DEGRADATION OF POLY- AND PER-FLUOROALKYL SUBSTANCES ($PFAS_S$) USING PHOTOCATALYST ZINC OXIDE

A Thesis

by

BILAL SAAD AZEEZ ABADA

Submitted to the Office of Graduate and Professional Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Chair of Committee,	Kung-Hui (Bella) Chu
Committee Members,	Sarbajit Banerjee
	Bill Batchelor
	Arul Jayaraman
Head of Department,	Robin Autenrieth

December 2016

Major Subject: Civil Engineering

ABSTRACT

Poly- and per-fluoroalkyl substances (PFASs) in the environment have raised a great public health concern because these compounds are persistent, bioaccumulative and toxic. Degradation of polyfluoroalkyl substances like fluorotelomer alcohols (FTOHs) can produce perfluoroalkyl acids (PFAAs). Previous studies have reported biodegradation of 6:2 FTOH by several FTOH-degrading bacteria to various shorter-chain PFASs. Some transition metals, like zinc oxide (ZnO), have some interesting semiconducting, adsorbing and optical properties in addition to their ability to photocatalyticly degrade contaminants. Accordingly, we hypothesized that an approach that combines biological and chemical treatment will be an effective way to degrade PFASs.

This study focused on photodegradation of PFASs using ZnO under environmentally friendly conditions, particularly near neutral pH and room temperature. Two types of ZnO were used: the commercial microscale ZnO and the tetrapod nanoscale ZnO. Results showed that photo-defluorination efficiency for 5:3 polyfluorinated acid was about 14.9% and 13.8% using commercial and tetrapod ZnO, respectively. Either type of ZnO could not successfully degrade any of the three PFAAs used in this study, i.e. PFOA, perfluorohexanoic acid (PFHxA) and perfluorobutyric acid (PFBA). Adding persulfate with tetrapod ZnO improved the defluorination efficiency for PFOA, but it reduced the defluorination of 5:3 acid and 6:2 FTOH. High doses of persulfate (27 mM) without ZnO led to a significant improvement in defluorination of PFOA, PFHxA and PFBA, with PFBA defluorination as high as about 40%.

Defluorination of 5:3 acid by ZnO was eliminated when the experiments took place in a growth medium. The competition of these ions with PFASs for adsorption and the high ionic strength were proposed as possible reasons for this elimination. 5:3 Acid defluorination was not much affected by the presence of PFOA in the solution, which indicates that PFOA does not adsorb strongly enough on ZnO to inhibit adsorption of the 5:3 acid. Finally, solutions of the 5:3 acid that had undergone photodegradation with

tetrapod ZnO were further examined for their treatability by biological processes. Biodegradation trials using *P. flurescens* DSM 8341 did not show a significant defluorination improvement, which in part due to the presence of growth medium. This is the first report studying the photodegradation of PFASs using ZnO.

DEDICATION

This work is dedicated to everyone helped me throughout my entire life. All the praise is due to Allah for his mercy, blessings and guidance. I ask Allah to make this work useful for my life as well as for the hereafter. A special feeling of appreciation is to my heroes, my parents. They were, and are still, the candles that lighted my path. Thanks to my soulmate and my love, my wife Farah, for being patient and supportive. I will never forget your support, darling. Love to my little boy Rami who was born during the first semester of my MS studies, and changed our entire life. Thanks to my lovely brother and sister. I wish that you will be more successful than your older brother.

I would like to thank my country and my sponsor, the Higher Committee for Education Development in Iraq (HCED) for giving me the opportunity to study in the US with my family. Their monitoring and efforts were crucial in reaching my goals. Special thanks to my chair, Dr. Chu, for her advice and mentoring. I really appreciate her awesome ideas and continuous follow-ups during my time spent pursuing my MS. Appreciations to my committee members, Dr. Banerjee, Dr. Batchelor and Dr. Jayaraman for accepting being on my committee and offering help whenever needed.

Finally, I would like to thank all my family members inside and outside Iraq. You were the best family that anyone could ever have. My appreciation is to all my teachers and advisors from my first year at school until this day. Your motivation is what made me achieve what I achieved. Ultimately, Regards to all my friends, colleagues, lab mates and peers. I was lucky to have you in my life.

ACKNOWLEDGEMENTS

I would like to thank the Higher Committee for Education Development in Iraq (HCED) for offering me a scholarship to get the MS degree. I would like to thank my committee chair, Dr. Chu, and my committee members, Dr. Banerjee, Dr. Batchelor and Dr. Jayaraman, for their guidance and support throughout the course of this research.

Thanks also to my friends and colleagues and the department faculty and staff for making my time at Texas A&M University a great experience.

Finally, thanks to my mother and father for their encouragement and to my wife for her patience and love.

CONTRIBUTORS AND FUNDING SOURCES

This work was supported by a thesis committee consisting of Dr. Kung-Hui Chu [advisor] and Dr. Bill Batchelor of the Department of Civil Engineering and Dr. Sarbajit Banerjee of the Chemistry department and Dr. Arul Jayaraman of the Department of Chemical Engineering.

The synthesis of tetrapod ZnO, and the data analyzed by EDX, XPS and XRD were done by Dr. Banerjee and his lab group from the Department of Chemistry at Texas A&M University. The powdered ZnO was supported by Dr. Banerjee's lab as well. All other work conducted for the thesis was completed by the student independently.

Graduate study was supported by a scholarship (not covering lab expenses) from the Higher Committee for Education Development in Iraq (HCED). Lab expenses (materials and analysis) to do experiments were offered by Dr. Kung-Hui Chu.

NOMENCLATURE

AFFF	Aqueous Film Forming Foam
AOP	Advanced Oxidation Process
ARP	Advanced Reduction Process
BTEX	Benzene, Toluene, Ethylbenzene and Xylene
EDX (or EDS)	Energy-Dispersive X-ray spectroscopy
FTOH	Fluorotelomer Alcohol
GAC	Granular Activated Carbon
GO	Graphene Oxide
hr	hour
HPLC	High Performance Liquid Chromatography
HRP	Horseradish Peroxidase
MB	Methylene Blue
MG	Methyl Green
MS	Mass Spectrometry
NMS	Nitrate Mineral Salts medium
NRGO	Nitrogen-doped Reduced Graphene Oxide
PBS	Phosphate Buffer Saline
PFAA	perfluoroalkyl acid
PFBA	perfluorobutyric acid
PFBS	perfluorobutyric sulfonate
PFHxA	perfluorohexanoic acid
PFOA	perfluorooctanoic acid
PFOS	perfluorooctanesulfonate
PFPeA	perfluoropentanoic acid
ppm	parts per million
PS	Persulfate
TCE	Trichloroethylene

UV	Ultra Violet
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction
ZnO	Zinc Oxide
ZVI	Zero Valent Iron

TABLE OF CONTENTS

Page

LIST OF FIGURES

Page

LIST OF TABLES

Page

1. INTRODUCTION

1.1 Project Description

1.1.1 Project goal

The goal of this project was to investigate the potential of using zinc oxide (ZnO), especially tetrapod ZnO, to photodegrade poly- and per-fluoroalkyl substances (PFASs) under natural pH and room temperature conditions, and to determine the possibility of linking this photocatalytic process with biodefluorination for effective removal of PFASs.

