes pH to decrease. The decrease in pH was similar between 1-d and 5-d reactions and between 50 and 60 °C in 5-d reactions except for GenX (Table 4-4). As pH drops, there is an increasing probability of losing some F- through HF volatilization (HF has a $\text{pK}_a = 3.2$ (Burgher et al., 2011)). For example, for PFBA and PFHxA at the final 5-d pH values, $> 50\%$ of any F- that may have been present in the aqueous phase would have been as HF and thus had potential to transfer to the headspace. Therefore, while some F- may have been lost due to HF volatilization, it is unlikely to account for the deficit in the fluorine mole balance given $\sim 100\%$ recovery of most PFAS at room temperature. Overall, for all PFAS, losing F- as HF into headspace may have contributed to some of the shortfall on fluorine mole balance, but more likely incomplete fluorine mole balance was due to the difficulty in identifying and quantifying low levels of unknown fluorinated products without standards for optimizing MS and MS/MS sensitivity.

Temperature Effect. The effect of temperature on transformation was PFAS-dependent. The % transformation in 5-d reactions at 50 °C were higher or equal than observed at 60 °C for PFOA, 6:2 FTS, 8:2 FTS, and GenX while for PFBS, transformation was higher at 60 °C (Figure ES-6A). Previously, we observed a substantial increase in PFOS transformation when the reaction was decreased from 60 °C to 50 °C (Zenobio et al., 2020) whereas in the current study with other PFAS, the increase in % transformation was either lower, not significant, or in the case of PFBS, actually decreased significantly (Fig. ES-6A). PFAA sorption is expected to increase at the lower temperature, thus, it would seem that energetics may play a greater role especially for the PFASs as hypothesized by (Bentel et al., 2019). Fluorine mole mass calculated for all PFAS tested at 50 °C ranged from 35% to 104% with the lowest ones being for 6:2 and 8:2 FTS (42 % and 35 %, respectively); the trend was similar to what was observed at 60 °C. Only PFOS that F mass balance was closed being close to unity, as found by our previous study (Zenobio et al., 2020). This latter implies that there are some fluorinated organic intermediates that are not detected or quantified in these systems. Defluorination % relative to moles of PFAS transformed was linear with increasing perfluorocarbon chain length (Figure ES-6B).

Organic products from transformation of other PFAS by $n\text{Ni}^0\text{Fe}^0\text{-AC}$. Organic products detected from PFHxS and PFBS degradation were only detected in the 5-d reactions; transformation in 1-d reactions were ($<15\%$). These products included single bonded polyfluoroalkyl sulfonates ($[\text{C}_n\text{HF}_{2n}\text{SO}_3]$, $n = 6$ from PFHxS and $n = 4$ from PFBS), which exemplify F/H exchange as observed previously with PFOS (Zenobio et al., 2020) (Figure 4-17a, Table A1 and A2). Two other and shorter chain polyfluoroalkyl sulfonates ($\text{C}_4\text{HF}_8\text{SO}_3$ and $\text{C}_5\text{HF}_{10}\text{SO}_3$) were also observed in the PFHxS reactions; however, we believe these likely resulted from transformation of two impurities: PFBS (6.9 $\mu\text{g/L}$ PFBS, 0.23% relative to PFHxS stock)

1-d and 3-d reactions (~ 17%) but increased to $36.7 \pm 4.7\%$ in 5-d reactions. Fluorine mole balance (Eq. 5) was 95 ± 6 , 97 ± 3 , and $103 \pm 6\%$ for 1-d, 3-d, and 5-d reactions, respectively.



Temperature affected % transformation of the PFAAs as a mixture was similar to what was previously observed in single PFAA batch reactions with 60 °C having a lower or equal % transformation than 50 °C for most PFAAs. Between the two reaction temperatures, % defluorination (Eq. 5) and % F^- generation (Eq. 6) are not statistically different with 27 ± 8.3 and $86 \pm 25\%$, respectively, at 60 °C versus 36.7 ± 4.7 and $107 \pm 13\%$, respectively, at 50 °C (p values > 0.05). Closure of F mole balance was again achieved (96 ± 8.8).

$$\% \text{ defluorination or } \% \text{ desulfonation per initial PFAS} = \frac{nF^- \text{ or } SO_3^{2-}}{\sum nPFAS_{initial}} \times 100 \quad (5)$$

$$\% \text{ fluoride or } \% SO_3^{2-} \text{ generated per transformed PFAS} = \frac{nF^- \text{ or } SO_3^{2-}}{\sum (nPFAS_{transformed} \times N)} \times 100 \quad (6)$$

PFAS transformation by nNi^0Fe^0 -AC in an AFFF-contaminated groundwater. A PFAS-contaminated groundwater sample was obtained from a study conducted on western Cape Cod, Massachusetts at the U.S. Geological Survey Toxic Substances Hydrology Program Cape Cod Research site. Groundwater samples were collected from a former fire-training area and near to a wastewater treatment plant located on Joint Base Cape Cod (Barber et al., 2017; Weber et al., 2017). PFAS were transformed in the groundwater samples, but overall, the % transformation for a given PFAS was generally lower than what was observed in single PFAS DI water solutions, except for PFBA (Figure ES-7). Initial concentrations of the analyzed PFAS were 0.20 – 38.08

nM (Table 4-5). The pH of the samples was 5.12, similar to the initial pH used for the DI water solutions (pH = 5.6). The concentrations detected in the groundwater samples were all well below the concentration used in the single solute studies (0.9 - 6 μ M). Thirteen PFAS were quantified including six PFCAs (C4-C9), five PFSAAs (C4-C8), and two FTSs (6:2 and 8:2 FTS). Several anions (Cl^- , Br^- , SO_4^{2-} , and NO_3^-) and cations (K^+ , Na^+ , Mg^{2+} , and Ca^{2+}) were also quantified with concentrations ranging from 0.92 to 341 μ M (Table 4-5). As shown in Weber et al. (2017), dissolved organic carbon (DOC) was found in the groundwater samples at 1.3 mg L^{-1} .

Table 4-5. Initial PFAS concentration (left) and inorganic ions (right) in Cape Cod AFFF-impacted groundwater sample.

PFAAs	nM	Ions	μM
PFBA	0.58	Chloride	174.42
PFPeA	1.34	Bromide	0.92
PFHxA	3.47	Sulfate	147.76
PFHpA	1.43	Nitrate	83.44
PFOA	2.68	Potassium	31.86
PFNA	0.2	Sodium	341.37
PFBS	1.2	Magnesium	86.40
PFPeS	3.64	Calcium	62.44
PFHxS	13.95		
PFHpS	0.23		
PFOS	38.08		
6:2 FTS	0.97		
8:2 FTS	3.77		
FOSA ^a			

^aPerfluorooctane sulfonamide (FOSA)
reported for a sample by USGS [1]

Several water parameters can impact PFAS transformation efficiency including pH, organic matter, and inorganic ions normally present. Organic matter could be an important sorbent of PFAS or a competitor for reactive sites on the nanoparticle surface, decreasing transformation rates. Also, the net positive charge on the nanoparticle surface at pH = 5.12, due to the metal corrosion ($\text{pHzpc} = [6-9]$), can promote anions attraction impacting transformation efficiency. Transformation of PFSAAs decrease ~23% in the groundwater system, probably relate to the impact of the groundwater parameters. But, the increase of concentration of three PFCAs (C7- C9) suggests that PFCAs are generated during the reductive treatment. Fluorotelomer precursors commonly degrade to PFCAs forming C8-C6 from 8:2 FTS transformation and C6-C4 from a 6:2 FTS solution (Carrillo-Abad et al., 2018; Shaw et al., 2019; Weber et al., 2017). However, the increased concentration of PFNA points to the presence of other PFAS precursors not quantified here. The presence of PFAS precursors in the same sample was previously confirmed by Weber et al. (2017) after performing the total oxidizable precursor (TOP) assay with the complete transformation of FTSs and increase of PFCA concentrations.

