DEGRADATION OF AQUEOUS PERFLUOROOCTANOIC ACID BY IRON-ACTIVATED
PERSULFATE OXIDATION

by

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STATEMENT BY AUTHOR

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TERMS, ABBREVIATIONS, AND ACRONYMS

ASC – Ascorbic Acid.

AFFF –Active Film-Forming Foam.

CECs –Contaminants of Emerging Concerns.

DNA – Deoxyribonucleic Acid.

EPA – Environmental Protection Agency.

Fh – Ferrihydrite.

FZ – FerroZine.

IAPO – Iron-Activated Persulfate Oxidation.

ISCO – In-Situ Chemical Oxidation.

ICP- MS – Inductively Coupled Plasma Mass Spectrometry.

Koc – Organic-Carbon Partition Coefficient.

PFOA –Perfluorooctanoic Acid.

PFOS – Perfluorooctanesulfonic Acid.

PFCs – Perfluorinated Compounds.

PHAs – Provisional Health Advisories.

PS- Persulfate.

UCMR 3 – Third Unregulated Contaminant Monitoring Rule.

UPLC–qTOF-MS/MS – Ultra-Performance Liquid Chromatography Coupled with Quadrupole

Time of Flight Mass Spectrometry.

ABSTRACT

Perfluorinated compounds (PFCs) are a class emerging contaminants that have been implicated in bladder cancer and other human health problems. Due to the widespread exposure to humans, persistence in the environment, and their negative effects on human health, we need to develop a treatment method to degrade these chemicals into harmless species. Perfluorooctanoic acid (PFOA, $C_8HF_{15}O_2$) is one of the top representatives of PFCs commonly reported to be found in water sources, hence it was chosen as the model compound and focus in this project. We examined an iron-activated persulfate oxidation (IAPO) method to decompose aqueous PFOA, and tested the reaction under various conditions, including: oxic, anoxic, and anoxic/dark conditions. We observed *ca*. 64% of PFOA (beginning with solution phase concentration fo *ca.* $1.64*10^{-6}$ mol L^{-1}) was transformed after four hours under anoxic conditions. This was about seven times higher than measured under oxic conditions, and about five times higher than anoxic/dark conditions. Therefore, we concluded that IAPO can decompose PFOA at 25 ^{o}C, the ambient condition temperature. This method can potentially be used as an inexpensive and environmentally-friendly PFOA remediation method, with potential application to other PFCs in groundwater and soil. In addition, this method may be applicable for surface water sources such as potable water reservoirs, waste water effluent, and extracted groundwater.

CHAPTER I- INTRODUCTION

1.1 Context

From a survey in 1999, groundwater is considered the primary source for potable water in the U.S, and approximately half of the U.S population use these sources.[1] However, these water sources may contain potential risks that can be harmful for human health. These potential risks can include heavy metals, toxic organic compounds, and pathogenic microorganisms. A suite of chemicals recently synthesized and utilized in industry or residential contexts, and now known to be increasingly ubiquitous in the environment, with potential risk to human and environmental health are referred to as contaminants of emerging concern (CECs). Public water suppliers are required to meet specific water standards under the Safe Drinking Water Act of 1986. The list of CECs for groundwater continues to expand as new chemicals are synthesized and become introduced into the environment, and most of these CECs are unregulated by EPA.

Perfluorinated compounds (PFCs) are among the CECs now recognized by EPA, and they are commonly found on military bases since they are effective flame retardant compounds and Perfluorooctanoic acid (PFOA) is the most common active ingredient in the aqueous film forming foam. This has become a big challenge for environmental scientists who are trying to remediate PFCs in the environmental sources. The problems are not only because of the heterogeneity, complexity and uncontrollable characteristic of natural systems; but also because PFCs are among the most stable and persistent of synthetic chemicals; they are resistant to most natural degradation processes.

Finding an environmentally-friendly method that is feasible to apply in natural water systems to degrade PFCs to harmless species has become an urgent task. In all of the developed groundwater remediation techniques, chemical oxidation is the technique, which has been reported

most frequently as being capable of rapidly degrading persistent organic compounds. Iron-activated persulfate oxidation (IAPO) is a newly utilized chemical oxidation method that has been reported to be capable of decomposing most organic contaminants, such as 1,4-dioxane, and trichloroethene.[2,3] Recently, this technique has been widely used for in-situ chemical oxidation (ISCO). Therefore, we hypothesized that IAPO would be a candidate for ISCO to remediate PFCs in groundwater. This study was designed to test its efficacy in a laboratory environment under controlled conditions.

1.2 Literature Review

1.2.1 PFCs as emerging environmental contaminants

PFCs have been manufactured for more than 50 years. Because of their unique molecular properties, thermal stability and their repellent properties, PFCs have been widely used to make a variety of products that require resistance to stains, water, and grease. For example, Teflon cookware is coated with PFOA to keep food from sticking to it; sofas are coated with PFCs to help them become more waterproof, and PFCs may also be used in some food packaging. Moreover, perfluorooctanesulfonic acid (PFOS), one the chemicals in PFCs family, was commonly used as an active ingredient for active film-forming foam (AFFF) to treat petroleum fires at manufacturing sites, military bases, firefighting training facilities, and airports since 1970.[4] Therefore, many of these areas are highly contaminated by PFOS. In a recent report, it was estimated that 4,600,000 gallons in 2004 and 1,972,000 gallons in 2011 of PFOS based AFFF was used.[5]

PFCs are extremely stable in nature, they are highly soluble in water, and they have low volatility.[6] PFCs have been found in soil, groundwater, air, sea water, animal tissues and human blood serum.[7] Although PFCs have low volatility, they can still be released directly to the atmosphere and adsorb to aerosols and then settle to the ground through deposition processes.[8,9] They are highly soluble in water, so they can migrate rapidly from soil to groundwater through hydrologic processes such as infiltration associated with rainfall and snowmelt, and they can be transported long distances.[10,11]

Up to 1 ppb of PFCs were detected in fresh waters in the vicinity of PFCs industries; $1*10^{-5}$ - $1*10^{-4}$ ng/g of PFCs were measured in the oceans;[12] and U.S. Environmental Protection Agency (EPA) Region 5 has detected about $2*10^{-3}$- $5*10^{-3}$ ng/g of PFOS in municipal tap water in Chicago and Cleveland. Interestingly, 1,700 – 4,000 ng/g PFOS was detected in the liver of the

Canadian Arctic polar bear.[13-15] Other studies reported about 2-8 ng/g of PFOA had been found in human serum from industrialized countries and about $5*10^3$ $-12*10^4$ ng/g of PFOA had been reported in public water systems.[11,16-23] Potential PFC exposure pathways to humans include ingestion from food and water, using PFCs based commercial products, or by inhalation of PFCs contaminated aerosols from the air.[6,24] The wide distribution, long-term accumulation and the persistence of PFCs has provided an opportunity for bioaccumulation and bio-concentration as they are transferred from low to higher trophic level organisms in the food chain.[25,26]

PFCs have many potential pathways to enter the environment. There is clear evidence that humans and wild animals are exposed to PFCs; and they have potential negative effects to human health and the environment, described below.