1.1.2 Background and problem statement

PFASs represent a wide group of aliphatic compounds that have the fluorine substituting partially (poly) or fully (per) for hydrogen [1]. Fluorine itself has some interesting and unique characteristics. It has Van der Waals radius similar to oxygen, rather than to other halogens [2]. In addition, fluorine is the 13th most ubiquitous element and the largest available halogen in the planet [2]. Fluorine as an element has the highest "electronegativity" [3]. This potential places elemental fluorine on the top of inorganic oxidants in terms of strength [3]. Moreover, the C-F bond has bond disassociation energy of 116 kcal/mole, which is approximately 25 kcal/mole higher than C-Cl bond [2, 4, 5]. Thus, some PFASs can be categorized as "extremely persistent". PFASs physical and chemical properties are still not fully understood and recorded [6]. However, most of these contaminants contain both hydrophobic and hydrophilic parts [7]. PFASs have been detected in different environments as well as in humans [4]. This group of contaminants has been used for longer than six decades in several applications including paintings, clothing, electrical conductors and Teflon coatings [8]. Their great resistance to thermal energy made these PFASs preferable [9]. PFASs are known for their toxicity and negative effects on humans, animals and plants' health [5, 10, 11]. The advisory levels in Germany for groundwater, as an example, are 0.23 µg/L for PFOS and 7 µg/L for PFBA [12].

Advanced Oxidation Processes (AOPs), or Advanced Reduction Processes (ARPs), are based on the concept of producing radicals to degrade persistent pollutants [9, 13] and have been explored to degrade PFASs. Radicals have "unpaired" electrons that will make required reactions more kinetically feasible [14]. There are several types of catalysts and different activation methods like heat, UV irradiation, ultrasound, transition metal ions, microwave energy and metallic oxides [13-16]. Photocatalysis is one of these advanced processes [17]. Photocatalysts absorb photons from a light source depending on their absorption spectra, and the energy from the photons will activate the generation of the radicals [14]. When these photocatalysts absorb the photons' energy, electrons transfer from the valence to the conduction bands, generating radicals that can oxidize, or reduce, the targeted contaminants [18]. Therefore, photocatalysis is a combination of both redox processes. Among many available photocatalysts, like titanium, indium and other metallic oxides, zinc oxide is capable of degrading different compounds and groups of contaminants like TCE and some dyes [13, 19-21].

Bak *et al* found that adding laponite to nano ZnO caused it to form a "porous ball composite" that improved adsorption of TCE on the composite, and therefore enhanced the removal by •OH that is produced on the ZnO surface [21]. In addition, shorter wavelengths of UV light and more alkaline pH conditions more efficiently removed TCE [21]. ZnO synthesized by electrolysis and heat showed potential to be used as an oxidant, with better quality and reusability than ZnO synthesized by electrolysis [13]. Methylene blue dye was 79% removed by heat-synthesized ZnO exposed to 365 nm UV light at 30 C° and pH = 6.5 for one hour [13]. Rhodanine dye was almost fully removed by 1 g/L of nano ZnO after exposure to a high-pressure mercury lamp for 1.5 hours at pH 10 [20]. Montazerozohori and Pour found that for each pH value in the range of 9-13, there is an optimum ZnO dose ranging between 0.5-1.5 g/L [20]. Moreover, Methyl Green dye was efficiently removed with 0.25 g/L of ZnO when two visible-light lamps were used for about 16 hours [19]. However, based on the author's best knowledge, there is no published document reporting on the use of ZnO to remove PFASs.

Consequently, the main purpose of this work was to investigate ZnO as a catalyst to degrade this group of persistent contaminants.

There were two main motivations for this work. First, most reported methods for treatment of PFASs remain unsatisfactory. PFASs were either transferred from one medium to another without being degraded or high energy consumption or extreme pH ranges were required for their degradation. For example, the treatment conditions for PFOA degradation were considered unrealistic for application to large scale contaminated sites [3]. Second, biodegradation of polyfluorinated compounds, mainly the precursors to PFAAs, is known and can produce PFASs. Accordingly, it might be possible to combine the biological with the photochemical processes to achieve better removal of PFASs. The aim of this project was to investigate a potentially feasible treatment train for PFASs that combines a novel photocatalytic process with biodegradation for effective removal of PFASs within more realistic conditions. The major question addressed in this study was whether or not ZnO can photocatalically degrade a single PFAS or a mixture of PFASs under more environmentally friendly conditions, such as lower energy input and near neutral pH.

1.2 Hypotheses and Objectives

The objectives of this project can be summarized as follows:

Objective 1: Test the removal of PFASs by ZnO

Hypotheses: ZnO can defluorinate PFASs when activated by UV light. Moreover, lab-synthesized tetrapod nanoscale ZnO will defluorinate PFASs more effectively than commercial microscale ZnO, since tetrapod ZnO has more surface area per volume than that of the commercial ZnO.

Task 1a. Determine the ability of two types of ZnO (tetrapod and commercial) to defluorinate selected individual PFASs.

Task 1b. Study the effects of ZnO dose, pH and addition of persulfate on the defluorination of individual PFASs.

Task 1c. Evaluate the ability of ZnO to remove PFASs in a mixture.

Task 1d: Determine time-course defluorination of some PFASs by tetrapod ZnO

Task 1e. Demonstrate the structural stability of ZnO.

Objective 2: Evaluate the extent of PFASs removal using a combination of tetrapod ZnO-assisted photodegradation and FTOH-degrading bacteria.

Hypotheses: Metabolites produced from ZnO-assisted photodegradation of PFASs might become more biodegradable.

Task 2a. Determine the effects of growth medium on PFASs defluorination by tetrapod ZnO.

Task 2b. Examine biodegradation potential of the metabolites generated from tetrapod ZnO-assisted photodegradation of PFASs.