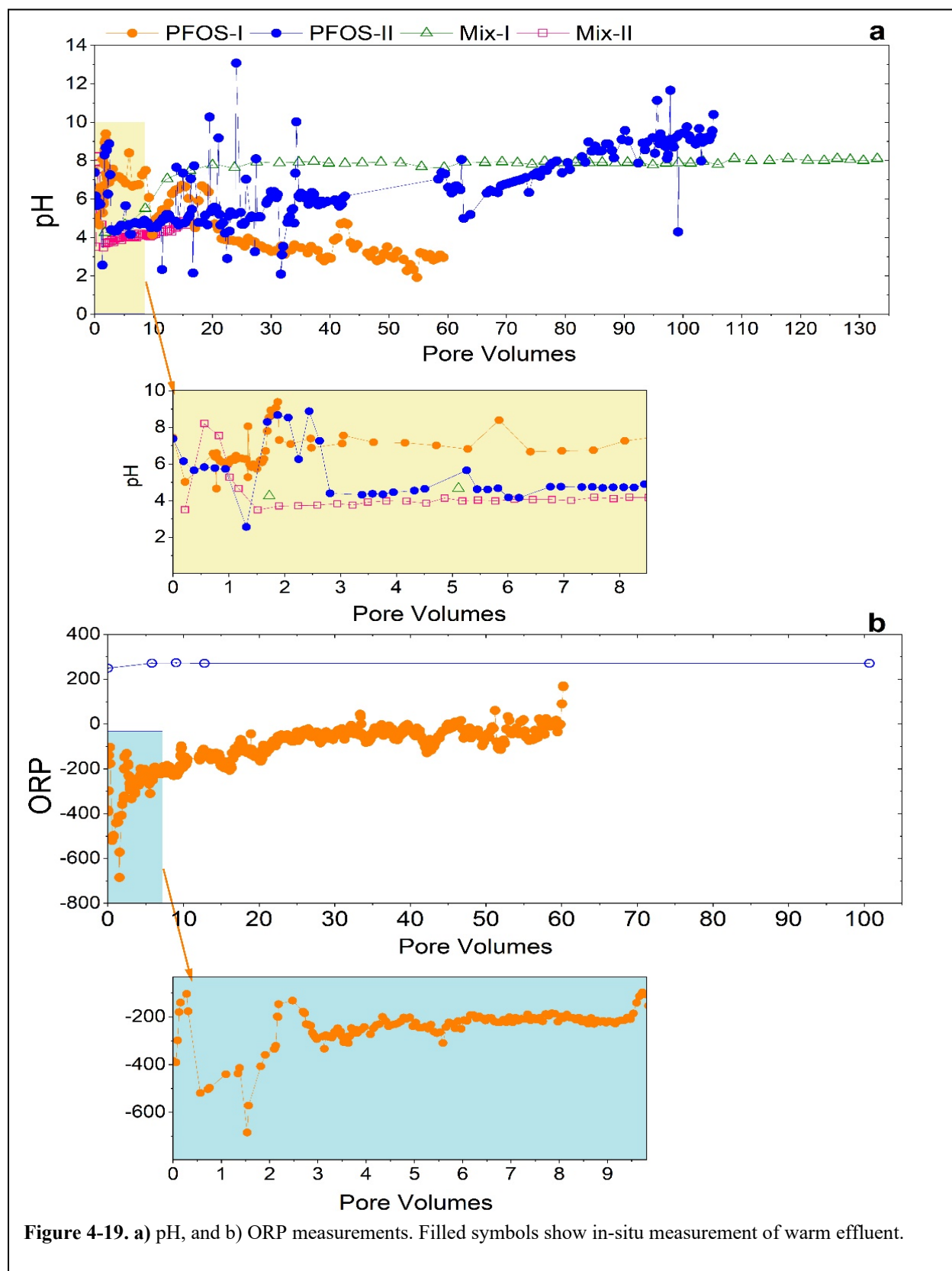
nNi⁰Fe⁰-AC Column Studies. We conducted two PFOS-only columns at different flow rates and two PFAA mixture columns under different conditions (Table 3-3 and 4-6). In the first couple PVs, in-line ORP values of PFOS- I fluctuated substantially in the -103 mV to -650 mV range but subsequently increased to ~0 mV (Figure 4-19). pH profiles varied between columns likely due to a combination of flow-rate, temperature and influent reactions. For example, effluent pH of PFOS- I fluctuated in the first ~2 PVs in the 5-9.4 range but gradually decreased to ~3 (Figure 4-19a). Although hydroxyl ions are generated upon H₂ generation in an anaerobic environment where water serves as the primary (Zenobio et al., 2021, 2020) , these ions are subsequently consumed through the formation and precipitation of iron oxides. For PFOS- II operated at a three times higher flow rate than PFOS- I (Table 3-3), pH fluctuated but generally increased from 3 to 10 throughout the study (Figure 4-19b). At this higher flow rate, metal hydroxide precipitation did not have time to occur within the column (Zenobio et al., 2020). For Mix- I with a buffered influent (pH = 7.5), pH gradually increased from 4 to ~8 in the first ~16 PVs then plateaued at ~8 while pH in Mix- II increased from ~4 to ~8 in <1 PV and then decreased to a plateau of ~5 within 2 PVs.

Table 4-6. Average of initial concentrations of PFAAs in batch, Mix-Col-I and -II

Compound	Concentration (ng mL ⁻¹)				
	PFOS-Col-I & -II	Mix-Col-I *	Mix-Col-II *	Batch at 60 °C	Batch at 50 °C
PFBS		190.4 ± 11.7	107.6 ± 10.2	175.4 ± 10.7	170.4 ± 3.6
PFPeA		136.1 ± 8.4	207.1 ± 16.7	110.0 ± 14.0	131.0 ± 2.8
PFHxA		165.3 ± 14.9	255.8 ± 22.8	163.0 ± 2.2	166.6 ± 0.6
PFHpA		157.2 ± 10.2	201.9 ± 14.6	148.9 ± 1.5	151.8 ± 4.5
PFHxS		122.5 ± 30.4	111.9 ± 9.3	255.0 ± 7.0	150.5 ± 9.2
PFOA		129.1 ± 20.9	179.9 ± 15.8	145.8 ± 1.8	127.5 ± 3.9
PFOS	~2006.6 ± 38.8	63.9 ± 26.5	61.3 ± 5.1	38.5 ± 0.6	61.8 ± 2.8
PFNA		31.3 ± 11.3	165.6 ± 14.6	123.5 ± 2.1	107.5 ± 12.8

*The averages are for ~5 and ~30 samples corresponding to sub-sampling of freshly prepared PFAA solution, and influent left in the eluent bottle (LC pump) for Mix-Col-I or influent left in the syringe (Harvard pump) for Mix-Col-II, respectively.

Retardation factors (R) for each PFAA were calculated for the whole column as well as just the reaction bed using mass weighted sum of sorption coefficients (K_d , L kg⁻¹). K_d was estimated using mass weighted averages of K_d values for nNi⁰Fe⁰-AC and sand (Eq. 7). The K_d values for nNi⁰Fe⁰-AC ($K_{d, nNiFe-AC}$) were calculated from the 5-d batch reactions at the temperature of interest based on the PFAA measured in the supernatant and particle extracts. $K_{d, nNiFe-AC}$ of the longer chain PFAAs were estimated assuming a log-linear correlation derived using data for the shorter chain PFAAs because supernatant concentrations were < LOQ. The sorption by sand ($K_{d, sand}$) was only measured for PFOS using 3-concentration coefficients (2, 5 and 10 ppb). For the other PFAAs, the $K_{d, sand}$ values were estimated assuming a similar log-linear correlation to number of fluorocarbons as $K_{d, nNiFe-AC}$ (Figure 4-20).



The initial break-through of each PFAA ($PV_{initial\ break-through}$) was estimated assuming the estimated R represented the number of PVs at which $C_{eff}/C_0=0.5$ (Eq. 8) (Brusseau et al., 1991). To validate the approach, estimated values for the short chain PFAAs were compared to observed values (when PFAA was first detected in the column effluents). Initial breakthrough for some of the longer chains did not occur during the experimental period for some columns. The reaction time for each PFAA in reaction bed was estimated using the PV of the reaction bed ($PV_{reaction\ bed}$) and the PFAA-specific retarded velocity (Eq. 9).

$$R = 1 + (\% mass_{nNiFe-AC} \times K_{d,nNiFe-AC} + \% mass_{sand} \times K_{d,sand}) \frac{\rho_b}{\theta_w} \quad (7)$$

$$Initial\ break-through = \frac{R}{\frac{PV_{C_{eff}/C_0=0.5}}{PV_{initial\ break-through}}} \quad (8)$$

$$Reaction\ time = \frac{PV_{reaction\ bed}}{\frac{Q_{water}}{R}} \quad (9)$$

In Eqs. 7-9, C_s (nmol kg⁻¹) and C_w (nmol L⁻¹) represent the concentrations extracted from particles and found in solution, respectively, in the batch reactors at 20 and 50 °C after 5-d reaction, C_{eff} and C_0 represent the concentrations in the column effluent and influent concentrations, respectively, ρ_b (g cm⁻³) and θ_w (ml cm⁻³) are measured bulk density and water content, respectively; and Q_{water} is the actual column influent flow-rate. For all four columns, ρ_b and θ_w were approximately 1.6 g cm⁻³ and 0.4 mL cm⁻³, respectively.

For both PFOS- I (59 PVs) and PFOS -II (105 PVs), PFOS remained <LO D in the effluent. Also, no fluorinated intermediates were detected in the effluent even after concentrating the effluent (15×) using solid phase extraction (SPE). In both PFAA mix columns, PFAA break-through time increased with increasing chain length (Figure 4-21). Shorter chain PFAAs with sorb less thus have lower retardation factors than longer chain PFAAs. Higher retardation factors translate to longer reaction times in the column for the longer chain PFAAs during which transformation can occur, which can lead to even longer times before breakthrough. The break-through of PFBS, PFPeA and PFHxA occurred within ~20 PVs (Figure 4-21). In Mix- I with total number of ~ 105 PVs, longer chains broke through within last 20 PVs.