1.2.2 Potential toxicity of PFCs

In animal research, PFCs have been reported to disrupt the normal endocrine activity; reduce the function of the immune system; cause negative effects on multiple organs, such as liver and pancreas; and cause developmental problems for rodent offspring where the parents have been exposed to PFCs.[12,31] A report in 2011 found that PFOA delays the development of the mammary gland in mice.[32] One study in 2003 concluded that PFOS can cause negative effects on brain neurotransmitters in the neuroendocrine systems of rats.[33] Long term exposure to PFOA and PFOS can cause tumor development in the liver of rats.[6,34] Both PFOA and PFOS have a very high affinity to bind liver fatty acid-binding protein and the B-lipoproteins.[17] Indeed, several other animal studies shown that PFCs can inhibit the fatty acid metabolism and potentially deregulate the metabolism processes on lipids and lipoproteins.[35,24]

For humans, it was reported that a continuing exposure to low levels of PFOA in drinking water can result in adverse health effects.[11] Unlike other recalcitrant chemicals that accumulate in

fat, fluorinated chemicals bind to proteins in blood and can accumulate and damage organs such as the liver.[16,17] From toxicology studies, PFOA and PFOS can be absorbed rapidly after oral exposure and be accumulated mainly in the serum, kidney and liver with no further metabolism.[24,25] The human body cannot metabolize or rapidly eliminate PFCs. The estimated half-life of PFOA and PFOS in the human body ranged from 2 – 9 years, depending on the study.[17] This long half-life with the continued exposure can result in levels that would cause negative outcomes on human health .[6,24,36,37] A retrospective cohort mortality study involving more than 6,000 PFOA exposed employees at an industrial plant showed high mortality ratios for kidney cancer and statistically higher diabetes mortality for male workers.[13,38] Other studies have shown that PFCs can cause negative effects on reactive oxygen species and can damage the deoxyribonucleic acid (DNA) in human liver cells.[39,40] A study from the U.S. National Health and Nutrition Examination Survey indicated that higher concentrations of serum PFOA and PFOS are related with thyroid disease in the general adult population.[41] Other epidemiologic studies show relationship between PFOS exposure and bladder cancer.[13,42] Another study of West Virginia and Ohio populations showed a relationship between exposure to PFOA from contaminated water and testicular cancer, kidney cancer, clinically raised cholesterol level in adults and children, changes in thyroid hormone levels, pregnancy induced hypertension, and ulcerative colitis.[43] A general public study has shown that PFOA is potentially associated with decreased sperm count, low birth weight, and current thyroid disease.[12] There was no clear conclusion from mentioned studies that PFCs will cause fatal health problems to humans in these studies. However, these studies have shown PFCs are related with negative effects on humans.

Based on gathered PFOA cancer data, in May 2015, the EPA Science Advisory Board suggested that PFOA is "likely to be carcinogenic to humans", however additional research is

required for a final conclusion.[44,45] Based on animal research, PFOA has been classified as a Group A3 carcinogen by the American Conference of Governmental Industrial Hygienist.[46] PFCs are recently considered as emerging contaminants by EPA. In January 2009, the U.S. EPA issued provisional health advisories (PHAs) for short term exposure level for both PFOA and PFOS in drinking water. These values are $0.2*10^6$ ng/g for PFOS and $0.4*10^{-6}$ ng/g for PFOA.[27] After these PHAs, in the same year, $6*10^3$ ng/g for PFOS and $16*10^3$ ngg for PFOA was chosen by U.S. EPA as the residential soil screening levels.[28] Since 2002, U.S. EPA has enforced manufacturers to phase out or limit the use of PFCs, including PFOA and PFOS.[29] In 2002, monitoring of PFOA and PFOS by U.S. EPA has begun under the third Unregulated Contaminant Monitoring Rule (UCMR 3).[30] Most recently, in 2015, PFOA and PFOS were listed by U.S. EPA on its Draft 4th Contaminant Candidate List.[6]

1.2.3 Persistence of PFCs in the environment

PFOA and PFOS are the end products of abiotic and biotic transformation of PFCs precursor substances, such as fluorotelomer alcohols, fluorotelomer iodides, and fluorotelomer olefins, and they are very stable.[47] Their unique chemical structure makes PFCs chemically and biologically stable from environmental degradation processes, including photo-oxidation, direct photolysis and hydrolysis; this makes them become extremely persistent in the environment.[34,48]

A study, which were performed from 1972 to 1978, concluded that PFOA is completely resistant to biodegradation.[49] These studies suggested that PFCs are likely to persist in the environment for a very long time despite microbial catabolism.[50] Other studies shown that PFOA will not break down in water through either aqueous photolysis or hydrolysis.[51,52] These studies also indicate PFOA does not degrade by any known natural degradation mechanism, including hydrolysis, photolysis, or biodegradation.[51,52]

PFCs will not be degraded in human or animal gut, and remain unchanged in the body for a long time. A study in 1970s showed that PFOA and PFOS are not biodegradable even in an activated sewage sludge; this study was performed on a medium rich in microbes.[50] For comparison, consider that another well-known persistent chemical, DDT has half-life of seven hours in activated sewage sludge,[53] Aroclor 1242 is 28 days in activated sewage sludge,[53] and the half-life of Dieldrin is 15 years in soil field plots.[53] Only PFOA, PFOS, and other terminal breakdown products of PFCs are not degraded at all, even with the activated sewage sludge and hence are considered to have an infinite half-life.[54]

Another study showed that some PFCs can break down, but the breakdown chain will stop at PFOA and PFOS where they become non-biodegradable.[55] From all the mentioned evidence, PFCs, especially PFOA and PFOS, are extremely persistent chemicals which are persistent over very long time frames in the environment.

1.2.4 Chemical Properties of PFOA

Perfluorooctanoic acid

Figure 1: The chemical structure of PFOA
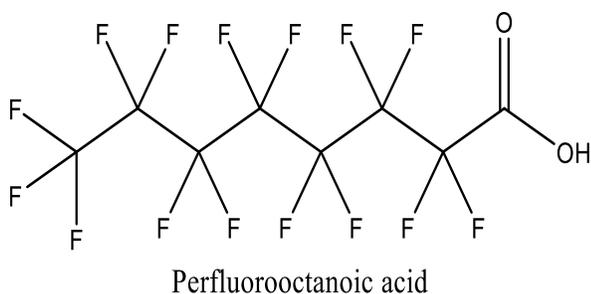
Unlike most of the organic compounds, PFCs are organo-fluorine compounds where some or all of the alkyl positions on the carbon chain are occupied by fluorine (instead of hydrogen), and usually the molecule will also contain a terminal oxygen-containing functional group (Fig. 1).[30] PFCs have very unique properties due to the fluorocarbons bonds in their chemical structures.

PFCs are highly polar compounds with very strong bonds due to the high dipole moment of the carbon-fluorine bond.[56] This contributes to them being very recalcitrant compounds, i.e. highly resistant to natural breakdown processes such as hydrolysis, photolysis and thermal- and bio-degradation.[50]

PFOA is a perfluoralkyl carboxylate, which is produced as a salt; and ammonium salt is the most common produced form.[8,35] PFOA has a very low volatility (Table 1) because of its ionic nature (pKa = 2.8). In the anionic form, PFOA are soluble in water and they can migrate rapidly from soil to groundwater and travel long distances from there.[10,11] This is consistent with the low organic-carbon partition coefficient (Koc) (Table 1). The Koc value indicates the ratio of mass of the target organic compound that is adsorbed in the soil per unit mass of organic carbon which present in the soil at the equilibrium condition. The low Koc value indicates that PFOA transport is not retarded by sorption to organic matter in the soil environment. Contaminated food and drinking water are considered to be the main PFOA contributors.[17] There is evidence that PFOA in drinking water has resulted in elevated blood levels with a biomagnifying factor of 100.[17] PFOA also has a very long half-life in water (Table 1), therefore, it has become a concern for the environment.