1.3 Technical Approach

1.3.1 Overview of experimental design

Five targeted PFASs were investigated in this study. The first contaminant is the 6:2 Fluorotelomer Alcohol (6:2 FTOH) and it is an example of a volatile, biodegradable fluoro-organic alcohol. Many studies refer to FTOHs as sources or parent compounds for the perfluoroalkyl acids (PFAAs) in the environment [10, 22]. The second contaminant is the perfluorooctanoic acid (PFOA), which is a representative of the PFAAs. EPA has proposed a health advisory for PFOA to be below 70 ng/L in drinking water, which is much lower than the concentrations at many contaminated sites in the US [23]. The third contaminant is the 5:3 acid, an example of a polyfluorinated PFAS, which is one of the biotransformed PFASs from biodegradation of 6:2 FTOH in aerobic and anaerobic environments [10, 11, 22, 24]. The last two PFASs are perfluorobutyric acid (PFBA) and perfluorohexanoic acid (PFHxA), which are short chain PFAAs that are also produced as a result of biological and chemical degradation of the parent fluorotelomer alcohols and long chain PFAAs. Two types of ZnO were used. The first one is the tetrapod ZnO. It is a nanoscale material synthesized in the lab and has a diameter of less than 1 micron in

the center with tapered ends that have less than 100 nm diameter. The second type is the commercial ZnO, which is a microscale material that can be purchased commercially.

Objective 1: Test the removal of PFASs by ZnO

The general experimental procedure can be summarized as adding ZnO and PFASs to specified concentrations and under conditions detailed in the materials and methods chapter. Samples were shaken for less than an hour in the dark and then incubated over the UV lamp. Vials were sacrificed at specific time steps and stored in a – 20 C° freezer for later analysis.

Task 1a. Determine the ability of two types of ZnO (tetrapod and commercial) to defluorinate selected individual PFASs.

The main purpose of this experiment was to evaluate how the tetrapod ZnO prepared is different from commercial ZnO when samples exposed to the UV light for 3 days.

Task 1b. Study the effects of ZnO dose, pH and addition of persulfate on the defluorination of individual PFASs.

The purpose of this experiment was to find the best ZnO dose to improve overall defluorination. In addition, different pH values and addition of persulfate revealed some assumptions that can be placed regarding the removal mechanism and radicals preference/scavenging.

Task 1c. Evaluate the ability of ZnO to remove PFASs in a mixture.

The purpose of this experiment was to find how the removal would be when two or more PFASs were together in the same solution. Each contaminant constituted an equal share of the total concentration based on a molar basis to address the competition between them.

Task 1d. Determine time-course defluorination of some PFASs by tetrapod ZnO.

The purpose of this task was to have some ideas about the kinetics of defluorination. The approach of this experiment would be similar to the experimental flow in task 1a. However, samples were sacrificed at different selected time steps.

Task 1e. Demonstrate the structural stability of ZnO.

This task depended on the XRD measurements for selected samples to examine if the structure of the solid ZnO remained the same after the end of the experiment, so that it may be reused again directly or after simple pretreatment.

Objective 2: Evaluate the extent of PFASs removal using a combination of tetrapod ZnO-assisted photodegradation and FTOH-degrading bacteria

Task 2a. Determine the effects of growth medium on PFASs defluorination by ZnO

This task was basically a replication to the main experimental flow. The only modification was different growth media were used instead of using DI water to check the significance of adding ZnO to a solution with many compounds.

Task 2b. Examine biodegradation potential of the metabolites generated from ZnO-assisted photodegradation of PFASs

Another approach worthy of the application was to check reversing the sequence of the treatment train. In this task, the efforts directed to examine the photo defluorinated PFASs if they can be further defluorinated by bacterial strains.

1.3.2 Chemical analysis and surface characterization of ZnO

Fluoride measurements: Detection of free fluoride by the fluoride probe is an indication of the mineralization of the contaminants. High percentages of defluorination are not expected, because of the possibility of having intermediates. For instance, according to the literature, a possible degradation pathway is to have one carbon (CF2) removed in a step-by-step approach. Following that approach for our targeted contaminants, 13-29 % defluorination efficiency may be complete removal of the parent contaminant, and transformation to shorter chain contaminants. Nevertheless, this assumption cannot be considered unless it is verified by other tests like LC/MS/MS.

XRD (X-ray diffraction): XRD importance was to identify if deformations took place to the chemical structure of the spent ZnO. This test was done for samples that

showed the highest defluorination efficiency to check if there was a shift or addition/removal of peaks as compared to fresh ZnO.

For the quantification part of the solids, XPS (X-ray Photoelectron Spectroscopy) or EDX (Energy-Dispersive X-ray spectroscopy) analysis were utilized depending on experimental conditions. Because we tried to lower PFASs concentrations as much as possible, it was not possible to detect fluorine on the surface of ZnO. Consequently, there were separate samples with higher concentrations to take a look at the effects of adsorption and the adsorption capacities of the ZnO with the selected PFASs.

1.4 Thesis Overview

This thesis starts with this first chapter as an introduction and demonstration of the goals and tasks. **Chapter 2** focused on the literature review. It covered topics regarding PFASs general properties, sources, distribution and more importantly approaches for their removal. **Chapter 3** is a detailed listing of the materials and equipment needed in this study, and the methods and protocols for experimental and analytical purposes. Then, **Chapter 4** was dedicated for the obtained results, and it covered the discussion and critical analysis of these results. Finally, **Chapter 5** summarized the conclusions with recommendations for future work. Appendix included details about calculations for the experiments and some side experiments.

2. LITERATURE REVIEW

2.1 Introduction

As the main focus of this thesis was to evaluate a treatment method for PFASs, it was important to layout the commonalities and fate of these contaminants. This was followed by introducing common research methodologies and problems. Then, the focus was directed on the main targeted PFASs that were intended to be used in the experiments. After that, there was a discussion of the literature review of biological and chemical removal processes in two separate subsections. Finally, the last section provided a detailed explanation of the catalysts that were used in this research.

2.2 PFASs Fate and Sources

Many of PFASs are persistent to biological, thermal and acidic degradation [3, 9]. Even incineration may not yield full removal of these compounds [9]. Nevertheless, It has been found that some contaminants like PFOA have higher outlet concentrations than the inlet concentrations of some treatment facilities [25]. This may be due to the break-up of longer chain, degradable, PFASs into PFOA. In general, non-ionic PFASs can be more easily treated than the ionic ones [9]. PFASs adsorption to soil may cause plants toxicity and consequently affect humans' and animals' health [26]. Long-chain PFASs have a higher potential for adsorption than short-chain ones [27]. Currently, there is a growing trend of using shorter chain PFASs [28].