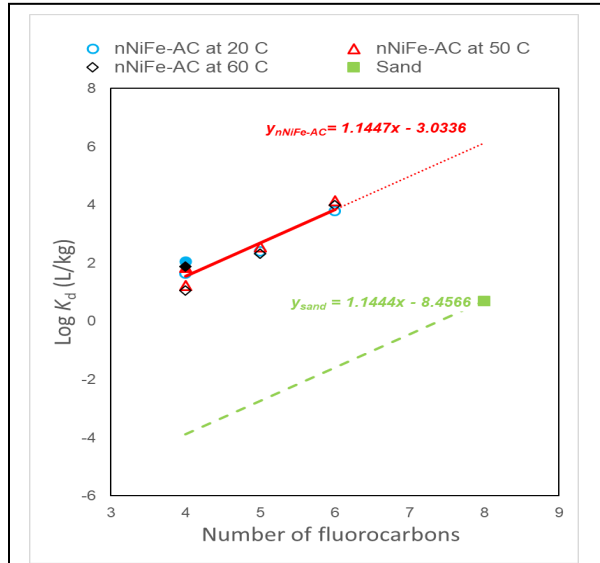
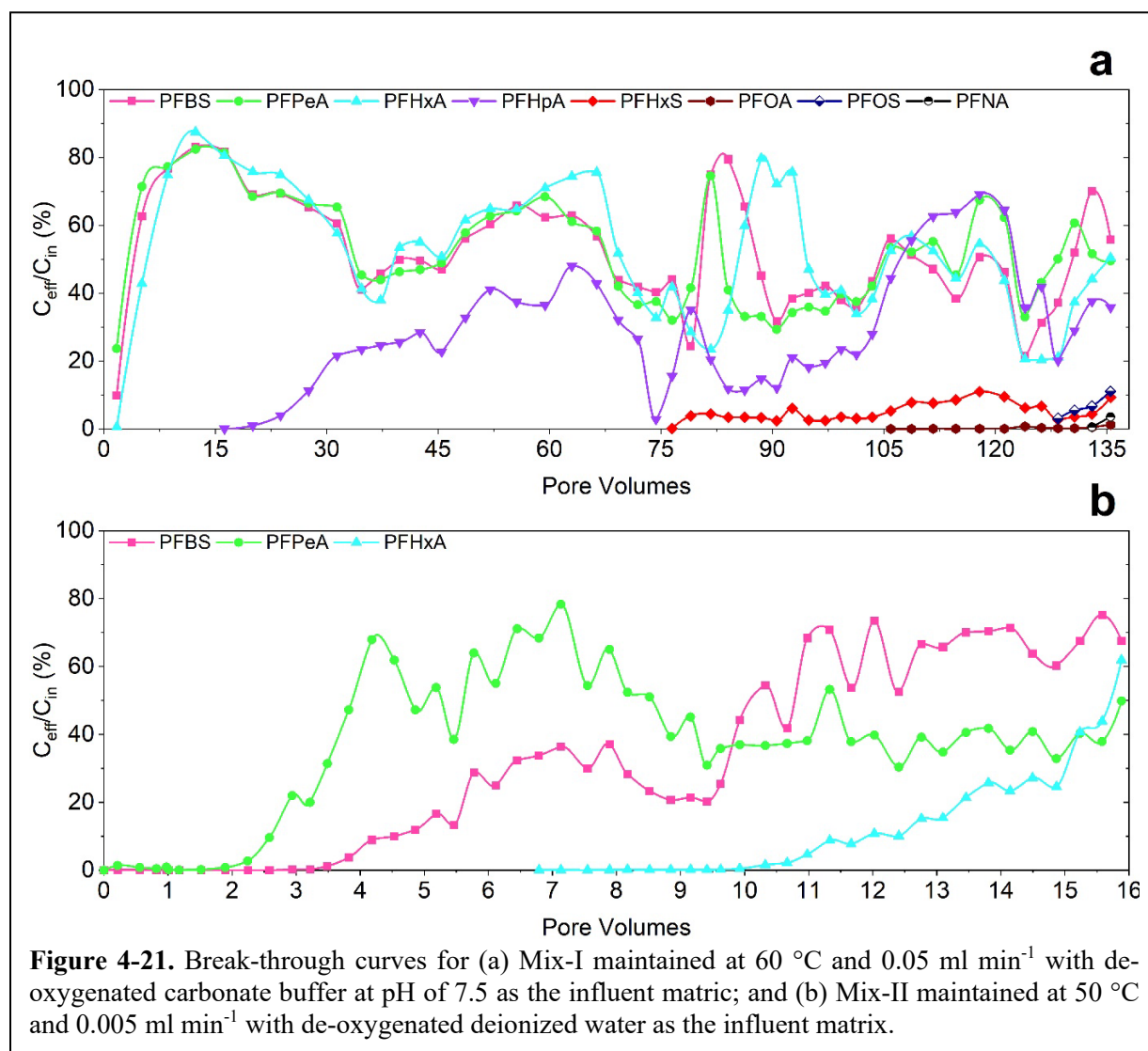
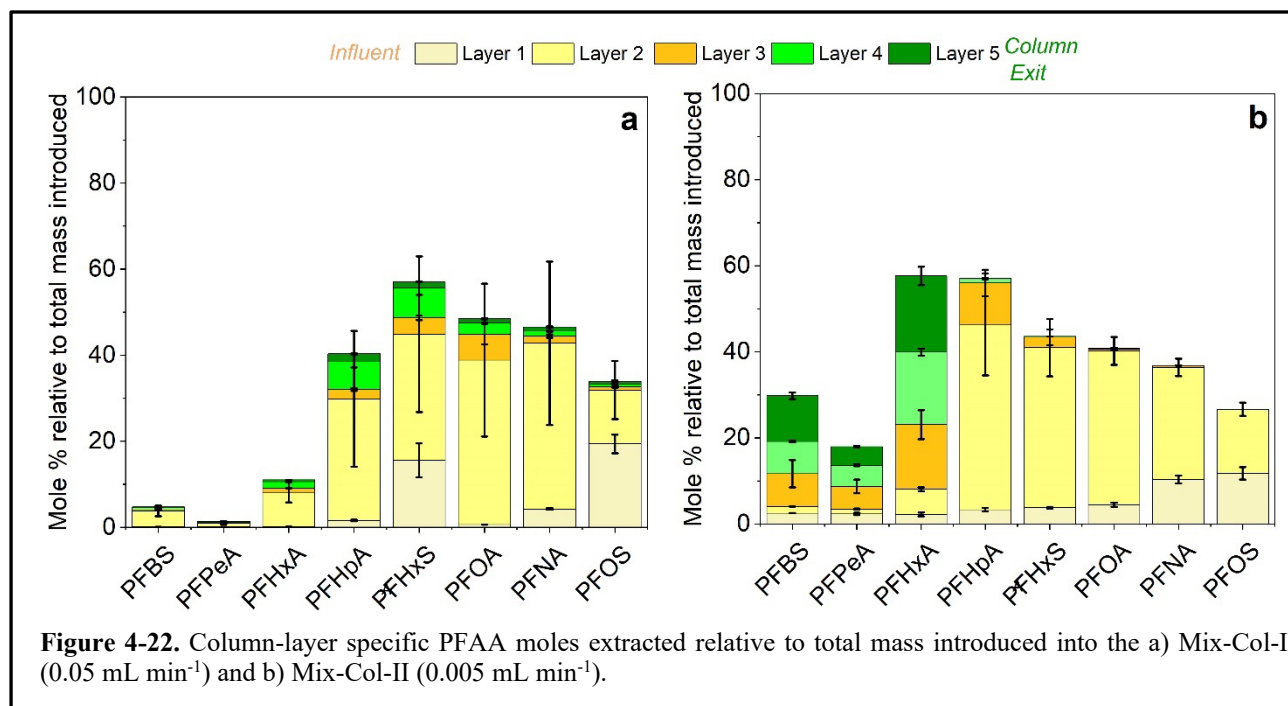


Figure 4-20. Log-linear correlation of K_d (L/kg) and number of fluorocarbons. K_d values for nNiFe⁰-AC are estimated from batch reactors at 20 and 50 °C. K_d values for sand was measured only for PFOS where a similar log-linear correlation as for nNiFe⁰-AC was assumed (green dotted line). For nNiFe⁰-AC, differentiation between the PFSA and PFCAs could not be accounted for with only one PFSA (PFBS)



The % of individual PFAAs recovered from each column layer relative to the total recovered all layers is summarized in Figure 4-22 and 4-23 for PFAA mix and PFOS only columns, respectively. For PFOS in single and mixed solute columns, the majority of PFOS mass was recovered from Layers 1 and 2 (the sand layer at the column inlet and the first layer of the reaction bed); PFOS residing in layer 1-3 made up 94-100% of the total extracted mass (Figure 4-22 for the PFAA mix and (Figure 4-23 for PFOS only columns). For the other PFAAs in the mixture columns, shorter chain PFAAs were found in layers closer to the column exit (Figure 4-22) as expected given their lower sorption affinity ($K_{d,PFAA}$ values). For Mix- II, recovery of the shorter chain PFAS was much higher in Layers 4 and 5 (50 to 60%) compared to Mix- I (< 25%). The latter was due to differences in how layers were separated differently in the two columns with layers 2 and 3 being thicker in Mix- I than Mix- II resulting in more of the shorter chains residing in Layers 2 and 3 in Mix- I compared to Mix- II.



The total moles of PFOS recovered from all columns was only 20-35% of the PFOS introduced; therefore, it was assumed that 65-80% was transformed. For the PFAA mix columns, % recovery, thus the % assumed to be transformed (Figure 4-24) was positively correlated to chain length (CF_n units) with $R^2 > 0.756$ for Mix- I and $R^2 > 0.878$ for Mix- II (Figure 4-25). The average total PFAA transformation was ~36 % and ~53 % for PFAA Mix I and -II, respectively (Figure 4-24, Tables 4-7 and 4-8). For each PFAA, % transformation was higher in Mix-II relative to Mix -I (Figures 4-24 and 25). The combined effects of longer residence times (> 5 days for all PFAAs, a generally more optimal temperature, and higher nNi⁰Fe⁰-AC to sand ratio likely enhanced the overall % transformation in Mix -II relative to Mix- I. Also supporting the role of longer residence times on % transformation is the fact that both 5-day batch studies and Mix-Col-I had lower residence times and lower % total transformation than Mix- II.

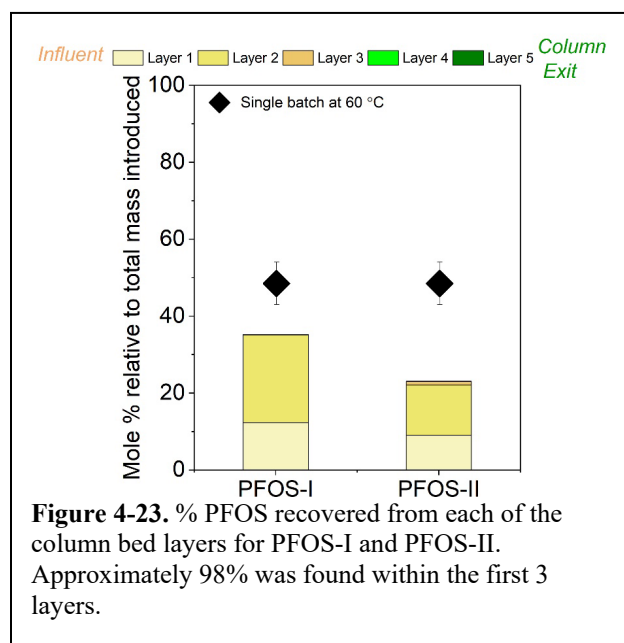


Table 4-7. PFAA and F mole balances for Mix-I. Italicized are generated products found in either column effluent or column extracts.