Property	PFOA
Chemical Abstract Service Number	335-67-1
Physical Description	White powder/ waxy white solid
Molecular Weight (g/mol)	414
Water Solubility at room temperature (mg/L)	9.500 (purified)
Melting Point (^{o}C)	45 to 54
Boiling Point (^{o}C)	188 to 192
Vapor Pressure at 20 ^{o}C (mm Hg)	0.017
Octanol-water Partition Coefficient (log K_{ow})	Not measurable
Organic-carbon Partition Coefficient (log K_{oc})	2.06
Henry's Law Constant (atm-m^3/mol)	Not measurable
pKa	2.8
Half-life	Atmospheric: 90 days Water: > 92 years (at 25 ^{o}C)

Table 1: Physical and Chemical Properties of PFOA. [17,24-28,30]

1.2.5 Iron-activated persulfate oxidation and PFCs

The persulfate anion is a strong oxidizing agent, and can be reduced to sulfate anions by two electron transfer with a standard half-cell potential of 2.12 V.[57]

$$S_2O_8^{-2} + 2e^- \rightarrow 2SO_4^{2-} \qquad [1]$$

Under high temperatures, persulfate can form sulfate free radicals that exhibit an even higher standard redox potential of 2.6 V, and these may be capable of degrading PFOA and PFOS at contaminated sites.[57]

$$S_2O_8^{2-} + heat \rightarrow SO_4^{\bullet -} \qquad [2]$$

Previous studies have tested the degradation of PFOA and PFOS under hydrothermal conditions or hydrothermal microwave for potential application to contaminated field sites.[57] However, these methods have several disadvantages, such as high energy cost, and they are not feasible for larger contaminated sites. A metal activator such as Fe^{2+} can be used in the absence of heat to also create free radical $SO_4^{\bullet -}$[57]:

$$Fe^{2+} + S_2O_8^{2-} \rightarrow Fe^{3+} + SO_4^{\bullet -} + SO_4^{2-} \qquad [3]$$
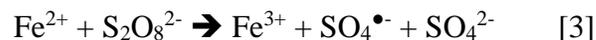
Introducing iron in water has been proposed to promote the hydrothermal decomposition of PFOS.[58] Thus, decomposition by IAPO could be an inexpensive, rapid, and feasible method for in-situ treatment, and an environmentally-friendly method which is used to remediate PFOA in soil and groundwater.

Moreover, persulfate may be the best oxidant that is feasible for ISCO for environmental applications. From common chosen oxidants by EPA for groundwater treatments, persulfate is one of the most persistent oxidants with high redox potential.[59] This is one of the most important factors for ISCO. The higher persistence of the oxidant the longer contact time for advective and diffusive transport processes to occur, so the oxidant can be delivered to the target zones.

1.3 Thesis formatting

This thesis is prepared to introduce the reasons for constructing experiments, methods and gathered results from the manuscripts in Appendix A. This manuscript is formatted for submission to *Environmental Science & Technology*. Most of the performed experiments and gathered results were prepared and done in ALEC. Both the persulfate and Fe^{2+} analyses in reactors were performed by appropriate colorimetric assays and the concentrations were measured by UV-VIS spectrophotometer. Total Fe concentration in reactors was measured by inductively coupled plasma mass spectrometry with the support from Mary Kay Amistadi. Fe^{3+} was determined from the difference between total Fe determined and measured Fe^{2+}. Concentration of PFOA in collected samples were analyzed by using ultra-performance liquid chromatography coupled with quadrupole time of flight mass spectrometry (UPLC–qTOF-MS/MS). Chromatographic separation was performed using a Waters XBridge C18 column (2.1 mm x 50 mm x 2.5 uM).

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CHAPTER II- PRESENT STUDY

Motivation and rationale to investigate the potential of IAPO reaction in degrading PFOA to less harmless species to humans and the environment are relayed in the following sections. A schematic about the rationale and impacts of the study to the environment are also included in this chapter, under the working assumption that the lab bench scale experiments gave positive results. A brief description of starting chemicals and their storage conditions chose for the study are also included. This chapter also presents the discussion of major findings in the study. The completed report which includes methods, gathered results, and discussion is presented in the Appendix A.

2.1 Rationale and Potential Environmental Impacts of the Study

Studying the feasibility of IAPO reaction in degrading PFOA at the lab bench scale is an essential to investigate whether the IAPO reaction is able to degrade PFOA in a cheap and environmentally-friendly way. This study gives us an opportunity to investigate several environmental factors that could potential alter the efficiency of the IAPO reaction in degrading PFOA, such as light, presence of oxygen or pH. Assessing the impact of these factors will allow us to determine if this reaction is feasible to be applied to the environment.

If these lab bench scale experiments in this study give us positive results, this will become a fundamental first step to applying the scheme at the field scale. In addition, this method could be applicable for surface water sources such as potable water reservoirs, waste water effluent, and extracted groundwater.

2.2 Study Objectives and Associated Approach

To determine the feasibility of IAPO reaction in degrading aqueous PFOA, the following tasks were performed:

1) Measure the changing PFOA concentration as a function of treatment and time.

2) Measure the changing persulfate (PS) concentration as a function of treatment and time.

3) Quantify the changing Fe^{2+}, Fe^{3+}, and total Fe concentration as a function of treatment and time.

4) Investigate the extent to which PFOA is absorbed to the surface of the neo-formed ferrihydrite nanoparticles (the potential final form of the starting material, Fe^{2+}, at the end of the IAPO reaction) under reaction conditions.

In this study, we tested the IAPO reaction in various conditions, including oxic, anoxic, anoxic/dark conditions. A number of controls were also tested in the study. These controls included:

(1) A PFOA solution alone to check the stability of PFOA as a function of time.

(2) A cocktail of PFOA with only Fe^{2+} to check the effect of Fe^{2+} on PFOA.

(3) A cocktail of PFOA plus PS to check whether PS alone could have any effect on PFOA

(4) A cocktail of PS plus Fe^{2+} to analyze levels of monitored analytes and rule out interactions between reactor vessels, lab equipment, and IAPO reactants.

In performed experiments, the concentration of PS in each reactor was determined by reacting with a cocktail of sodium bicarbonate (EMD, A.C.S. grade) and potassium iodide (Amresco, A.C.S. grade) for at least 20 min, followed by measurement of absorption at 400 nm using an UV-VIS Spectrophotometer (Shimadzu, UV-2501PC, Colombia, MD). Ferrous iron (Fe^{2+}) concentration of each reactor was determined by measuring the absorption at 562 nm of the

complexes between aqueous Fe^{2+} with FerroZine iron reagents (FZ, Acros Organics, 98 +% pure) using UV-VIS Spectrometry (as in PS analysis). Total Fe concentration of each reactor was measured by inductively coupled plasma mass spectrometry (ICP-MS, Perkin Elmer, Elan DRC-II, Shelton, CT). Ferric iron (Fe^{3+}) was calculated from the difference between total Fe determined by ICP-MS and Fe^{2+} measured by ferrozine assay. In all experiments, the concentration of PFOA in collected samples was analyzed using ultra-performance liquid chromatography (DIONEX, Ultimate 3000 RSLC, Sunnyvale, CA) coupled with quadrupole time of flight mass spectrometry (UPLC–qTOF-MS/MS, ABSciex, TripleTOF 5600, Framingham, MA). Chromatographic separation was performed using a Waters XBridge C18 column (2.1 mm x 50 mm x 2.5 uM; Milford, MA) maintained at 30°C. For the adsorption experiments, the reactants used to synthesize ferrihydrite included $Fe(NO_3)_3 \cdot 9H_2O$ (J.T. Baker, reagent grade 98.8%), and NaOH (Alfa Aesar, 10.0 N standardized).

2.3 Selected Reactants and their Chosen Storage Conditions for the Study

In this study, ascorbic acid (ASC) was chosen as a quencher for the IAPO reaction to allow us to get the accurate measurements on the changing of PFOA concentration over time during the course of the IAPO reaction. ASC is an unstable when in solution, especially in the presence of oxygen and degrades markedly in the presence of metal ions (particularly Cu and Fe).[1,2] Thus, in this study, any ASC solutions had restrictive conditions:

1) ASC solutions are very unstable at alkaline pH. Hence, all the pH of ASC solutions in this study was kept at 5-6. pH was adjusted by H_2SO_4.[1,2]

2) These solutions were kept in a dark condition. Thus, all ASC solutions in this study was kept in amber bottles.

3) These solutions were made on the same day before the experiment was performed.

4) According to previous studies, 4 mol of ascorbic acid can quench 1 mol persulfate.[3] Moreover, 4-40 mol of ascorbic acid will show no effect on LC-MS/MS analysis.[3] Thus, in this study, about 20 mol of ascorbic acid was used to quench 1 mol persulfate to ensure safety.