In addition to household wastes generated from populous and industrial areas [27], one of the main possible contaminated locations are airports and military sites where Aqueous Film Forming Foams (AFFFs) were used by firefighters [29-31]. AFFFs are essential in stopping fires that are generated from hydrocarbons [30]. Their importance is to resist the surface tension between the air and the foams [29]. They contain different PFASs depending on the manufacturer and year of production [30]. It is estimated that more than 500 sites in the US had activities included using AFFFs [31].

The analysis of these foams confirmed that some of the PFASs can be transformed within time into other fluorinated forms [29].

studies revealed that PFOA and PFOS were observed in almost all blood tests in the US in recent years [4]. PFASs distribution extends to areas as far as the arctic [3]. Surface waters may receive some of these contaminants from landfill leachates as a minor source [28]. PFASs have been found in the anaerobic sludge of WWTPs as well [24].

2.3 Common Research Approaches and Problems

Massive efforts were spent to study occurrence, transportation and fate of these contaminants. However, research was more complex for PFASs than many other groups of contaminants because of their characteristics. One of the analytical obstacles is the measurement of these contaminants. Until the date of publishing this thesis, most of the studies based their analysis on HPLC (high performance liquid chromatography) coupled with MS (mass spectrometry). However, many PFASs are still not identified and standardized analytical methods need to be developed for them. Some of these compounds can be generated as intermediate forms of the parent compound [10, 11]. Houtz and Sedlak adapted a method to measure total PFASs by simply transforming the precursors into carboxylic and sulfonic acids, which can be further analyzed by HPLC [8]. The method can be summarized as thermolysis of sufficient amounts of persulfate under alkaline conditions to transform long chain PFASs or precursors into shorter ones [8]. Another approach for lab applications is the indirect measurement of free fluoride released to have an indication of the mineralization of the contaminant. This can be done by using the ion chromatography or specific ion probes [10, 11, 14].

Another problem is the extraction of contaminants from solid or liquid phases to quantify the total amounts and close the mass balance. It is possible that some PFASs sorb into the experimental apparatuses or solid materials [5]. A common solution for that problem is to do the solid phase extraction (SPE) as illustrated by many references [29]. Nevertheless, Backe *et al* presented a new “liquid-liquid extraction method” for having

more efficient and less demanding extraction [29]. As a result, investigating PFASs will keep flourishing as new techniques and approaches are developed frequently.

2.4 Targeted PFASs

Details about the targeted PFASs (Abbreviations, molecular formula and chemical structures) are listed in Table 1.

2.4.1 6:2 fluorotelomer alcohols

Many studies emphasized that FTOHs, in general, are sources or parent compounds for the perfluoroalkyl acids (PFAAs) in the environment [10, 22]. FTOHs can be identified using the nomenclature "A:B FTOH", in which A is the number of carbon-fluorine functional groups and B is the number of carbon-hydrogen groups, i.e. the number of C molecules without fluorine [6]. There are around 12 million kilograms of FTOHs produced every year [7], and about 0.1 million kg is expected to be generated to the environment annually [6]. Wu and Chang described FTOHs as having "unique geometry" and interesting properties [6]. They are volatile organics, and their Henry's constants are not well documented [6], but some references stated that log K_{AW} (unitless) for 6:2 FTOH is 1.66 [32].

FTOHs are known for their high sorption to soil [10, 22]. 6:2 FTOH has been shown to be almost non-adsorbing to glass surfaces [6]. This biodegradable PFAS has a half-life in soils and aerobic environments of about 2 days or it may be even less [22], whereas it is about 30 days in anaerobic methanogenic conditions [24], and 20 days in the atmosphere [6]. One of the products of degradation of FTOHs, in general, is the perfluoroalkyl iodide, which was shown to have toxic effects to some cells in human [7].

2.4.2 PFOA

The PFASs that have 8 carbon molecules in their structure are amongst the most produced ones in the industry [8]. PFOA is one of these C8 PFASs. Its industrial importance is related to its optical properties and its ability to produce acids [33]. It can

be generated as a result of biotransformation of some precursors like 8:2 FTOH [27]. EPA stated that PFOA is a "likely carcinogen" and it may be related to liver and kidney cancer [7, 34]. Experimentally, high doses of PFOA caused toxicity to adrenocortical carcinoma cells in humans (H295R), which are responsible for producing genes needed for steroidogenesis [7].

PFAS (abbreviation)	Synonym	Molecular formula / weight (g/mole)	Source
6:2 Fluorotelomer Alcohol (6:2 FTOH)	1H,1H,2H,2H-Perfluoro-1-octanol	$C_8H_5F_{13}O$ / 364.1	Sigma-Aldrich, St. Louis, MO
5:3 Polyfluorinated acid (5:3 acid)	2H,2H,3H,3H-Perfluorooctanoic acid	$C_8H_5F_{11}O_2$ / 342.11	Synquest laboratories, Alachua, FL.
Perfluorooctanoic acid (PFOA)	Pentadecafluorooctanoic Acid	$C_8HF_{15}O_2$ / 414.07	TCI America, Portland, OR
Perfluorohexanoic acid (PFHxA)	Undecafluorohexanoic acid	$C_6HF_{11}O_2$ / 314.05	TCI America, Portland, OR
Perfluorobutyric acid (PFBA)	2,2,3,3,4,4,4-Heptafluorobutanoic acid	$C_4HF_7O_2$ / 214.04	Sigma-Aldrich, St. Louis, MO

Table 1 Summary of the PFASs that were used in this project

EPA has recommended that PFOA concentration should be below 70 ng/L in drinking water, which is much lower than the concentrations in many sites where AFFFs

were used (on the order of thousands of µg/L) [23]. Research is still burgeoning to address the health effects and the concentrations that would result in these adverse health effects in water, air and soils [34]. PFOA estimated half-life is more than 92 years in the atmosphere under standard conditions [3], 256 years in the ocean [5], and around 1 year with sunlight exposures at high altitudes [35]. It usually exists in deprotonated form because of its low pKa of 2.3-2.8 [4, 16, 36]. The protonated form represents less than 0.006 % under natural conditions of pH = 7 [37]. What makes PFOA more difficult to be degraded than many other PFASs is its low adsorption to soil [5], and high solubility [5, 34]. Solubility can be a dominant factor for degradation processes that need to have the reactions take place at or near the catalyst's surface. Solubility varies significantly within temperature changes [37]. Some studies found that PFOA was not successfully removed by some oxidation approaches [4]. Other studies suggested that hydroxyl radicals were not efficient in removing PFOA [16].