Solute	PFAA Introduced (nmol)	Effluent (nmol)	Total Extracted (nmol)	F atoms in PFAS	Total fluorine in PFAA not recovered (nmol)	Total Organic F Introduced (nmol)	Total Organic F Recovered (nmol)
PFBS	1598.9	1148.90	80.5	9.0	3325.4	14389.7	11064.3
PFPeA	1364.2	879.94	19.8	9.0	4180.6	12278.0	8097.5
PFHxA	1216.1	685.24	134.3	11.0	4361.7	13376.7	9015.1
PFHpA	1057.5	339.95	426.9	13.0	3779.0	13748.1	9969.1
PFHxS	684.2	29.33	390.2	13.0	3440.9	8894.4	5453.5
PFOA	681.9	0.98	330.6	15.0	5253.5	10227.8	4974.3
PFOS	328.4	0.42	111.5	17.0	3680.1	5582.8	1902.7
PFNA	115.8	0.23	53.9	17.0	1048.0	1968.5	920.5
<i>PFBA</i>	0	1.08	0	7	---	---	7.5
<i>PFPrA</i>	0	0.508	0	5	---	---	2.5
<i>C₄H₂F₇SO₃*</i>	0	0	3.5	7	---	---	25
<i>C₆H₃F₁₀SO₃*</i>	0	0	1.7	10	---	---	17
<i>C₆HF₁₂SO₃*</i>	0	0	0.3	12	---	---	3
<i>C₈H₃F₁₄SO₃*</i>	0	0	9.1	14	---	---	127
<i>C₉HF₁₆O₂*</i>	0	0	16.7	16	---	---	267
<i>C₉H₂F₁₅O₂*</i>	0	0	0.1	15	---	---	2
<i>C₉H₃F₁₄O₂*</i>	0	0	0.8	14	---	---	11
Total	7046.9	3086.6	1579.1	-	29069.2	80466.0	51859
				Total fluoride generated (nmol)			6770.6
				% F⁻ generation from transformed PFAAs			23.3
				Total F mole balance (%)			72.9

*Semi-quantitative concentration estimates made using PFOS but this is likely a poor estimation.

Table 4-8. PFAA and F mole balances for Mix-II. Italicized are generated products found in either column effluent or column extracts.

Solute	PFAA Introduced (nmol)	Effluent (nmol)	Total Extracted (nmol)	F atoms in PFAS	Total fluorine in PFAA not recovered (nmol)	Total Organic F Introduced (nmol)	Total Organic F Recovered (nmol)
PFBS	114.9	39.2	31.9	9.0	394.5	1034.1	639.6
PFPeA	309.5	102.3	41.8	9.0	1489.0	2785.3	1296.3
PFHxA	260.2	1.2	139.4	11.0	1315.8	2862.3	1546.5
PFHpA	178.4	-	96.4	13.0	1065.5	2318.7	1253.2
PFHxS	89.8	-	36.7	13.0	691.2	1167.8	476.6
PFOA	139.2	-	53.1	15.0	1290.8	2087.8	797.1
PFOS	39.4	-	9.9	17.0	502.0	670.0	168.0
PFNA	114.2	-	39.6	17.0	1267.3	1940.6	673.3
<i>PFBA</i>	0	0.02	0	7	---	---	0.15
<i>PFPrA</i>	0	0.306	0	5	---	---	1.5
<i>C₄H₂F₇SO₃*</i>	0	0	0.00	7	---	---	0.0
<i>C₆H₃F₁₀SO₃*</i>	0	0	0.0	10	---	---	0.0
<i>C₆HF₁₂SO₃*</i>	0	0	0.5	12	---	---	5.6
<i>C₈H₃F₁₄SO₃*</i>	0	0	0.5	14	---	---	6.8
<i>C₉HF₁₆O₂*</i>	0	0	11.9	16	---	---	190.7
<i>C₉H₂F₁₅O₂*</i>	0	0	0.0	15	---	---	0.0
<i>C₉H₃F₁₄O₂*</i>	0	0	0.1	14	---	---	2.0
Total	1245.5	143.0	461.7		8016	14867	7057.3
				Total fluoride generated (nmol)		1153.1	
				% F⁻ generation from transformed PFAAs		14.4	
				Total F mole balance (%)		55.2	

*Semi-quantitative concentration estimates made using PFOS but this is likely a poor estimation.

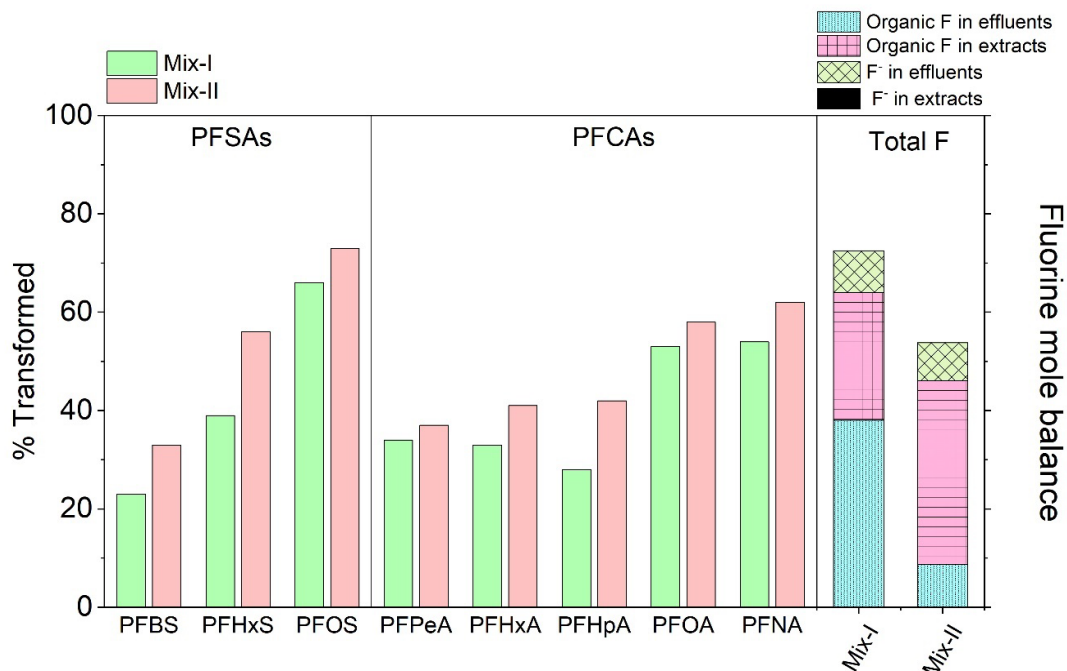


Figure 4-24. % Transformed (left axis) of each PFAA in Mix-Col-I and -II and total F mole balance (right axis) based on organic and inorganic F recovered from the effluents and extracted from column.

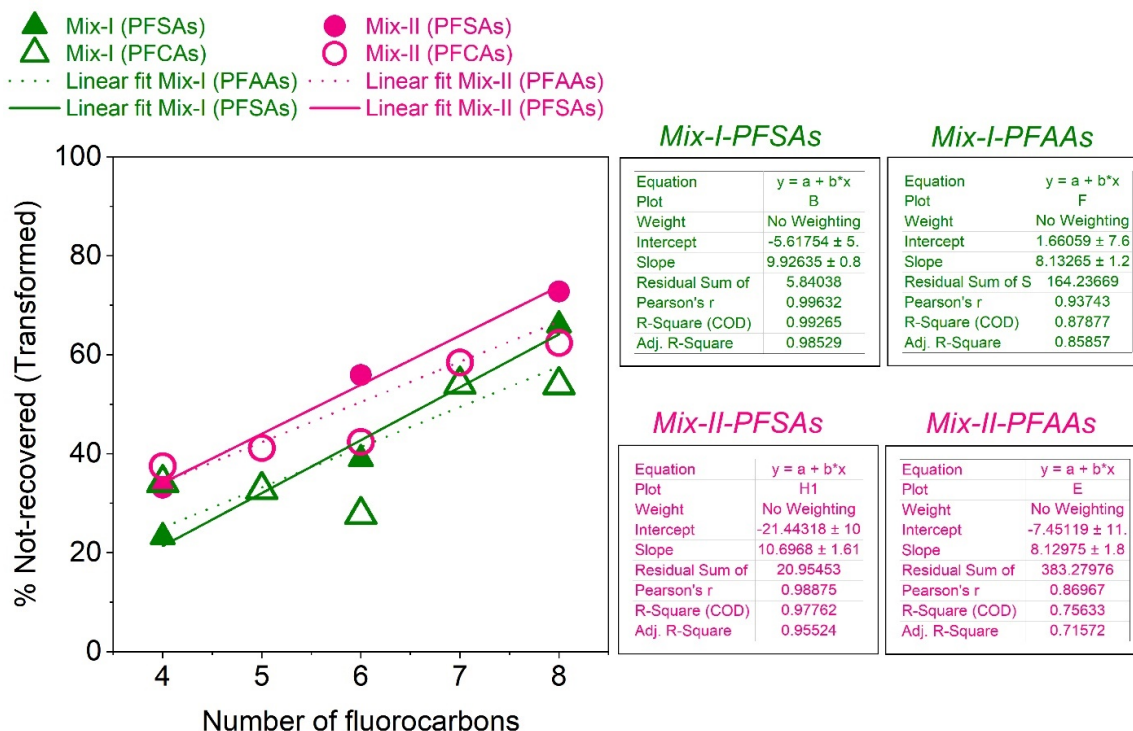


Figure 4-25. Correlation of % not-recovered (transformed) with the number of perfluoroalkyl carbons for Mix-I (60 °C, 0.05 mL min⁻¹) and Mix-II (50 °C, 0.005 mL min⁻¹).