Fe^{2+} solutions can be oxidized slowly by air when cold or rapidly when hot.[4,5] The oxidation rate will increase by exposing to light or alkali conditions.[4,5] Also, PS solution will not be stable under room temperature even under dark and anaerobic conditions.[4] Therefore, these solutions had some restrictive conditions in this study:

1) Solutions were kept at pH range from 2 to 4. pH was adjusted by H_2SO_4.

2) Solutions were kept in metal-free polypropylene tubes.

3) Reagent solutions were freshly made on the same day the experiment was performed.

2.4 Tested Conditions for Reactors of the Study

Fe^{2+} is rapidly oxidized to Fe^{3+} in the presence of dissolved oxygen, and Fe^{2+} is one of the starting materials in the IAPO reactions. Therefore, any factors that can affect the concentration of Fe^{2+} concentration at the beginning of IAPO reaction will also change the efficiency of IAPO reaction in degrading PFOA. Thus, in this study, we tested the efficiency of the IAPO reaction in degrading PFOA under oxic and anoxic conditions.

A previous study[6] showed that sunlight can reduce Fe^{3+} to Fe^{2+} by photocatalytic reaction. Thus, IAPO reaction was also tested under the anoxic condition without light to determine the effect of light on IAPO in degrading PFOA.

2.5 Summary of Obtained Results

2.5.1 PFOA removal during reaction treatments

From controls outlined in the previous section, this study observed that there was no significant change in concentration of PFOA in the controls, and the background contamination level contributed from the cocktail between PS and Fe^{2+} was negligible. Hence, this study concluded that either PS or Fe^{2+} alone has no effect on PFOA degradation, and the background contamination level from the interactions between reactants of IAPO, reactor vessels and lab equipment was negligible.

The gathered data indicated that *ca*. 64% of PFOA was degraded after 4 h under the anoxic condition, and only 9% was degraded under oxic condition; seven times less effective than the anoxic condition. From the anoxic/dark condition, only *ca.* 12% of PFOA was transformed by IAPO reaction after 4 h. A more detailed discussion of these finding is presented in Appendix A.

2.5.2 PS concentrations as a function of reaction time

From gathered data, we observed that PS concentration in each experiment rapidly decreased in the first 5 min and then more slowly over the next 4 h. In the first 5 min, *ca*. 67.7%, 64.3%, and 88.2% of PS was consumed under anoxic, oxic and anoxic/dark conditions respectively. This indicated more PS was consumed under the anoxic/dark condition, whereas anoxic and oxic conditions had similar PS consumption rates in the first 5 min of IAPO reaction.

After 4 h of IAPO reaction, *ca*. 89.5%, 90.7%, and 92.6% of PS was consumed under anoxic, oxic and anoxic/dark conditions respectively. These data indicate a relatively small increase in PS consumption between 5 min and 4 h. However, similar PS consumption rates in the various treatments did not result in comparable PFOA degradation rates. A more detailed discussion will be mentioned in Appendix A.

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2.5.3 Changing Fe^{2+}, Fe^{3+}, and Total Fe Concentrations at Tested Conditions

Similar to the trends observed in PS data, most of the major changes in concentration of Fe^{2+}, Fe^{3+}, and total Fe under oxic, anoxic, and anoxic/dark conditions were observed in the first 5 min of the reaction. For Fe^{2+} in the first 5 min, *ca.* 71.9%, 61.3%, and 94.8% of Fe^{2+} was consumed under anoxic, oxic and anoxic/dark conditions respectively. The total Fe concentration in these conditions were constant during the reaction, therefore, we believe most of consumed Fe^{2+} was transformed into Fe^{3+}. For Fe^{3+} in the first 5 min, *ca.* 170, 131, and 215 mg L^{-1} of Fe^{3+} was produced under anoxic, oxic and anoxic/dark conditions respectively. This indicated more Fe^{2+} was consumed and more Fe^{3+} was produced under anoxic/dark condition for the first 5 min.

After 4 h, *ca.* 61%, 99.5%, and 86.1% of Fe^{2+} was consumed under anoxic, oxic and anoxic/dark conditions respectively. For Fe^{3+}, *ca.* 144, 221 and 198 mg L^{-1} of Fe^{2+} was produced under anoxic, oxic and anoxic/dark conditions respectively. According from these final data points, they generally indicated Fe^{3+} was more dominant under oxic condition, and more Fe^{2+} remained under anoxic condition. We observed re-bound behavior of Fe^{2+} in all three conditions, especially under anoxic/dark conditions where 38% of Fe^{2+} was re-generated while the previous point showed only 1.9% Fe^{2+} was left in the reactor. From these gathered data, we observed that the IAPO reaction is a cycle reaction where Fe^{2+} was converted into Fe^{3+} at first, then Fe^{3+} will gain an electron from the oxidant to re-generate Fe^{2+}. See Appendix A for more detailed explanation.

2.5.4 PFOA Adsorption Test on Ferrihydrite

From the collected data, after 4 h reaction with Fh, only *ca.* 2 % PFOA was removed from solution. This implied that the adsorption process of PFOA on the surface of Fh was negligible in this study. Therefore, this confirmed that the major decreasing trend over time of PFOA observed

from anoxic IAPO reactors was mainly because of the oxidation interaction between starting materials from the IAPO reaction and PFOA.

2.6 Summary of Conclusions

The results of this study indicate that Fe^{2+} is a key factor controlling the efficiency of IAPO reaction in degrading PFOA. Fe^{2+} is rapidly oxidized to Fe^{3+} in the presence of dissolved oxygen, and Fe^{3+} will not donate any electron to PS form sulfate free radical to degrade PFOA.

In this study, we concluded that the IAPO reaction can degrade PFOA at ambient temperatures under anoxic conditions. This can be a cheaper, more efficient and environmentally friendly *in-situ* treatment for contaminated sites. However, this technique is still very situational for *in-situ* treatment. Therefore, further study is needed to investigate the performance of this technique at a real field scale. A more detailed conclusion can be found in Appendix A.

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APPENDIX A

Degradation of PFOA in water by Iron-Activated Persulfate Oxidation

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ABSTRACT: Perfluorinated compounds (PFCs) are highly resistant to natural breakdown processes such as heat, hydrolysis, photolysis and biodegradation. Due to their widespread exposure to humans, persistence in the environment, and potential toxicity, there is a need to develop methods to degrade these chemicals to less harmful species. Here we report that decomposition by ferrous iron-activated persulfate oxidation can be accomplished at ambient temperatures and potentially used as an inexpensive and environmentally-friendly method to remediate PFCs in soil and groundwater. In this study, we tested the reaction under oxic, anoxic, and anoxic/dark conditions. We found that ca. 64% of perfluorinated octanoic acid (PFOA, $C_8HF_{15}O_2$) (the initial concentration was $1.64*10^{-6}$ mol L^{-1}) was transformed after four hours under anoxic conditions. This degradation rate was about seven times greater than oxic conditions and about five times greater than anoxic/dark conditions.