2.4.3 5:3 polyfluorinated acid

There is limited research for 5:3 acid degradation as compared to that for FTOHs or PFOA. However, it is one of the intermediates from the biotransformation of fluorotelomer alcohols [11]. This acid has the tendency to combine with organic matter and become unavailable to microorganisms [38]. It can be biodegraded slowly under aerobic conditions, whereas anaerobic environments do not seem to be convenient for its treatment [22, 24, 38]. It is hypothesized also that 5:3 and 5:3 Uacid, 5:3 Uacid is the unsaturated acid with a double bond, are reversible [11].

2.4.4 PFBA and PFHxA

Perfluorobutyric acid (PFBA) and Perfluorohexanoic acid (PFHxA) are PFAAs that have shorter chain lengths than PFOA. They are more persistent than the longer chain PFAAs and they both represent intermediates resulted from many chemical [5, 16, 31, 33, 39] and biological [10, 11, 22, 24] transformation processes.

2.5 Biological Treatment Processes for Removing PFASs

Although some earlier studies showed no biodegradation of PFASs [40], recent observations found the opposite for some of them. C-F bond can be broken by 4 different enzymes and some of them have been isolated and studied [41]. 5:3 acid can be aerobically biotransformed by activated sludge [38], and by specific bacterial strains like *Pseudomonas fluorescens* DSM 8341[11]. Results showed that about 22 % of the 5:3 acid was transformed by activated sludge into other acids after 90 days by a mechanism of removing one carbon from the chain 4:3 acid, 3:3 acid, perfluoropentanoic (PFPeA) acid and perfluorobutyric acid (PFBA) were among the biotransformed PFASs [38].

Liu *et al* investigated 6:2 FTOH aerobic degradation by using cells from activated sludge with some previous exposure to fluorinated compounds [22]. Four major PFASs (PFBA, PFPeA, PFHxA and 5:3 acid) were detected among 13 metabolites after 90 days of incubation in bacterial culture, and after 180 days in soil [22]. In the same study, the 5:3 acid was tested for its aerobic degradation in soil. The results revealed a persistence to biological degradation, probably due to the strong sorption to soil [22]. Regarding anaerobic processes, applying methanogenic processes for 6:2 FTOH yielded mainly polyfluorinated acids, e.g. the 5:3 acid [24]. These results were considered as an evidence to support the assumption that perfluorinated acids found in anaerobic conditions are from sources other than biotransformation of fluorotelomer alcohols [24]. The percentage of the 5:3 acid degraded was higher anaerobically than aerobically[24].

Some studies were more focused on identifying and testing specific bacterial strains rather than using a group or microbial communities. Kim *et al* studied the biological defluorination of 4:2, 6:2 and 8:2 FTOHs by *Pseudomonas butanovora* and *Pseudomonas oleovorans*, two bacterial strains capable of degrading some alkane substances [10]. In that study, the first bacterial strain aerobically transformed FTOHs by removing three CF_2 groups to produce PFAAs in addition to ketones and sFTOHs, while the second strain yielded additional x:3 polyfluorinated acids and shorter chained PFAAs [10]. The differences between the pathways motivated the authors to further

examine other factors. They tested two additional strains as well, *Pseudomonas fluorescens* DSM 8341, which can remove fluoroacetate [41], and *Mycobacterium vaccae* JOB5 [11]. The results showed that DSM 8341 has the potential to slightly degrade the 5:3 acid and that JOB5 was not affected by the type of inducer [11]. The two strains from their earlier study were affected by the inducers in terms of the number of intermediates and the degradation pathway [11].

Kwon *et al* isolated an aerobic strain, almost identical to *Pseudomonas aeruginosa,* capable of degrading 67% of PFOS in 2 days with the presence of 0.1% glucose, under conditions otherwise similar to the natural environments [42]. The study found that there was no free fluoride released during the experiment, and PFBS with PFHxA were detected [42]. Therefore, some biological processes have the potential to treat some PFAS. However, most of these processes involve biotransforming the targeted contaminants into shorter chain PFASs, which need to be further treated to achieve complete mineralization.

2.6 Physical and Chemical Processes for Removing PFASs

2.6.1 Processes related to water and wastewater treatment

Most conventional water and wastewater treatment plants are unable to degrade PFASs. However, enhanced treatments like membranes can remove long chain PFASs [43]. PFOA could be removed by coagulation mechanisms that are applied to drinking water treatment with few adjustments. For example, low pH of 4, adding 1 mM of NaCl and the existence of PAC led to remove about 90% of PFOA [4]. PFOA and PFOS could adsorb on the “fine flocs” formed during enhanced coagulation, which is basically using higher amounts of coagulant, depending on pH and coagulant type and dose [44]. This indicates the importance of surface charge and ionic strength to remove PFASs.

Activated carbon is currently one of the most economic solutions to remove PFOA and other PFASs from water [3, 45]. However, temperature, seasonal effects, the age of the adsorbent and desorption possibility within time are some of the drawbacks [25, 43]. Four mechanistic steps controlled PFOA removal by GAC: two diffusion

steps, “mass transfer” and sticking on the solid’s surface [3]. Wang *et al* found that PFOA adsorbed on activated carbon fibers with pH inversely affecting the adsorption capacity [36]. One of the novel ideas to remove PFASs from water, especially the hydrophobic ones, is what is known as the “fluorous microgel star polymer” which was able to remove about 98% of PFOA by “encapsulating” the acid in the center of the polymer [46]. Consequently, there are existing approaches to remove these contaminants from water. The major disadvantage is these applications usually remove the PFASs from the water to another medium without degrading or mineralizing the contaminants themselves.

2.6.2 Remediation treatment processes

It is worthy to begin with PFASs degradation studies by different forms of iron due to its wide applications in treating different groups of contaminants. Many PFASs removal experiments by zero valent iron (ZVI) were based on extreme conditions of temperature, pressure, pH or adding some catalysts [7]. Arvaniti *et al* coated nanoscale zero valent iron (nZVI) with positively charged elements to avoid particles’ aggregation and reduce their surface activity [7]. PFOA was 38% removed at pH=3, 20 C°, 1000 pm coated nZVI and 200 µg L^{-1} of PFOA [7]. Another approach was mixing persulfate with ZVI to expedite sulfate radicals generation by applying high-temperature conditions ,90 C°, and microwave energy [33]. The outcomes revealed that about 67% of PFOA removed with defluorination efficiency of 22.5% after 2 hours of reaction [33]. In that approach, persulfate addition was vital to the removal process, and the higher the persulfate dose or the temperature, the better was the removal.