Degradation products identified in the extracts of column material in Mix- I and Mix- II from the reductive transformation of the PFAA mixture solution are summarized in Tables 4-7 and 4-8. Non-target screening as survey scan over the mass range 100-1000 Da was carried out as described previously (Zenobio et al., 2020). We identified 7 degradation products after elucidation by mass error, isotopic pattern, retention time, and identification of daughter ions corresponding to fluorine-containing fragments. Only defluorinated fluoroalkyl products were identified corresponding to the degradation of PFBS ($\text{C}_4\text{H}_2\text{F}_7\text{SO}_3^-$), PFHxS ($\text{C}_6\text{HF}_{12}\text{SO}_3^-$ and $\text{C}_6\text{H}_3\text{F}_{10}\text{SO}_3^-$), PFOS ($\text{C}_8\text{H}_3\text{F}_{14}\text{SO}_3^-$), and PFNA ($\text{C}_9\text{HF}_{16}\text{O}_2^-$, $\text{C}_9\text{H}_2\text{F}_{15}\text{O}_2^-$, $\text{C}_9\text{H}_3\text{F}_{14}\text{O}_2^-$). In Mix- I, long-chain products (>C6) were mostly found in the first layer of the reaction bed (L2). While, the degradation product of C4 was only detected at layer 4 (L4). Similarly, in Mix- II long-chain products were mainly detected in L2 and no C4 products were found.

Total F mole balance for PFAA mix columns is tabulated in Tables 4-7 and 4-8. For both mix columns, F- was found to be the main transformation product. A total F mole balance (Eq. 3) of ~72 and 54 % was achieved by just the PFAAs and fluoride quantified. If we compare corrected intensities of the organic products with the intensity of PFOS and the PFOS standard curves to provide some estimate of the organic products identified, it appears that these products may only account for an additional 0.56 and ~1.4 % of the total F mole balance for Mix- I and -II, respectively. Shorter chain PFBA and PFPrA were also detected in effluents after ~100 and 12 PVs for Mix- I and -II, respectively, but the total was < 0.1% of the total organic F introduced. F- was also detected in all effluent fractions collected for both Mix- I and -II in addition the extracts of all layers of Mix- I but no F- was detected in extracts of Mix- II. A defluorination of ~8 % (Eq. 5) was achieved for both Mix- I and -II with % F- generated from transformed PFAAs at ~23 and 14% (Eq. 6), respectively. Higher total % transformation of PFAAs in Mix- II but lower % F- generation relative to Mix- I suggests that more organic intermediates could be generated in Mix- II which did not undergo defluorination. This is in line with estimated higher % of organic products at ~1.4% in Mix- II compared to ~0.56% in Mix- I. Although these values are relatively low to account for missing F in total F mole balance, it should be noted that organic intermediates were semi-quantified which can lead to considerable underestimation in organic products formation. In addition, the presence of some other undetected organic intermediates is also likely which can account for missing F.

Permanganate-based Systems. Permanganate (PM) has shown to be able to oxidize a range of organic contaminants including perfluorooctane sulfonate (PFOS). However, mechanisms of PFOS removal by PM have been questioned. To provide clarity to what may be happening to PFOS in PM systems, we evaluated the ability of PM to degrade PFOS by conducting studies similar to previous studies that reported PFOS destruction which included PM solutions (Table A6) and PM combined with persulfate (PS) with the latter being known as ScisoR Technology® (Ross, 2012; Yao et al., 2016). We also evaluated if addition of various soluble catalysts could enhance PM's potential to breakdown PFOS. We observed no PFOS destruction by PM regardless of buffer concentration or type used to control pH (Figure 4-26) or with the addition of selected catalysts (Figure 4-27). We investigated if the type (Na^+ or K^+) or concentrations of phosphate salt solutions (0~200 mM) affected the occurrence or stabilization of water-soluble MnO_2 colloids, which were hypothesized by previous work to enhance the PFOS transformation process by permanganate. We measured zeta potential and the size of MnO_2 colloids and found that increasing phosphate ions up to 50 mM resulted in increasingly larger MnO_2 colloids to a similar degree for both salt forms.

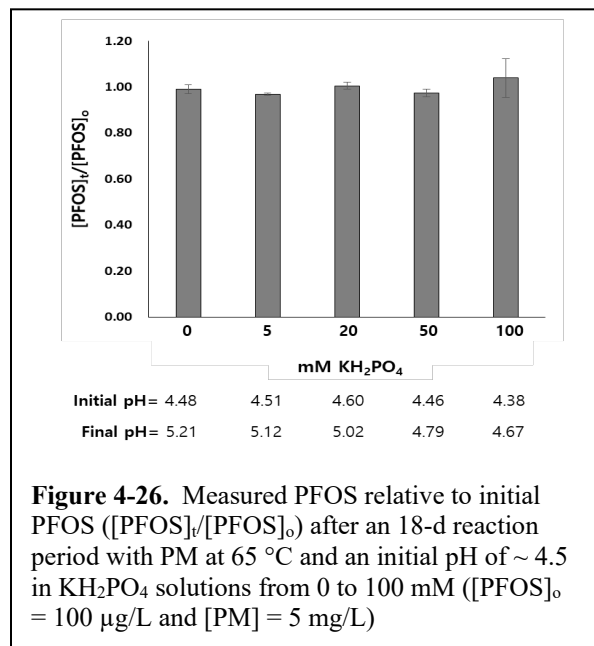


Figure 4-26. Measured PFOS relative to initial PFOS ($[PFOS]_t/[PFOS]_0$) after an 18-d reaction period with PM at 65 °C and an initial pH of ~4.5 in KH_2PO_4 solutions from 0 to 100 mM ($[PFOS]_0 = 100 \mu\text{g/L}$ and $[PM] = 5 \text{ mg/L}$)

Differences in quenching techniques also did not appear to alter results. We also show that the F^- and SO_4^{2-} generation provided in a published study (Liu et al., 2012) as evidence that PM was breaking PFOS bonds were below or not significantly higher than reported limits of quantitation. Also an unknown peak interfering with fluoride quantitation was observed. For SO_4^{2-} , impurities were found in technical PM bringing into question the reported SO_4^{2-} levels in the published work.

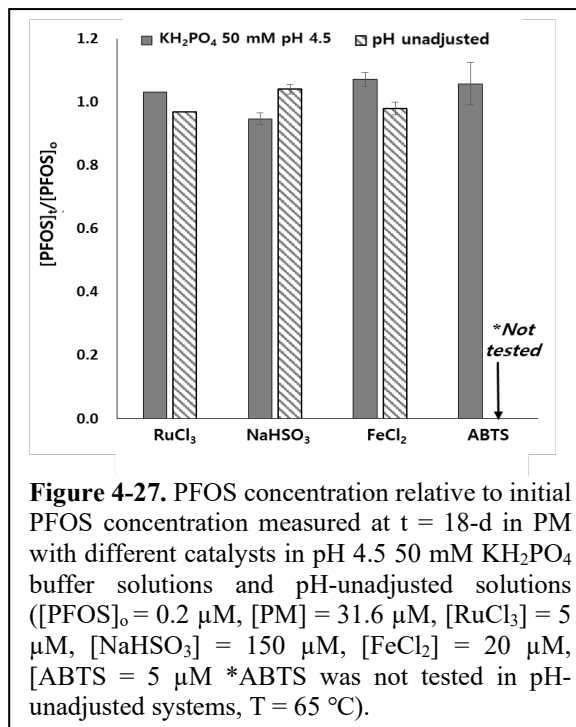


Figure 4-27. PFOS concentration relative to initial PFOS concentration measured at $t = 18\text{-d}$ in PM with different catalysts in pH 4.5 50 mM KH_2PO_4 buffer solutions and pH-unadjusted solutions ($[PFOS]_0 = 0.2 \mu\text{M}$, $[PM] = 31.6 \mu\text{M}$, $[RuCl_3] = 5 \mu\text{M}$, $[NaHSO_3] = 150 \mu\text{M}$, $[FeCl_2] = 20 \mu\text{M}$, $[ABTS] = 5 \mu\text{M}$ *ABTS was not tested in pH-unadjusted systems, $T = 65 \text{ }^\circ\text{C}$).

For PM-PS systems, the ability for PM and PS together to remove PFOS was evaluated over a 23-week period at room temperature ($22 \pm 0.5^\circ\text{C}$) in pH-unadjusted solutions (initial pH ≈ 6.5). (Figure 4-28). During the 4-weeks prior to PS addition, no PFOS removal was observed although several changes in the system (Figure 4-28a). The pH decreased over time to ~ 3 with concomitant increases in ORP from 415 to 650 mV (Figure 4-28b). Mn(VII) converted to Mn(IV) as evidenced by loss of absorbance at 525 nm of Mn(VII) (Waldemer and Tratnyek, 2006), color change of purple to colorless (Figure 4-29), and the formation of brownish MnO_2 precipitates in all samples by 4 weeks.

At the end of 4 weeks, addition of PS (104 mM) also did not lead to any PFOS removal over the next 17 weeks (Fig. 28a). For PM-PS systems (ScisoR Technology[®]), PFOS was not found to be degraded (Figure 4-28a), but rather PFOS distribution became heterogeneous as confirmed when subsampling reaction vessels at different depths ((Figure ES-10) and visual evidence of PFOS ‘salting-out’ ((Figure ES-10 insert). The decreasing changes in PFOS concentrations observed with both increasing persulfate concentrations or the salt products that form as persulfate is degraded (controls) further support the PFOS ‘salting out’ phenomena ((Figure ES 4-10, Figure 4-30). In addition, subsequent sonication and filtering of the samples led to the apparent disappearance of most of the PFOS, which was an artifact arising from the behavior of PFOS aggregates or potential hemi-micelle formation. Given these findings, it is clear that neither permanganate or the ScisoR Technology[®] destroy PFOS, but the addition of salts may have

application for collecting or concentrating PFOS and other PFAAs in a remediation or water treatment strategy. Additional details, tables, and figures can be found in (Park et al., 2020).