1. INTRODUCTION

Perfluorinated compounds (PFCs) are anthropogenic organic compounds with an aliphatic chain-like structure where all of the hydrogens atoms have been replaced by fluorine atoms and generally comprising one polar functional group at the end of the carbon chain.[1,2] Perfluorooctanoic acid (PFOA) is used in the manufacturing of Teflon® and is the most common active ingredient in the aqueous film-forming foam which was historically used for fire-fighting activities, particularly on military bases. Due to its remarkable degradation resistance, and its low affinity for adsorption to the surfaces of natural particles, PFOA has been found in drinking water, sea water, and other naturally occurring water sources.[2-9] PFOA is one the most common PFC found in groundwater.[2-4] Previous studies have shown large amounts of PFOA have been released in to the natural environment, about 2-8 ng/mL of PFOA has been found in human serum from industrialized countries and about 5-120 ng/L was reported in public water systems.[1-9] A recent study reported

that PFOA is one of the most difficult PFC compounds to degrade.[10] Therefore, due to its potential toxicity to humans there is a need to develop methods to degrade PFOA to harmless species.[1]

Persulfate (PS) oxidation is a relatively new remediation method that has been applied to the decomposition of many organic contaminants, and has promise as an *in situ* remediation technique. .[11-16] The PS oxyanion ($S_2O_8^{2-}$) is a strong oxidizing agent that can be reduced to sulfate anions, as shown in Eq. (1) below, with a standard half-cell potential of 2.0 V.

$$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-} \qquad (1)$$

Moreover, a metal activator such as Fe^{2+} can be used under ambient conditions to enhance PS to form the sulfate free radical ($SO_4^{\bullet-}$), as shown in Eq. (2). The half-cell potential for reduction of $SO_4^{\bullet-}$ has a higher redox potential of 2.6 V.[17-24]

$$Fe^{2+} + S_2O_8^{2-} \rightarrow Fe^{3+} + SO_4^{\bullet-} + SO_4^{2-} \qquad (2)$$

Previous studies have demonstrated the brake-down PFOA by coupling PS with Fe^{2+} under hydrothermal or hydrothermal microwave conditions.[19-23] However, this technique is only feasible under laboratory conditions and would be costly for larger contaminated sites and *in situ* remediation. Therefore, in this study we investigated the decomposition of PFOA by iron-activated persulfate oxidation (IAPO) at ambient temperatures to determine if the technique could be used as an inexpensive and environmentally friendly method to remediate aqueous PFOA. This method may also be relevant for other emerging persistent contaminants such as 1,4-dioxane, and estrogens. Additionally, this could be applicable for surface water remediation applied to potable water reservoirs, waste water effluent, and extracted groundwater.

2. EXPERIMENTAL METHODS

Materials and Preparation of Reactants. All lab supplies in contact with PFOA samples were polypropylene (PP) to avoid adsorption of to labware,.[25] All equipment and containers used for sample preparation were cleaned using established EPA methods.[25] A $2.17*10^{-6}$ mol L^{-1} PFOA (AccuStandard) stock solution was dissolved in LC-MS grade water (OmniSolv) and contained in a PP bottle and maintained under refrigeration (4^oC) until use. Potassium persulfate ($K_2S_2O_8$,EM Science) was used for the PS solution . Ferrous sulfate 7-hydrate ($FeSO_4·7H_2O$, J.T.Baker, A.C.S Reagent) was used for Fe^{2+}. $4.0*10^{-3}$ mol L^{-1} L-(+) ascorbic acid (ASC [$C_6H_8O_6$], Alfa Aesar 99+%) was used as a redox reaction quencher for the IAPO reaction in this study,[26] All reactants were dissolved in LC-MS grade water (OmniSolv) and contained in PP tubes. LC-MS grade water at pH 2 was used to dissolved PS and Fe^{2+}, with pH adjusted by 18 mol L^{-1} H_2SO_4 (BDH Aristar Plus, ≥ 95%). Solutions were prepared immediately before all performed experiments.

Reaction Procedures. Each experiment was carried out in triplicate in 15 mL PP tubes, referred to as reactors. Replicated reactors ran simultaneously at the same conditions and concentrations. In each experiment, *ca.* $1.69*10^{-6}$ mol L^{-1} PFOA plus $5.7*10^{-3}$ mol L^{-1} PS and $3.99*10^{-3}$ mol L^{-1} Fe^{2+} were added to each reactor. Aliquots were transferred from each reactor, at five time-points over 240 min total, to PP containers for analyses (PS, Fe^{2+}, total Fe, and PFOA). For PFOA analysis, $4.0*10^{-3}$ mol L^{-1} of ASC was used as a redox inhibitor to quench the reaction. The pH was monitored in the reactor with an ISFET silicon chip sensor pH probe (minilab, IQ125), was calibrated and checked by buffer solutions, pH 4 and 7 (J. T. Baker, Analyzed Reagent).

Three different treatment conditions were tested in this study: oxic under laboratory lighting, anoxic under laboratory lighting and anoxic in the dark. For the oxic-light experiment, all reactions were performed under ambient laboratory conditions. For anoxic reactions, all solutions−were

flooded by $N_{2(g)}$ to eschew the presence of oxygen, and reactions were conducted in an N_2 filled glove box (830-ABC, Plas-Labs, Lansing MI). The anoxic/dark conditions were the same as the anoxic-light experiment except that all the reactors were covered by aluminum foil to prevent light exposure.

Persulfate Analysis. Persulfate concentration of each reactor was measured as at designated time steps using the standardized method of Liang et al..[12-14] PS in each sample was determined by reacting with a mixture of sodium bicarbonate (EMD, A.C.S. grade) and potassium iodide (Amresco, A.C.S. grade) for 20 min, and absorption measured at 400 nm using an UV-VIS Spectrophotometer (Shimadzu, UV-2501PC, Colombia, MD).[12-14] The wavelength of 400 nm is not the most sensitive wavelength for PS; however, it was used because the interference by aqueous Fe is minimized.[13,14] Detailed procedures are described in the **SI**. A stock solution of PS was prepared, and this was then diluted to create calibration standards with concentrations ranging from 0 mol L^{-1} to $5.7*10^{-3}$ mol L^{-1} in PP tubes. Calibration curves were constructed based on linear regression of absorption at 400 nm versus PS concentrations in the standard solutions, and highly linear relations were obtained (e.g., $R^2 > 0.999$). Calibration standards were run prior to sample analysis.

Fe^{2+}, Fe^{3+} and total Fe Analysis. Ferrous iron concentration of each reactor was determined by FerroZine iron reagents measured at 562 nm (FZ, Acros Organics, 98 +% pure) using UV-VIS Spectrometry (as in PS analysis).[27,28] A buffer at pH 9.5 was made from 5 mol L^{-1} ammonium acetate (EMD, A.C.S crystals) with the pH adjusted with *ca.* 28-30 % ammonium hydroxide (Fisher Scientific, Certified A.C.S Plus) to stabilize all collected samples and standards. The detailed procedure is provided in the **SI**. The standards were made with a Fe^{2+} concentration range from $3.58*10^{-6}$ - $3.58*10^{-5}$ mol L^{-1} and contained in PP tubes. Calibration standards were run with

the collected samples ($R^2 > 0.999$). Any collected sample from reactors with an observed absorbance larger than 1 or outside the range of calibration curve was diluted by pH 2 LC-MS grade water before adding the FZ solution.

Total Fe concentration of each reactor was measured by inductively coupled plasma mass spectrometry (ICP-MS, Perkin Elmer, Elan DRC-II, Shelton, CT), with an ammonium gas dynamic reaction cell to destroy isobaric molecular interferences. Ferric iron (Fe^{3+}) was calculated from the difference between total Fe determined by ICP-MS and Fe^{2+} measured by Ferrozine assay.

PFOA Adsorption Test. During IAPO, Fe^{2+} is oxidized to Fe^{3+}, which is then precipitated as ferric hydroxide. It is expected that Fe^{3+} in the collected samples was ferrihydrite (Fh). Previous studies indicated that PFOA can adsorb to the surface of Fh.[29,30] Therefore, synthetic Fh was utilized as a control to assess potential adsorption of PFOA. The Fh was synthesized by a standardized procedure.[31] An aliquot of $5.33*10^{-6}$ mol L^{-1} of Fh was added to each reactor in triplicate, based on the maximum Fh that could precipitate assuming all added Fe^{2+} converted to Fh. The reactions were performed under the same conditions as described above. The final concentration of PFOA after 4 h was measured to test for potential absorption of PFOA to the surface of Fh.