One of the interesting studies is the use of 480 µM Fe(III) under natural sunlight conditions to degrade 48.3 µM of PFOA [5]. 97.8% of PFOA was degraded, with a defluorination efficiency of around 13%, after 4 weeks of reaction on the roof of a building in Houston, Texas [5]. The degradation was based on a stepwise removal of one carbon molecule from the chain [5]. Hydroxyl radicals (•OH) were thought to have the dominant role in the degradation process, based on radical scavengers analysis [5].

Adding persulfate or hydrogen peroxide hindered the degradation, yet promoted the defluorination of PFOA [5].

Trautmann *et al* could remove 45 to 98% of selected PFASs in less than two days by applying electrical current to boron-doped, diamond electrodes [12]. The removal was higher for PFASs of longer chains [12]. Zhang *et al* found that aluminum electrodes could remove up to 70 % of the PFASs mixture from leachates [47]. Lin *et al* concluded that a zinc hydroxide electrode was better than iron, magnesium, and aluminum electrodes for PFAAs removal by electrocoagulation at a low dosage and with different ranges of concentrations [45]. It could completely remove PFOA and PFOS regardless of pH changes, and the effluent Zn was below EPA maximum recommended levels [45]. The authors proposed that zinc hydroxide electrodes can be better used after pre-concentrating PFASs, and that was based on other studies showed that higher pollutants' concentrations needed lower energy consumption per amount of pollutant removed [45].

Furthermore, PFOA was about 70 % degraded by using horseradish peroxidase along with some phenolic organics, 4-methoxyphenol [48]. The overall reduction in toxicity was about 98 % [48]. The use of photocatalytic degradation has been investigated extensively. Ozone and UV energy in combination have been found capable of degrading the hydrophilic parts of selected PFASs [9]. It was possible to photo treat PFOA by UV and KI, but the system was highly depending on pH [49]. The authors of that study proposed that hydrated electrons along with UV light controlled the degradation [49]. Hydrated electrons of -2.9 V perform well in basic conditions to avoid conversion into H radicals of -2.1 V [49]. Additionally, sulfite and UV light in the absence of oxygen resulted in more than 88 % reductive defluorination efficiency of PFOA [50]. It was important for hydrated electrons to be in oxygen-free conditions to avoid radicals scavenging [50]. Finally, indium oxide showed better performance than titanium oxide to photodegrade 100 µmol/L PFOA [39]. The degradation took place in a glass reactor at 25 C°, pH around 4, 254 nm UV lamp of 23 W and 0.5 g/L indium oxide [39]. About 83 % of PFOA was removed with 33.7 % defluorination efficiency after 4 hours of reaction [39]. Consequently, there are many suggested methods to remove one

or a group of PFASs. However, many complexities and requirements accompanied these applications.

2.7 Literature for Catalysts that Are Intended to Be Used in this Research

2.7.1 Zinc oxide (ZnO)

ZnO is used in different applications. Its semiconducting properties with wide band gap (3.3 eV) made it preferable in many electrical applications [51]. Due to its relative inexpensive cost and abundancy [52], ZnO was a subject of focus for many studies as a photocatalyst and was favored relative to titanium oxide (TiO_2) in many cases [13, 19]. It consists of Zn^{2+} and O^{2-} ions, and radicals may form on the surface of ZnO, and perform the degradation after that [13]. The absorbed light energy will motivate the release of hydroxyl radicals, as well as other radicals, that played a vital role in degrading different contaminants [21]. The literature reported value of pH of zero point charge ($pH_{zpc)}$ is around 9, meaning that at pH higher than 9, surface charge will be negative and vice versa [19, 20]. PH will additionally control the availability of OH^- in water, which can be generated into hydroxyl radicals more easily by increasing pH values [20, 21].

Kinetics of reactions should increase as the concentration of reactants increases. However, it has been shown that when ZnO concentration is higher than 1 g/L, or 1.2 g/L, it may settle and form clumps that will decrease the available reaction sites; and therefore reduces its effectiveness [19, 20]. ZnO had a stable "structure" even after being mixed with other chemicals or materials for different purposes [21]. ZnO can be synthesized from Zn metal by using chemicals, UV light, pressure, temperature and electrolysis [13]. The efficiency and reusability of ZnO are proportional to the thickness of the ZnO synthesized layer [13].

Akhmal *et al* investigated the photo-degradation of 50 ppm methylene blue (MB) in 0.0667 g/L ZnO at 30 C° and initial pH of 6.5 [13]. The samples were shaken for some time in the dark for adsorption to take place, and then they were exposed to UV light of 365 nm and 100 W [13]. Experimental outcomes stated that ZnO synthesized by

electrolysis, which is also cheaper and easier to make than other processes, showed better removal of the dye, 84% removal within 1 hour [13]. In another study, methyl green (MG) dye was removed efficiently by 0.25 g/L of ZnO under visible light irradiation [19]. For the same study, optimum pH was found to be 10, and Cl^- and CO_3^{-2} addition decreased the efficiency [19].

Bak *et al* used ZnO nanoparticles with laponite to test the degradation of trichloroethylene (TCE) [21]. One of the interesting outcomes was increasing TCE concentration decreased the degradation efficiency [21]. The authors proposed two possible reasons; first, at higher concentration, all the binding sites might have TCE attached on them, allowing little or no •OH to adsorb on the ZnO surface [21]. Second, higher organic concentration means higher portion of the UV light absorption by the organic itself; therefore, ZnO will catch fewer photons [21]. However, another probable explanation is that with a constant light flux, there will be a constant production rate of radicals, resulting in a constant rate of degradation of TCE, as long as the fraction or radicals produced that react with TCE remains constant. This fraction might increase as TCE concentration increases, but it generally will not increase in proportion to the concentration of TCE. Therefore, as the concentration of TCE increases the same or only a little bit more TCE is degraded, resulting in a lower removal percentage. Rhodanine dye was also tested for photo-degradation by ZnO using a 400 W mercury lamp [20]. The results showed that for each pH, from 9 to 13, there is an optimum ZnO dose ranging between 0.5 to 1.2 g/L [20]. To sum up, ZnO as a photocatalyst was efficient in degrading different groups of contaminants.

2.7.2 Persulfate (PS)

Persulfate can be applied as the sole oxidant or as a co-catalyst to perform/improve the treatment. It is a good choice for AOPs because of its practical storage and high oxidation potentials (E_o = 2.1 eV, E_o for the radical $\bullet SO_4^-$ = 2.6 eV) [15, 16, 31, 33]. It can affect reactions both positively and negatively. For instance, it may promote the degradation of the adsorbed contaminants after they attach on the surface of

the other catalysts [15, 19]. However, Mai *et al*. found out that when persulfate exceeded specific concentration, it might compete with the contaminants in terms of the adsorption on the surface of ZnO [19]. This was also observed with PS addition to Fe (III) [5]. In addition, persulfate existence in water will change the chemistry and probably affect reactions or pathways that are expected.