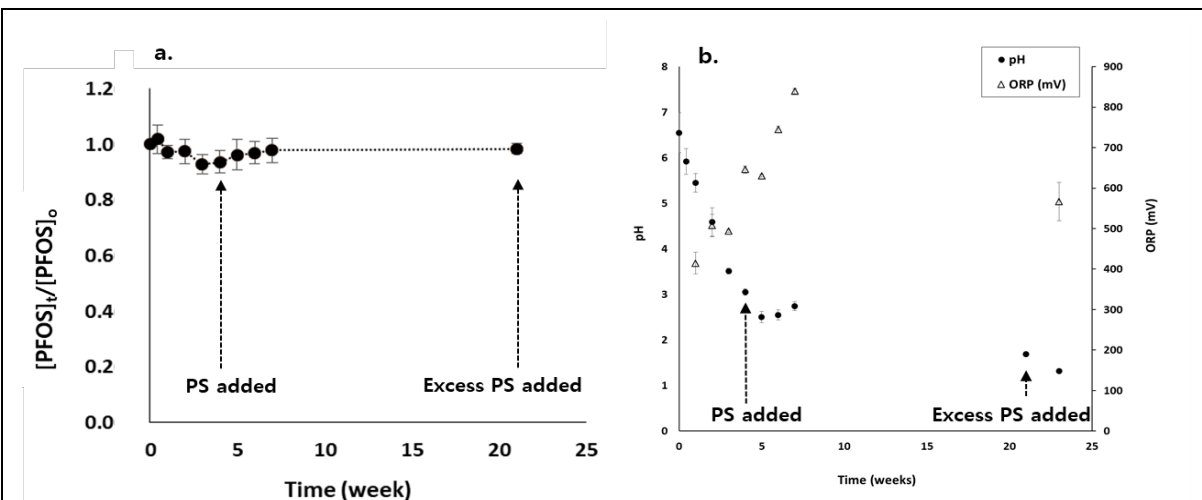


Figure 4-28. For 21-weeks at T = 22 °C with the Scisor Technology®, **(a)** PFOS and **(b)** pH and ORP measured at each sampling time. ($[PFOS]_o = 8 \mu\text{M}$, $[PM] = 1.82 \text{ mM}$, $[LA] = 0.44 \text{ mM}$ with $[PS] = 104 \text{ mM}$ added at the 4 weeks). UV-Vis spectra confirmed Mn(VII) conversion to Mn(IV).

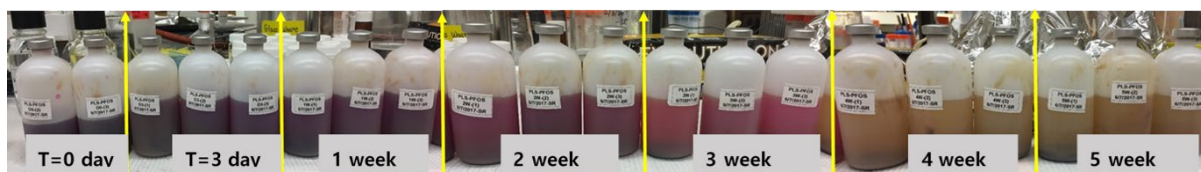


Figure 4-29. Batch reactors used in the evaluation of permanganate-persulfate oxidative/reductive technology to degrade PFOS and exemplifying color change of the samples in the process showing oxidation to reductive conditions.

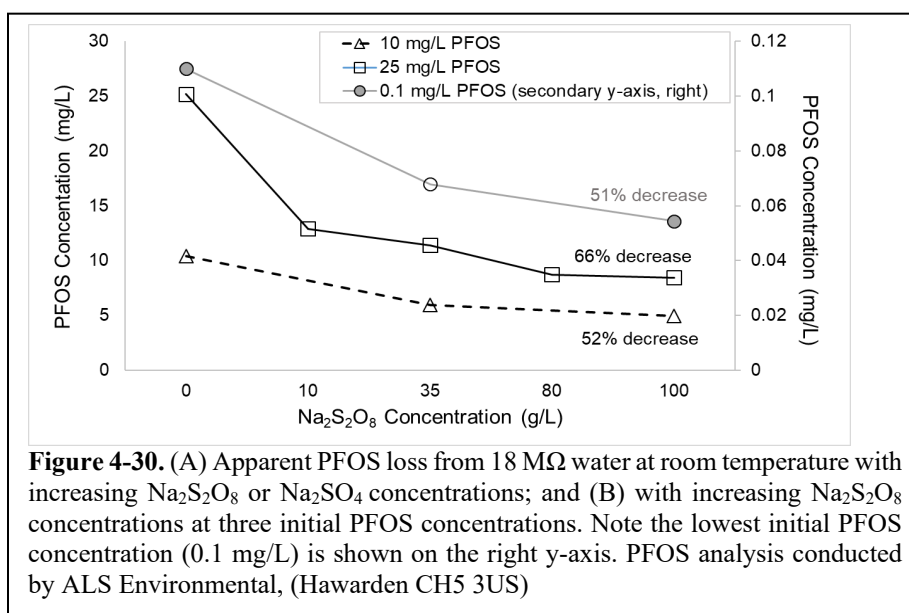


Figure 4-30. (A) Apparent PFOS loss from 18 MΩ water at room temperature with increasing $\text{Na}_2\text{S}_2\text{O}_8$ or Na_2SO_4 concentrations; and (B) with increasing $\text{Na}_2\text{S}_2\text{O}_8$ concentrations at three initial PFOS concentrations. Note the lowest initial PFOS concentration (0.1 mg/L) is shown on the right y-axis. PFOS analysis conducted by ALS Environmental, (Hawarden CH5 3US)

SECTION 5: CONCLUSIONS AND IMPLICATIONS FOR FUTURE RESEARCH/IMPLEMENTATIONS

At the start of this ER-2426 project, the primary approach to mitigate PFAS transport and contamination of drinking water was sorbents, which came with challenges to effectively capture shorter chain PFAAs. Also the sorbent still had to be disposed of as a hazardous waste or regenerated in a way that brought back its sorbent abilities and destroyed the sorbed PFAS. Very little was known about potential technologies that could destroy PFAS, in particular PFOS, which had been identified as the most recalcitrant PFAS for even abiotic technologies. What we did know at the time was that microbial degradation of PFAS would lead to terminal PFAAs. Also, the abiotic technologies that had been evaluated at some level for destruction of PFOS and PFOA were either unsuccessful, had questionable results or were simply not amenable for use in situ remediation of groundwater. The large PFAS-contaminated plumes being generated from military bases due to the frequent use of AFFFs called for the need to identify in situ destructive remediation technologies to mitigate PFAS transport offsite.

Key Findings:

- Vitamin B12 systems are not effective at degrading L-PFOS, which appears to be due to steric hindrances that limit L-PFOS complexation with VB12.
- Neither PM, persulfate or a combination of the two (ScisoR Technology®) can transform PFOS. Apparent PFOS loss appeared to be due to clustering and ‘salting out’, which leads to sampling artifacts, thus underestimates of PFOS concentrations. We also determined that fluoride impurities in reagents used as well as peaks that interfere with proper fluoride quantitation led to wrong conclusions that fluoride was being generated.
- The initial promise that $n\text{PdFe}^0$ was able to degrade PFOS was proven to be an artifact of changes in sorption affinity during iron corrosion. Some of the iron released during corrosion precipitated as Fe-oxides causing PFOS to be strongly sorbed (not methanol extractable), and thus, appear transformed. As the oxides changed forms over longer reactions times, PFOS was released revealing it had not been transformed.
- PFOS was found to complex with Fe released to solution during corrosion, which reduced quantifiable PFOS levels by LC-MS/MS. Elevating solution pH to > 10 released PFOS for quantification. Complexation increased with Fe concentration and valence state ($\text{III} > \text{II}$). Complexation was greater for longer chain PFAAs.
- Of the metals (single, bi and tri) evaluated, $n\text{Ni}^0\text{Fe}^0$ -AC nanocomposites synthesized with a 3-h synthesis stirring time using sodium borohydride to reduce and precipitate the metals to zero valence were the most effective at degrading L-PFOS with $> 97\%$ of unrecovered PFOS accounted for by the fluoride and sulfite generated. PFOS transformation and defluorination was $\sim 94\%$ at 50°C .
- $n\text{Ni}^0\text{Fe}^0$ -AC nanocomposites also transformed other PFAS, which transformed and defluorinated to varying degrees. For the PFAAs, transformation rates and % fluoride generated relative to moles of parent transformed decreased with a decreasing number of perfluorocarbons. Overall, F- generation was greatest for the PFSAs. For fluorotelomer sulfonates (6:2 and 8:2 FTS), more than half of the substances were transformed with C-S cleavage, but % defluorination was low indicating that once the C-S bond was cleaved, propensity to defluorinate was low. GenX was the least transformed PFAS evaluated.
- In bench-scale PRBs (saturated columns systems), sorption and transformation limited

PFAA breakthrough according to chain length with the longer chain PFAAs remaining near the inlet.

Implications and Benefits:

- Our studies showed that there are many artifacts that can lead to wrong conclusions regarding PFAS removal, this it is imperative that multiple lines of evidence be required when assessing PFAS remediation technology potential.
- The salting out phenomena that was observed as an artifact leading to wrong conclusions of PFOS removal indicates that exploiting the ‘salting out’ may have potential for treating PFAS-contaminated water – forcing PFAS to precipitate with addition of salts. Precipitates could be filtered out and the salty water processed to remove salts using standard technologies.
- AC serves to immobilize or reduce PFAS mobility through sorptive processes, thus increasing proximity to the nNi^0Fe^0 nanocomposites facilitating reductive transformation. To date, these are the first such nanocomposites that have shown to transform and defluorinated PFAS.
- Application of nNi^0Fe^0 -AC nanocomposites in PRBs for use in PFAS capture and transformation in groundwater plumes especially where groundwater is already fairly reduced has potential and warrants further investigation.
- The use of nNi^0Fe^0 -AC nanocomposites can also be used in column reactors above ground in place of just AC, which is what is currently used the most.
- In situ injection of nNi^0Fe^0 -AC nanocomposites is also plausible. The main concern with regards to toxicity for any in situ use of these nanocomposites would likely be nickel concentrations in groundwater. However, < 2% Ni in total was observed in column effluent after more than 138 pore volumes, thus the use of these nanocomposites will likely not lead to Ni levels of concern in groundwater.
- Lastly, while it is evident that nNi^0Fe^0 -AC technology may be very successful at rapidly defluorinating the longer chain PFASs like PFOS, it is unlikely to be sufficient on its own for degrading the range of co-occurring PFAS, thus would be best considered as part of a treatment train coupled with other treatment technologies. For example, once the sulfonate group is cleaved, attack by oxidative technologies may be more effective.