PFOA Analysis. To generate the calibration standards, PFOA stock solution in methanol was diluted to final concentrations ranging from $2.42*10^{-7}$ to $2.17*10^{-6}$ mol L^{-1} by LC-MS grade water. Calibration samples were run the same day as samples using ultra-performance liquid chromatography (DIONEX, Ultimate 3000 RSLC, Sunnyvale, CA) coupled with quadrupole time of flight mass spectrometry (UPLC–qTOF-MS/MS, ABSciex, TripleTOF 5600, Framingham, MA). Chromatographic separation was performed using a Waters XBridge C18 column (2.1 mm

x 50 mm x 2.5 uM; Milford, MA) and the column was kept at 30°C. Detailed procedure is provided in the **SI**.

3. RESULTS AND DISCUSSION

PFOA removal during reaction treatments. A number of controls were conducted in this study including (1) a PFOA solution alone to check the stability of PFOA, (2) PFOA with only Fe^{2+} to check the effect of Fe^{2+} on PFOA, (3) PFOA plus PS to check whether PS alone could have any effect on PFOA, and (4) PS plus Fe^{2+} to analyze levels of monitored analytes and rule out interactions between reactor vessels, lab equipment, and IAPO reactants. The controls were performed under anoxic condition, which was the condition with highest degrading rate of PFOA observed. The monitored concentrations in the controls remained stable, indicating no positive or negative interferences. No significant change in concentration of PFOA was observed in these controls, and the background contamination level contributed from the cocktail between PS and Fe^{2+} was negligible because the PFOA concentration below the detection limit was observed in this mixture (Figure 1a). From this study we concluded PS and Fe^{2+} alone will have no effect on PFOA, and the background contamination level from the interactions between reactants of IAPO, reactor vessels and lab equipment was negligible.

The concentrations of PFOA in the IAPO reactors were measured under oxic, anoxic, and anoxic/dark conditions. The data indicate that *ca.* 64% of PFOA was degraded after 4 h under anoxic condition, and only 9% was degraded under oxic condition; seven times less effective than the anoxic condition (Figure 1b). Fe^{2+} is a key factor in the formation of $SO_4^{\bullet-}$ and necessary to enhance the decomposition rate of PFOA by IAPO. Fe^{2+} is rapidly oxidized to Fe^{3+} in the presence of dissolved oxygen (DO), and Fe^{3+} does not promote the conversion of PS to $SO_4^{\bullet-}$. Earlier studies[18,23] of IAPO on PFOA show that there was no significant decrease in PFOA concentration

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at ambient temperature under oxic conditions. Our PFOA results (Figure 1b) demonstrate that IAPO on PFOA can be done at ambient temperature under anoxic conditions.

From previous studies[34], it was shown that sunlight can reduce Fe^{3+} to Fe^{2+} by photocatalytic reaction. Thus, we performed IAPO reactors under the anoxic condition without light to determine the effect of light on IAPO in degrading PFOA. Indeed, only *ca.* 12% of PFOA was reduced by IAPO reaction after 4 h under the anoxic/dark condition (Figure 1b). However, it was not clear that photocatalytic reaction of Fe was the reason for this effect. Under anoxic/dark conditions, more Fe^{2+} was still be consumed in the first 5 minutes but with the faster rate compared to the other two conditions. By comparisons, Fe^{2+}, under anoxic/dark conditions, was also quicker to rebound to a higher concentration, especially at *ca.* 90 min which will be shown in the next part. The PFOA decomposition efficiency was decreased during IPAO implied that the high quantity of Fe^{2+} ions might compete with sulfate free radicals and PFOA interaction to cause a lower decomposition efficiency of IAPO reaction on PFOA, this trend was also observed in a previous study.[23]

We also checked the efficiency of ASC in quenching the IAPO reaction. A pretreatment of ASC with PFOA, at similar concentration to that used in previous performed experiments, was added to each reactor before adding PS and Fe^{2+} under anoxic conditions. We found that ASC slowed, but did not stop, the IAPO reaction (Figure 1b). The anoxic reaction still exhibited a higher IAPO degradation rate than that observed in the oxic condition, whether ASC added before or after adding PS and Fe^{2+} in the reactors.
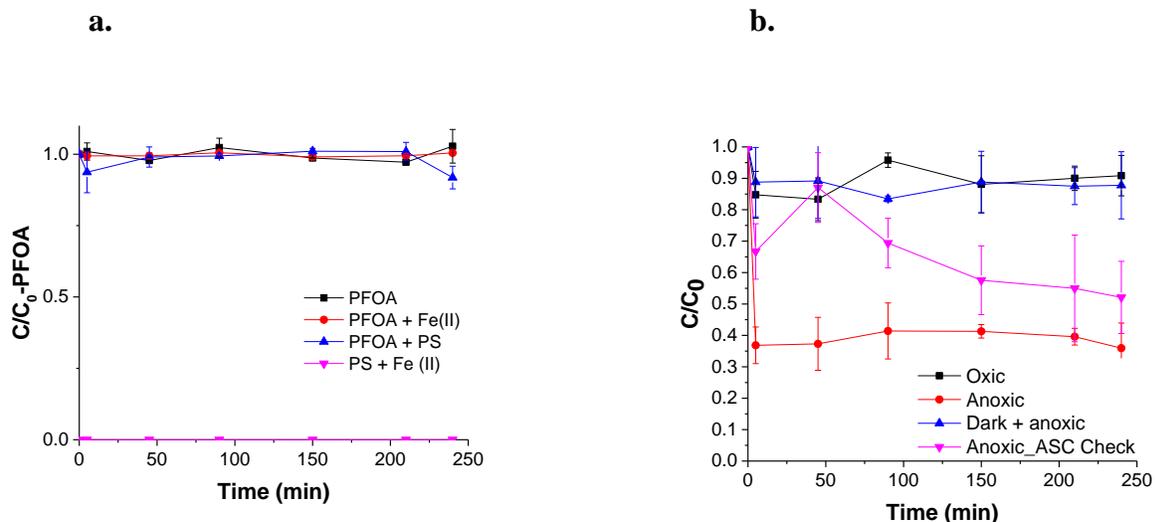
Figure 1. PFOA concentrations over time (C/Co) measured at different conditions for 4 h, including (a) controls performed under anoxic condition (oxygen free) to ensure the quality control and quality assurance of the study (b) at oxic (presence of oxygen), anoxic, anoxic/dark (oxygen free without light), and anoxic-ASC check (ASC at pH 5 was added in advance in the reactors with PFOA before adding the reactants of IAPO). Error bars indicate the standard deviation of triplicate reactors run at the same time with the same conditions and starting materials.

PS concentrations as a function of reaction time. PS was the chosen oxidant in this study, and along with ferrous iron, is one of the main reactants that will create sulfate radicals to degrade PFOA. Therefore, the concentrations of PS were measured in each experiment. IAPO is a very fast reaction; the PS concentration in each experiment rapidly decreased in the first 5 min and then more slowly over the next 4 h (Figure 2). This indicated PS was consumed by IAPO reaction to form the sulfate radical that effectively degrades PFOA. This followed the same trend as PFOA because the concentrations of PFOA degraded rapidly in the first 5 min.

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The anoxic/dark condition consumed PS at a faster rate compared to the oxic and anoxic conditions, which had very similar and slower PS consumption rates (Figure 2). This could indicate that a higher concentration of free radical sulfate was formed under the anoxic/dark conditions. Since Fe^{2+} was rebounded earlier with higher concentration later in the IAPO reaction under anoxic/dark conditions (Figure 3b), sulfate free radicals can interact with both Fe^{2+} and PFOA at the same time, so more persulfate will be consumed. Also, Fe^{2+} was consumed at the higher rate in the first 5 min under anoxic/dark conditions compared to the other two conditions, so more Fe^{3+} was produced under this condition (Figure 3b + 3c). PS can potentially donate an electron to Fe^{3+} to form persulfate radical and Fe^{2+} which shown in the Eq. (3).

$$Fe^{3+} + S_2O_8^{2-} \rightarrow Fe^{2+} + S_2O_8^{\bullet -} \qquad (3)$$
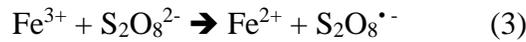
This explains the higher consumption rate of PS under anoxic/dark conditions compared to the other two conditions.