Houtz and Sedlak found that one dose of 10 mM persulfate was enough to transform all PFASs precursors found in runoff samples to PFOA or PFOS [8]. In addition, Park *et al* noticed that persulfate can degrade PFOA, PFOS and 6:2 fluorotelomer sulfonate when it is pre-activated by heat [31]. In the latter study, conditions of natural environments were simulated in terms of concentrations, slurry soil conditions and the existence of other groups of contaminants like BTEX [31]. The molar ratio of persulfate to PFOA was very high, around 170,000 [31]. However, it was mentioned that increasing persulfate concentration reduced the effectiveness due to the competition and "scavenging" of the radicals [31]. The experiments in soil slurry indicated that several injections are needed because of PFOA sorption to the soil [31]. Lee *et al* found that activated carbon, as an adsorbent and a catalyst, will enhance the degradation of PFOA by persulfate, in which PFOA was completely mineralized instead of being transformed into other intermediates [16]. This approach revealed many advantages in terms of fewer requirements of time (around 12 hrs), temperature (25 C°) and activation energy (26.1 kJ/mol, rather than 66.8 kJ/mol) [16].

Wang *et al* described their hydrothermally prepared Nitrogen Doped Reduced Graphene Oxide, NRGO, as "Bifunctional" due to its adsorbing and activating functions [15]. NRGO is more effective than graphene oxide (GO) [15]. In their publication, 0.175-0.385 mM of bisphenol was added to 120 ppm NRGO at 25 C° and stirred in dark for 10 minutes, followed by the addition of PS [15]. The adsorption of bisphenol on NRGO reached equilibrium within a few minutes only [15]. NRGO was pretreated by vacuum filtration and water and methanol and used again for experiments. Results showed that NRGO kept highly effective even after 5 cycles of reuse [15]. Moreover, it was found that there was a continuous adsorption-degradation cycle in which the

degraded contaminants were released to solution, leaving a space for the non-degraded remaining fraction to be adsorbed and further treated [15].

3. MATERIALS AND METHODS

3.1 Introduction

This chapter begins with listing all chemicals and equipment used in this project. Then, detailed experimental procedures and analytical approaches will be presented afterward.

3.2 Materials

3.2.1 Chemicals and standards preparations

PFASs: 1H, 1H, 2H, 2H perfluorooctanol (6:2 FTOH, CAS # 647-42-7, 97% pure) and perfluorobutyric acid (PFBA, CAS # 375-22-4, 98% pure) were purchased from Sigma-Aldrich (St. Louis, MO). 2H,2H,3H,3H-Perfluorooctanoic acid (5:3 acid, CAS # 914637-49-3, 99% pure) was purchased from Synquest laboratories (Alachua, FL). Pentadecafluorooctanoic Acid (PFOA, CAS # 335-67-1, >98.0% purity) and Undecafluorohexanoic Acid (PFHxA, CAS # 307-24-4, >98% pure) were purchased from TCI America (Manufactured in Japan). All PFASs were dissolved in DI, except for the 5:3 acid and the 6:2 FTOH (in 33% and 50 % Ethanol (v/v), respectively).

Catalysts: Commercial powdered ZnO and lab prepared tetrapod ZnO were supplied from Dr. Banerjee's lab of the Department of Chemistry at Texas A&M University. Commercial ZnO (CAS# 1314-13-2) was purchased from Sigma-Aldrich (St. Louis, MO). Tetrapod ZnO (Figure 1) was prepared in the lab by heating 99% Zn metal to 950 C° after being cut into pieces, and then let the pieces cool down to be collected. Sodium persulfate (CAS # 7775-27-1) was purchased from MP Biomedicals (Santa Ana, CA)

Other chemicals: Sodium fluoroacetate (SFA, CAS # 62-74-8) was purchased from MP Biomedical (Santa Ana, CA). 1-Butanol (CAS # 71-36-3, 99.4% pure) was purchased from Fisher Scientific (Fair Lawn, NJ). *n*-octane (CAS # 111-65-9, 97% pure) was purchased from Acros Organics (Geel, Belgium). Ethanol (CAS # 64-175, pure) was purchased from VWR (Radnor, PA).

Bacterial strains: *P. fluorescens* DSM 8341 was purchased from the German Collection of Microorganisms and Cell Cultures (DSMZ, Germany) and was grown in Luria broth medium.

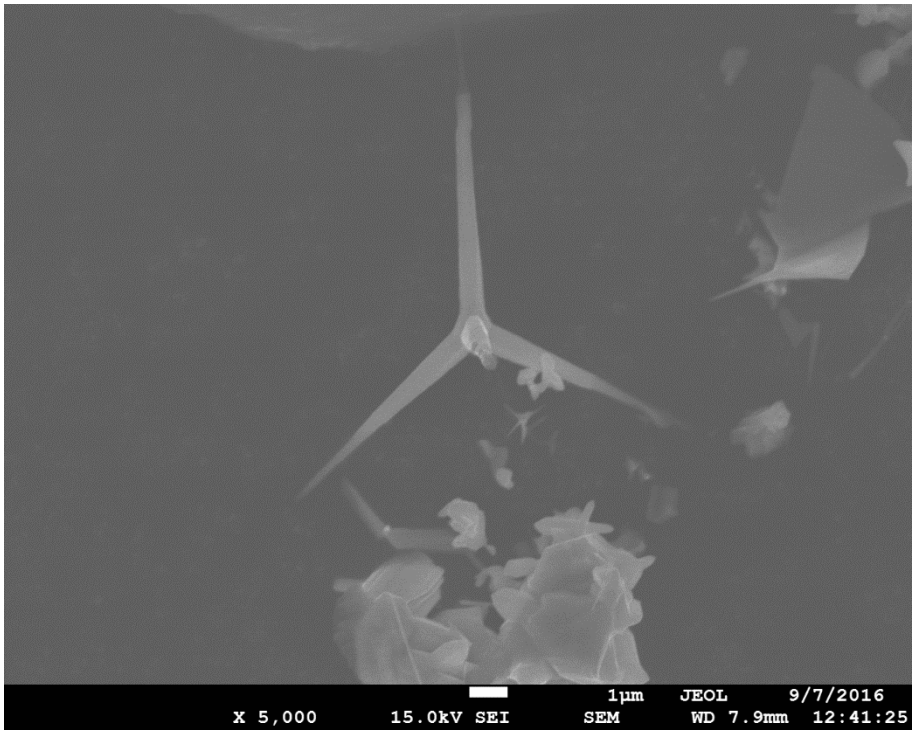

Figure 1 SEM image for the tetrapod ZnO

3.2.2 Equipment and apparatuses

All photocatalytic experiments were conducted using UV lamps placed below the samples. The lamps are Compact 4-watt with 365nm wavelength (Cat # 36582-045) purchased from VWR (Radnor, PA). Crimp-top head space borosilicate glass vials of 5 and 20 ml volume and their aluminum crimp seals, butyl and PTFE/silicone septa were also purchased from VWR. Spectroscopy system used was Agilent G1103A. DI water was prepared with Barnstead Thermolyne D4754 NANOpure Water Filtration System.