Future work:

- Additional studies at longer reaction times (> 5 d) are needed to evaluate if transformation and defluorination of some of the less-transformed PFAS will increase.
- Additional column studies using AFFF-impacted groundwater are needed and are underway.
- Studies to evaluate regeneration potential of the nNi^0Fe^0 -AC nanocomposites are needed and are underway, which would improve chances of adoptability in PRBs and above ground column reactors.
- nNi^0Fe^0 -AC technology in a field-scale pilot study at an AFFF-impacted site are warranted and may be funded through an ESTCP-type project. We currently have companies interested in our nNi^0Fe^0 -AC technology pending patent.

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APPENDICES

SUPPORTING DATA TABLES

Table A1. Transformation products (parent m/z) detected after individual 6 μ M solutions of PFBS and PFHxS reacted with nNi0Fe0-AC at 60 °C for 1 d or 5 d in single solute reactions. Corresponding fragmentation shown in Table S19. Degradation products were detected using QToF ESI-. All samples were concentrated 3 times to increase product detection.

PFSA	Molecular Formula	Theoretical m/z	Observed m/z	Error (ppm)	RT (min)
PFBS (C ₄ F ₉ SO ₃ ⁻ ; m/z 298.9416) RT = 7.68 min	Polyfluoroalkyl sulfonate with single bond				
	C ₄ HF ₈ SO ₃ ⁻	280.9519	280.9521	0.80	6.83
	Perfluorobutyl carboxylic acid				
	C ₄ F ₇ O ₂ ⁻	212.9787	212.9789	1.12	6.45
PFHxS (C ₆ F ₁₃ SO ₃ ⁻ ; m/z 398.9373) RT = 9.48 min	Polyfluoroalkyl sulfonate with single bond				
	C ₆ HF ₁₂ SO ₃ ⁻	380.9455	380.9450	1.25	9.16
	C ₅ HF ₁₀ SO ₃ ⁻	330.9487	330.9487	0.08	7.90
	C ₄ HF ₈ SO ₃ ⁻	280.9519	280.9534	5.46	7.43
	Perfluoroalkyl carboxylic acid (PFCAs)				
	C ₆ F ₁₁ O ₂ ⁻	312.9723	312.9730	2.35	8.43
	C ₄ F ₇ O ₂ ⁻	212.9787	212.9788	0.70	6.42

Table A2. Fragmentation patterns for the transformation products from Table A3-15 identified after nNi⁰Fe⁰-AC reacted at 60 °C in single PFSA reactions using accurate-mass identification. Precursor and daughter ions were identified by QToF. In table column one, the number in parenthesis is the observed m/z of the precursor ions.

Initial PFSA	Molecular Formula	Theoretical m/z	Observed m/z	Error (ppm)	Molecular Formula
PFBS C ₄ F ₉ SO ₃ ⁻ m/z 298.9416	C ₄ HF ₈ SO ₃ ⁻	79.9574	79.9581	8.75	SO ₃ ⁻
		98.9552	98.9555	2.83	FSO ₃ ⁻
PFHxS C ₆ F ₁₃ SO ₃ ⁻ m/z 398.9373	C ₆ HF ₁₂ SO ₃ ⁻	79.9574	79.9574	0.00	SO ₃ ⁻
		98.9552	98.9543	9.30	FSO ₃ ⁻
		118.9926	118.9915	9.24	C ₂ F ₅ ⁻
		168.9894	168.9885	5.33	C ₃ F ₇ ⁻
		298.9424	298.9411	4.35	C ₄ F ₉ SO ₃ ⁻
	*C ₅ HF ₁₀ SO ₃ ⁻	79.9574	79.9577	3.75	SO ₃ ⁻
		98.9552	98.9554	1.82	FSO ₃ ⁻
	*C ₄ HF ₈ SO ₃ ⁻	79.9574	79.9573	1.25	SO ₃ ⁻
		98.9552	98.9550	2.22	FSO ₃ ⁻
	C ₆ F ₁₁ O ₂ ⁻	68.9958	68.9967	13.04	CF ₃ ⁻
		118.9926	118.9918	6.72	C ₂ F ₅ ⁻
		268.9824	268.9814	3.84	C ₅ F ₁₁ ⁻
	C ₄ F ₇ O ₂ ⁻	168.9894	168.991	9.50	C ₃ F ₇ ⁻

*degradation products of impurities found in the PFHxS stock solution.

Table A3. Measured concentrations of PFCAs in ng/L for 6:2 FTS and 8:2 FTS at 50 and 60 °C in extracts from single solute reactions which were diluted 2 and 10× for 6:2 FTS and 8:2 FTS, respectively, from batch reactions.

PFAS	Temperature (°C)	PFBA	PFPeA	PFHxA	PFHpA	PFOA
6:2 FTS	60	<LOQ*	<LOQ	100 ± 80	590 ± 130	<LOD
8:2 FTS		<LOD	<LOD	<LOD	<LOD	98 ± 2
6:2 FTS	50	<LOQ	<LOQ	<LOQ	<LOQ	<LOD
8:2 FTS		<LOD	<LOD	<LOD	<LOD	115 ± 2

*LOQ values are reported in Table A3-20.

Table A4. Transformation products (parent m/z) detected after individual 6 μ M solutions of PFBA, PFHxA, PFOA reacted with $n\text{Ni}^0\text{Fe}^0\text{-AC}$ at 60 $^\circ\text{C}$ for 1 d or 5 d single solute batch reactions. Corresponding fragmentation shown in Table A1. Degradation products were detected using QToF ESI. Degradation products were detected using QToF ESI. All samples were concentrated 3 times to increase product detection.

PFCA	Molecular Formula	Theoretical m/z	Observed m/z	Error (ppm)	RT (min)
PFBA ($\text{C}_4\text{F}_7\text{O}_2^-$: m/z 212.9787) RT = 6.45 min	Perfluoropropanol with single bond				
	$\text{C}_3\text{F}_7\text{O}^-$	184.9837	184.9840	1.43	6.45
	Perfluoropropanol with double bond				
	$\text{C}_3\text{F}_5\text{O}^-$	146.9869	146.9870	0.48	6.45
PFHxA ($\text{C}_6\text{F}_{11}\text{O}_2^-$: m/z 312.9723) RT = 8.45 min	Perfluoropentanol with single bond				
	$\text{C}_5\text{F}_{11}\text{O}^-$	284.9773	284.9774	0.18	8.42
	Perfluoroalkyl alcohol with double bond				
	$\text{C}_6\text{F}_{11}\text{O}^-$	296.9773	296.9767	2.18	8.42
	$\text{C}_5\text{F}_9\text{O}^-$	246.9805	246.9808	1.05	8.42
	$\text{C}_4\text{F}_7\text{O}^-$	196.9837	196.9841	1.85	7.56
	Perfluoroalkyl acids (PFCAs)				
	$\text{C}_5\text{F}_9\text{O}_2^-$	262.9755	262.9758	1.30	7.55
	$\text{C}_4\text{F}_7\text{O}_2^-$	212.9787	212.9786	0.24	6.44
	Polyfluoroalkyl carboxylate with single bond				
	$\text{C}_6\text{H}_4\text{F}_7\text{O}_2^-$	241.0100	241.0095	1.87	8.27
PFOA ($\text{C}_8\text{F}_{15}\text{O}_2^-$: m/z 412.9659) RT = 10.22 min	Perfluoroalkyl acids (PFCAs)				
	$\text{C}_7\text{F}_{13}\text{O}_2^-$	362.9691	362.9696	1.46	9.35
	$\text{C}_6\text{F}_{11}\text{O}_2^-$	312.9723	312.9708	4.67	8.46
	$\text{C}_4\text{F}_7\text{O}_2^-$	212.9787	212.9791	2.11	6.45
	Perfluoroalkyl alcohol with double bond				
	$\text{C}_7\text{F}_{13}\text{O}^-$	346.9742	346.9750	2.44	9.36
	$\text{C}_6\text{F}_{11}\text{O}^-$	296.9773	296.9779	1.86	8.45
	$\text{C}_4\text{F}_7\text{O}^-$	196.9837	196.9845	3.88	7.58
	$\text{C}_3\text{F}_5\text{O}^-$	146.9869	146.9874	3.20	6.47
	Polyfluoroalkyl carboxylates with single bond				
	$\text{C}_8\text{HF}_{14}\text{O}_2^-$	394.9753	394.9761	2.03	9.88
	$\text{C}_8\text{H}_2\text{F}_{13}\text{O}_2^-$	376.9847	376.9853	1.54	9.55
	$\text{C}_8\text{H}_3\text{F}_{12}\text{O}_2^-$	358.9941	358.9945	1.00	9.32
	$\text{C}_8\text{H}_4\text{F}_{11}\text{O}_2^-$	341.0036	341.0036	0.11	8.69
	$\text{C}_8\text{H}_5\text{F}_{10}\text{O}_2^-$	323.0130	323.0137	2.21	8.42
	$\text{C}_8\text{H}_6\text{F}_9\text{O}_2^-$	305.0224	305.0225	0.30	7.98
	$\text{C}_8\text{H}_7\text{F}_8\text{O}_2^-$	287.0318	287.0317	0.45	7.78
	$\text{C}_8\text{H}_8\text{F}_7\text{O}_2^-$	269.0413	269.0415	0.93	7.74
	$\text{C}_8\text{H}_9\text{F}_6\text{O}_2^-$	251.0507	251.0514	2.90	7.70
	$\text{C}_8\text{H}_{11}\text{F}_4\text{O}_2^-$	215.0695	215.0698	1.32	7.47
	$\text{C}_8\text{H}_{12}\text{F}_3\text{O}_2^-$	197.0789	197.0791	0.82	7.45
	$\text{C}_7\text{HF}_{12}\text{O}_2^-$	344.9785	344.9801	4.66	7.36
	$\text{C}_6\text{HF}_{10}\text{O}_2^-$	294.9817	294.9808	3.00	7.36
	Polyfluoroheptanol with double bond				
	$\text{C}_7\text{HF}_{12}\text{O}^-$	328.9836	328.9829	2.05	8.99

Table A5. Fragmentation patterns for the transformation products from Table A4 identified after nNi⁰Fe⁰-AC reacted at 60 °C with single PFCAs using accurate-mass identification. Precursor and daughter ions were identified by QToF. In column one, the number in parenthesis is the observed m/z of the precursor table ions.