Also, there was a similar PS consumption rate between oxic and anoxic, but it did not mean similar amount of sulfate free radicals were formed, since it requires the donation electron from Fe^{2+} (Eq. 2). The concentrations of Fe^{2+} in the oxic and anoxic conditions did not behave the same, this will be shown in the next section of the report.
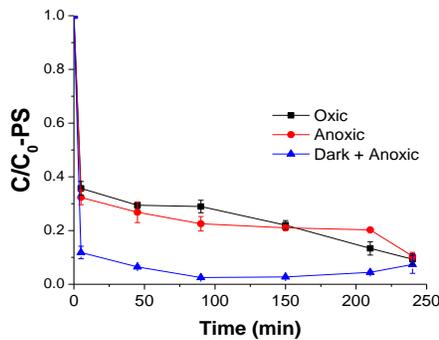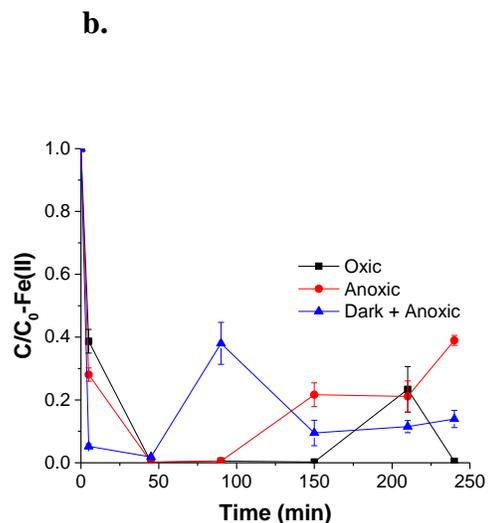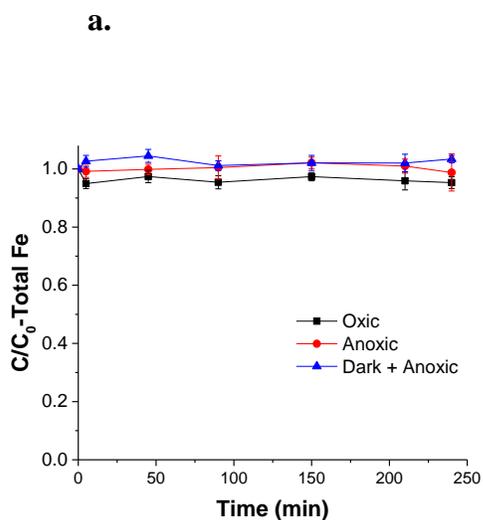
Figure 2. Concentrations (C/Co) of persulfate (PS) over time measured at different conditions for 4 hours, including under oxic (black), anoxic (red), and anoxic/dark conditions (blue). Error bars indicate the standard deviation of triplicate reactors run at the same time with the same conditions and starting materials.

Changing Fe^{2+}, Fe^{3+}, and Total Fe Concentrations at Tested Conditions. In this study, Fe^{2+} and Fe^{3+} are the two dominant species of Fe in the IAPO reactors. In this study, we observed that IAPO is a redox cycle reaction where oxidized Fe^{3+} can be reduced back into Fe^{2+} by gaining the electron from persulfate ions ($S_2O_8^{2-}$) (Figure 3b and 3c). Most of the Fe^{2+} was oxidized to Fe^{3+} in the first 5 min under oxic, anoxic and anoxic/dark conditions (Figure 3b and 3c). However, the redox cycle in the anoxic/dark condition had the earliest rebound of Fe^{2+} compared to the other two conditions (Figure 3b). This might indicate higher Fe^{2+} concentration was present in the reactors or more Fe^{3+} was produced in the first 5 min under anoxic/dark conditions (Figure 3c) compared to the other two conditions resulting in more PS consumed under this condition.

All these reasons could result in more PS consumed under anoxic/dark conditions compared to the other two conditions, which explained from the previous part. It was clearly shown that the redox cycle under the oxic conditions had the slowest Fe^{2+} rebound, and Fe^{3+} was stabilized for a longer time before it was reduced back to Fe^{2+}. This indicates that under oxic conditions, Fe is subjected to both oxygen and IAPO reactions in parallel. Therefore, Fe^{3+} was stabilized longer under the oxic condition which explains why less PFOA was degraded under this condition compared to other tested conditions. More Fe^{2+} observed under the anoxic/dark condition coincides with a decrease in the PFOA decomposition efficiency. This indicates that the dark condition is also an interference factor that can lower the efficiency of the IAPO reaction which will become a

challenge for in-situ remediation. However, the reason which caused the increase in Fe^{2+} concentrations in the IAPO redox cycle under anoxic/dark condition still remains unclear in this study. In this study, the concentration of Fe^{2+} is considered as the most important parameter that will influence the efficiency of IAPO in degrading PFOA.
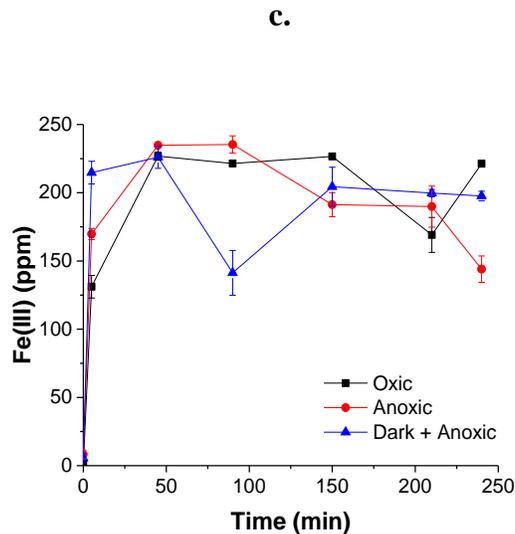
a.

b.

c.

Figure 3. Concentrations of Fe species, (a) total Fe, (b) Fe^{2+}, and (c) calculated Fe^{3+} in IAPO reactors over time (C/Co) measured at different conditions for 4 hours, including at oxic (black), anoxic (red), and anoxic/dark (blue). Error bars indicate the standard deviation of triplicate reactors were run at the same time with same the conditions and starting materials.

There was a large drop in pH to *ca.* 2.4 in the IAPO reactors in the first 5 min (Figure 4). This followed the same trend with other gathered data that IAPO reaction took place in the first 5 min. According to simulations performed using Geochemist's Workbench (version 10.0), [35] hydrolysis of Fe present at the concentrations measured in this experiment is capable of depressing the pH to about 2.5. Also, it has been reported that the hydrolysis constant of Fe^{3+} is about 2.19, and this should be the pH of a Fe solution where Fe^{3+} and $Fe(OH)^{2+}$ are at equilibrium.[36,37] Therefore, we believed the main reason that for this is from Fe^{3+} hydrolysis reaction where Fe^{3+} interacts with water to form $Fe(OH)^{2+}$ and releases hydrogen ions, which is shown in Eq. (4). [37]

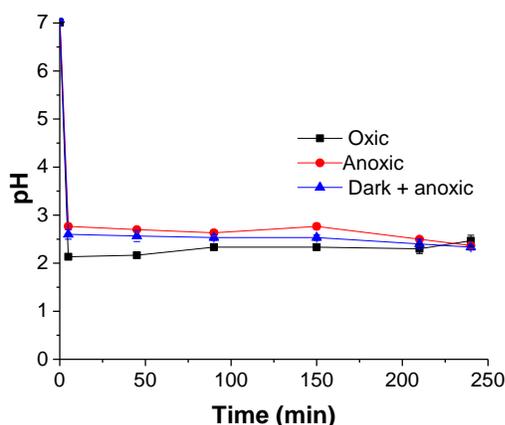$$Fe^{3+} + H_2O \rightarrow Fe(OH)^{2+} + H^+ \qquad (4)$$

Figure 4. pH in IAPO reactors run for 4 hours under oxic (black), anoxic (red), and anoxic/dark (blue) conditions. Error bars indicate the standard deviation of triplicate reactors run at the same time under the same conditions and with the same starting materials.