Initial PFCa	Molecular Formula	Theoretical m/z	Observed m/z	Error (ppm)	Molecular Formula
PFBA (C ₄ F ₇ O ₂ ⁻ : m/z 212.9787) RT = 6.45 min	C ₃ F ₇ O ⁻	68.9958	68.9975	24.6	CF ₃ ⁻
		134.9869	134.985	14.3	C ₂ F ₅ O ⁻
PFHxA (C ₆ F ₁₁ O ₂ ⁻ : m/z 312.9723) RT = 8.45 min	C ₅ F ₁₁ O ⁻	118.9926	118.9922	3.4	C ₂ F ₅ ⁻
		168.9894	168.9878	9.5	C ₃ F ₇ ⁻
	C ₆ F ₁₁ O ⁻	130.9920	130.9916	3.1	C ₃ F ₅ ⁻
		180.9888	180.9884	2.3	C ₄ F ₇ ⁻
		230.9856	230.9860	1.6	C ₅ F ₉ ⁻
	C ₅ F ₉ O ⁻	84.990124	84.9895	7.3	CF ₃ O ⁻
		118.9926	118.9923	2.5	C ₂ F ₅ ⁻
		130.9920	130.9921	0.7	C ₃ F ₅ ⁻
		146.9869	146.9876	4.6	C ₃ F ₅ O ⁻
		180.9888	180.9885	1.8	C ₄ F ₇ ⁻
		196.9837	196.9826	5.8	C ₄ F ₇ O ⁻
		118.9926	118.9921	4.2	C ₂ F ₅ ⁻
	C ₄ F ₇ O ₂ ⁻	118.9926	118.9921	4.2	C ₂ F ₅ ⁻
PFOA (C ₈ F ₁₅ O ₂ ⁻ : m/z 412.9659) RT = 10.22 min	C ₇ F ₁₃ O ₂ ⁻	68.9958	68.9958	0.0	CF ₃ ⁻
		118.9919	118.9918	0.8	C ₂ F ₅ ⁻
		168.9894	168.9882	7.1	C ₃ F ₇ ⁻
		318.9792	318.9796	1.1	C ₆ F ₁₃ ⁻
	C ₆ F ₁₁ O ₂ ⁻	118.9919	118.9931	10.1	C ₂ F ₅ ⁻
	C ₄ F ₇ O ₂ ⁻	118.9926	118.9921	4.2	C ₂ F ₅ ⁻
	C ₇ F ₁₃ O ⁻	68.9958	68.9964	8.7	CF ₃ ⁻
		84.9901	84.9908	8.0	CF ₃ O ⁻
		118.9926	118.9922	3.4	C ₂ F ₅ ⁻
		130.9920	130.9921	0.7	C ₃ F ₅ ⁻
		134.9869	134.9869	0.2	C ₂ F ₅ O ⁻
	C ₇ F ₁₃ O ⁻	146.9869	146.9869	0.2	C ₃ F ₅ O ⁻
		168.9894	168.988	8.3	C ₃ F ₇ ⁻
		180.9888	180.9882	3.4	C ₄ F ₇ ⁻
		184.9837	184.9849	6.3	C ₃ F ₇ O ⁻
		196.9837	196.9823	7.3	C ₄ F ₇ O ⁻
		218.9862	218.9876	6.4	C ₄ F ₉ ⁻
		230.9856	230.9856	0.1	C ₅ F ₉ ⁻
		280.9824	280.9832	2.7	C ₆ F ₁₁ ⁻
	C ₆ F ₁₁ O ⁻	118.9919	118.9919	0.0	C ₂ F ₅ ⁻
		130.9920	130.9924	3.0	C ₃ F ₅ ⁻
		134.9869	134.9851	13.6	C ₂ F ₅ O ⁻
		168.9894	168.991	9.5	C ₃ F ₇ ⁻
		180.9888	180.9885	1.8	C ₄ F ₇ ⁻
	C ₄ F ₇ O ⁻	230.9856	230.9857	0.3	C ₅ F ₉ ⁻
		130.9920	130.9912	6.2	C ₃ F ₅ ⁻
		130.9912	130.9912	0.0	C ₃ F ₅ ⁻
	C ₈ HF ₁₄ O ₂ ⁻	68.9958	68.9971	18.8	CF ₃ ⁻
		118.9926	118.9923	2.5	C ₂ F ₅ ⁻
		168.9894	168.9896	1.2	C ₃ F ₇ ⁻
	C ₈ H ₃ F ₁₂ O ₂ ⁻	68.9958	68.995	11.6	CF ₃ ⁻
		118.9926	118.9932	5.0	C ₂ F ₅ ⁻
	C ₇ HF ₁₂ O ₂ ⁻	130.992	130.9928	6	C ₃ F ₅ ⁻
	C ₇ HF ₁₂ O ₂	280.9824	280.9841	5.9	C ₆ F ₁₁ ⁻
	C ₆ HF ₁₀ O ₂ ⁻	230.9856	230.9833	10.1	C ₅ F ₉ ⁻
	C ₇ HF ₁₂ O ⁻	180.9888	180.9944	13.8	C ₄ F ₇ ⁻

Table A6. Comparison of experimental conditions and results of this study with (Liu et al., 2012)

	Parameters	This study	Liu et al. (2012)
Experimental conditions	[PFOS] ₀	C ₈ F ₁₇ SO ₃ -K 100 µg/L	C ₈ F ₁₇ SO ₃ -H 100 µg/L
	[PM] ₀	5 mg/L	0.1 ~10 mg/L (mainly 1 mg/L used)
	pH	KH ₂ PO ₄ or NaH ₂ PO ₄ 0 ~ 200 mM 4.5	Phosphate buffer solution (Fisher) 4.2
	Temperature (°C)	65	65
	Shaken for reaction period	Hand-shaken once/day	Stationary remained
	Sampling	Cool down to room T using ice box	Cool down to room T using 4 °C water
	Quenching method	0.1-mL of 0.1 M NH ₂ OH•HCl was added to 10-mL aliquot	0.5-mL of 1 M L-ascorbic acid was added to 1-mL aliquot
	Filtration	0.2 µm Whatman inorganic membrane	0.2 µm Polypropylene filter
	Isotopically mass-labelled PFOS Internal standard	M8PFOS (¹³ C ₈)	None
Results	PFOS removal%	No removal for 18 d	46.8% for 18 d
	F ⁻ yield%	No F ⁻ generation	5.4 % F ⁻ generation for 18 d
	SO ₄ ²⁻ yield%	No SO ₄ ²⁻ generation	36.9 % SO ₄ ²⁻ generation for 18 d

LIST OF SCIENTIFIC/TECHNICAL PUBLICATIONS:

Articles in peer-reviewed journals

- Zenobio, J.E., Modiri-Gharehveran, M., Perre, Chloe, Vecitis, C.D., Lee, L.S. 2020. Rates and Products of Reductive Transformation of Perfluorooctanesulfonate by nNiFe⁰-Activated Carbon. *J. Haz. Mat.* <https://doi.org/10.1016/j.jhazmat.2020.122782>.
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None

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- Mahsa Modiri Gharehveran and Linda S. Lee. 2021. PFAS Destruction in 1-Dimensional Bench-Scale Permeable Reactor Barriers Containing Zero Valent Nickel-Iron Activated Carbon Nanocomposites. REMTEC, March 9-11, 2021
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- Lee, L.S. 2020. Two Research Snapshots: (1) PFAS Occurrence in Commercial Biosolids-base Soil Amendments and (2) Reductive mineralization of PFAS using nNiFe⁰-activated carbon Particles, Oregon State University (Invited), May 6, 2020.
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None

Other significant outputs/awards:

Park, Saerom. 2017. Lab-scale exploration of abiotic transformation approaches for

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Zenobio, Jenny. 2019. Reductive degradation of per-and polyfluoroalkyl substances (PFAS) by synthesized activated carbon-supported bimetals. PhD Dissertation, West Lafayette, IN

Provisional Patent. Activated carbon supported Ni^0Fe^0 nanoparticles for reductive transformation of perfluoroalkyl-containing compounds. EFS ID#30188706; Application #62550265; Confirmation #6140, Aug. 25, 2017.

Pending patent. Activated carbon supported Ni^0Fe^0 nanoparticles for reductive transformation of perfluoroalkyl-containing compounds. EFS ID#30188706; Application #62550265; Confirmation #6140, Aug. 25, 2017. Patent in process.

Geosyntec's Technology and Innovation and Applied Research program (TAC) award (\$20K)

AF Ax-Nano LLC (AF STTR Phase I), Reactive Bimetallic-Carbon Media For Destruction Of PFAS-Containing Aqueous Fire Fighting Foam Stockpiles, \$50K, Jan 2021-June 2021, A. Carpenter (PI), L.S. Lee (co-PI).