PFOA Adsorption Test on Ferrihydrite. From the collected data, only *ca.* 2 % PFOA was removed from solution after 4 h reaction with Fh at the pH *ca.* 3.0 (Figure 5), implying that the adsorption process of PFOA on the surface of Fh is negligible under the experimental conditions. From this study, we conclude the major decreasing trend over time of PFOA observed from anoxic IAPO reactors was mainly because of the oxidation interaction between sulfate free radicals from the IAPO reaction and PFOA.
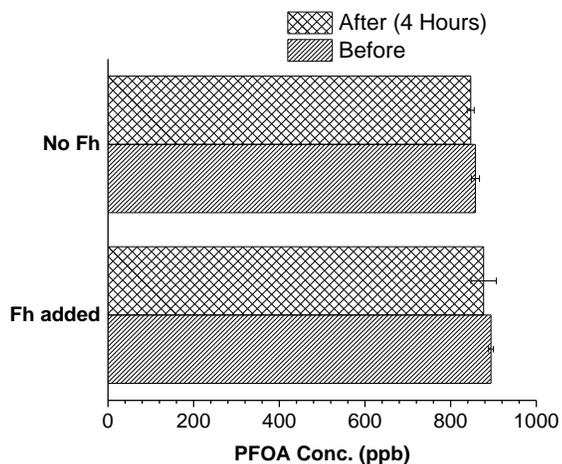
Figure 5. A comparison in PFOA concentration when no Fh and Fh were added for *ca.* four hours with the pH approximate at 3. Experiments were performed in under conditions with similar physical conditions to prior experiments where no rotation or mechanical mixing was applied. Error bars indicate the standard deviation of triplicate samples. The reactors in this experiment only contained PFOA and Fh. The amount of Fh in each reactor was similar to the amount of Fe^{2+} in reactors from prior experiments.

Environmental Implication. In this study, we discovered that IAPO reaction can degrade PFOA at ambient temperature under anoxic condition. This can be a cheaper, more efficient and environmentally friendly *in-situ* treatment for contaminated sites. Although, this technique is still very situational for *in-situ* treatment since exclusion of light and oxygen are the two main factors that cause the reduction in the PFOA decomposition efficiency in this study. Therefore, further study is needed to investigate the performance of this technique at the field-scale. Also, an isolation technique should be developed where reactants in the IAPO reaction can be isolated under anoxic condition before it can be delivered and interact with the contaminated plume at the site. Moreover, since this was an analytical experiment, all the starting materials was adjusted at the optimal pH, such as pH 2 for PS and Fe^{2+} solutions. This can be another challenge as the pH in subsurface systems would unlikely be able to be maintained at such low pH. Therefore, further study is needed to investigate the performance of this technique at a real field scale.

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Supporting Information

Degradation of Aqueous Perfluorooctanoic Acid by Iron-Activated Persulfate Oxidation

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Number of Figures: 0

- **EXPERIMENTAL METHODS**

Persulfate Analysis. Persulfate concentration of collected samples was determined using the developed method of Liang et al. [1-3] Collected samples were reacted with a cocktail of sodium bicarbonate ($NaHCO_3$, EMD, A.C.S. grade) and potassium iodide (KI, Amresco, A.C.S. grade) for 20 min, followed by measurement of absorption at 400 nm, where the interference by aqueous Fe is minimal, [1-3] using an UV-VIS Spectrophotometer (Shimadzu, UV-2501PC, Colombia, MD).

$NaHCO_3$ was dissolved in LC-MS grade water (OmniSolv) at a concentration of $5.95*10^{-2}$ mol L^{-1}. Then, KI was dissolved in the $NaHCO_3$ solution to the concentration of 0.6 mol L^{-1}. All the mentioned solutions were massed on the analytical balance to get the most accurate concentrations for stock solutions. 0.5 mL of collected sample was then transferred and mixed well with 9.5 mL of the KI-$NaHCO_3$ mixture in the polypropylene (PP) tube for 20 mins. Then, the absorbance value of the mixture was measured by UV-VIS Spectrophotometer at the wavelength of 400 nm. Calibration standards were also measured using the same procedure and they were always run prior to sample analysis.

Fe^{2+}Analysis (Ferrozine Assay). Fe^{2+} concentration of collected sample was determined by standardized method. [4-7] Collected samples were reacted with FerroZine iron reagents (FZ, Acros Organics, 98 +% pure) for 5 mins, followed by measurement of absorption at 562 nm using the same UV-VIS Spectrometer as for PS analysis. This mixture is stable at pH 4-10. [4-7] Also, this method is only applicable for solutions with concentrations of Fe^{2+} ranging from $1.79*10^{-7}$ – $5.37*10^{-5}$ mol L^{-1}. Therefore, any sample with an observed absorbance larger than 1 was diluted by pH 2 LC-MS grade water before adding the FZ solution. The pH of the LC-MS grade solution was adjusted by using sulfuric acid (BDH ARISTAR ULTRA, $\geq$ 95% pure). All containers which

came in contact with samples, calibration standards and reagents for the assay were cleaned with 10% nitric acid solution.

FZ was dissolved in LC-MS grade water at a concentration of 0.01 mol L^{-1} in a PP tube. This solution was freshly made on the same day prior to the experiments. A buffer at pH 9.5 was made by dissolving ammonium acetate (EMD, A.C.S crystals) in LC-MS grade water to a concentration of 5 mol L^{-1} with the pH adjusted with *ca.* 28-30 % ammonium hydroxide (Fisher Scientific, Certified A.C.S Plus). All the mentioned activities were massed on the analytical balance to get the most accurate concentrations for stock solutions. 1 mL of collected sample was mixed with 100 uL of the FZ solution, after which 50 uL of buffer solution was added. This cocktail stood for at least 5 mins for the color to fully develop. Then, the absorbance value of the mixture was measured by UV-VIS Spectrophotometer at a wavelength of 562 nm. Calibration standards were also measured using the same procedure and they were always run prior to sample analysis.

PFOA Analysis. All PFOA analysis activities was performed by using ultra-performance liquid chromatography (DIONEX, Ultimate 3000 RSLC, Sunnyvale, CA) coupled with quadrupole time of flight mass spectrometry (UPLC–qTOF-MS/MS, ABSciex, TripleTOF 5600, Framingham, MA). Chromatographic separation was performed using a Waters XBridge C18 column (2.1 mm x 50 mm x 2.5 uM; Milford, MA) and the column was kept at 30ºC. Chromatographic measurement was performed using a gradient elution program with $2*10^{-3}$ mol L^{-1} ammonium acetate in a mixture of aqueous solution H2O:MeOH (95:5) (solvent A) and $2*10^{-3}$ mol L^{-1} ammonium acetate in MeOH (solvent B) as a binary mobile phase mixture, with flow rate at 0.35 mL/min. The gradient elution started with 25% solvent B held for 5 min, and increased linearly to 85% solvent B in 0.1 min, and then to 100% in 3.7 min, and held until 9 min. Then, solvent B reverted back to 25% in 5 min, with 14 min total run time. The electrospray

ionization (ESI) operating parameters spray voltage were 4.5 kV, and the nebulizer gas (N2), heater gas (N2), and curtain gas (N2) were set at 55, 55, and 30 psi respectively. The source temperature and declustering potential were applied at 700 oC and -80 V respectively. An ESI negative TOF MS- product ion experiment was used to analyze for PFOA. The parent-ion and product-ion for PFOA analysis were 412.9660 Da and 368.9767 Da respectively and the collision energy was set at -15V. An injection volume of 10 uL was applied per sample or standard. Data were gathered by TF 1.7.1 (Analyst) and processed with MultiQuant 2.1 (MultiQuant) software.

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