Additional information about vials efficiency of different light wavelengths absorbance is available in the appendix.

3.3 Experimental Approaches

3.3.1 Testing ZnO for PFASs removal

3.3.1.1 Determining the ability of two types of ZnO (tetrapod and commercial ZnO) to defluorinate selected PFASs.

This experimental procedure was applied for most of the experiments of tasks 1 and 2, except for some modifications that will be illustrated for each task accordingly. First, ZnO was added to DI water to have a concentration of 1 g/L, and 6 ml of that solution was then transferred to a 20 ml borosilicate glass vial. Second, individual PFASs were added to the vials by using a precision syringe. The vials were capped to eliminate the possibility of volatilization. Contaminants' concentrations in samples were selected to get an approximated total theoretical fluorine concentration of approximately 5 ppm (details available in the appendix). This concentration was chosen to enable the fluoride probe to detect fluoride in concentrations that yield defluorination efficiencies as low as 1%. For task 1a, there should be three sets of samples for each contaminant: PFAS + tetrapod ZnO, PFAS + commercial ZnO and PFAS+ DI water only as a control. Samples were triplicated for all the experiments of task1.

Vials were sacrificed at specific time steps and stored in a – 20 C° freezer until analysis. Three time points are selected for task 1 experiments (except time-course experiments): at the beginning of the experiment to check whether there is already free fluoride in the samples, after 30 minutes of shaking at 30 C° and 200 rpm in the dark to allow for attachment of contaminants to the solid and after 3 days of UV light exposure at room temperature and 250 rpm of shaking. Vials needed additional shaking by hand for a few seconds on a daily basis to re-suspend the ZnO. The vials' holder was placed in a slightly tilted position to allow for more turbulence and mixing of the samples.

When ready for analysis, vials were taken out of the freezer. Then they were centrifuged for 10 minutes at approximately 7,000 rpm. After that, 0.5 ml, or 1 ml

depending on expected defluorination efficiency, was taken by syringe from each vial to a 2 ml microcentrifuge tube for fluoride probe measurements. Then by using a pipette, the remaining suspension (should be less than 2 ml) was mixed and transferred to a 2 ml microcentrifuge tube. Consequently, the transferred solution was centrifuged at 13,000 rpm for 15 minutes, followed by discarding the supernatant, and vacuum drying the pellets for 2-5 hours in the vacuum dryer using low dry rate without heat. Ultimately, the spent ZnO was kept in dark until it was taken for analysis.

3.3.1.2 Determining effects of ZnO dose, pH and addition of persulfate on defluorination of PFASs.

This task consisted of three experiments. The first experiment studied the effects of changing ZnO dose on 5:3 acid defluorination. Concentrations of 0.25, 0.5, 1 and 1.5 g/L were selected for tetrapod ZnO. Concentrations of 0.25, 0.5 and 1 g/L were selected for commercial ZnO. The 5:3 acid was selected among the other PFASs because preliminary results showed higher removal for this acid. The second experiment studied what the defluorination of the 5:3 acid in 1 g/L tetrapod ZnO will be when the only variable was pH of the samples. pH was be adjusted to either 3, by adding H_2SO_4, or to 10, by adding NaOH.

The third experiment evakuated whether persulfate (PS) addition would improve or hinder the photocatalytic defluorination. After 30 minutes of samples shaking in the dark, PS was added. For each PFAS, PS was added to a final concentration of 50 µM, as per literature recommended PS concentration with ZnO [19]. Another set of samples included adding PS to a final concentration of about 2.1 mM.

3.3.1.3 Evaluating the ability of ZnO to remove PFASs mixture.

This task was basically a repetition of commercial and tetrapod ZnO comparison experiments with only one modification. The only difference was to add a mixture containing equal molar concentrations of both the 5:3 acid and PFOA. The stock solution concentrations and details are included in the appendix.

3.3.1.4 Determining time-course defluorination of some PFASs by tetrapod ZnO.

3 days period of UV exposure was selected for most of the experiments based on preliminary experiments findings. That approach did not reveal information about the kinetics of experiments. Therefore, it was beneficial to do a time step experiment based on pH, ZnO dose and PS concentrations that yielded highest defluorination efficiencies.

3.3.1.5 Determining structure stability of ZnO.

For this task, samples with higher defluorination efficiencies were selected for the XRD analysis. The obtained curves for fresh and spent ZnO were compared to check if peaks were shifted, added or removed.

3.3.2 Evaluating the extent of PFASs removal using a combination of tetrapod ZnO-assisted photodegradation and FTOH-degrading bacteria

3.3.2.1 Determining the effects of growth medium on 5:3 acid defluorination by tetrapod ZnO.

The goal of this task was to try repeating 5:3 acid experiment, but with having 1 g/L of tetrapod ZnO solution in a bacterial growth medium rather than in DI water. Nitrate Mineral Salts medium (NMS), P1 medium and Phosphate Buffer Saline (PBS) were selected for this task to replace the DI water.

3.3.2.2 Examining biodegradation potential of the metabolites generated from tetrapod ZnO-assisted photodegradation of PFASs.

Because the photodegradation pathways were not studied in this research, it is unknown whether the generated intermediates are biodegradable or not. Therefore, in this task, the biological processes took place after the photocatalytic process. 3 ml of the supernatant of 5:3 acid tetrapod ZnO-photodegraded samples for 2 days were used for these experiments. *P. fluorescens* DSM 8341 was grown first on Luria broth medium (LB) until it reached a high optical density (around $O.D_{600}$ = 1.0). Then the cells were centrifuged at 5,000Xg for 5 minutes and re-suspended in 457 medium with 0.1 g/L SFA

and 0.5 g/L Yeast Extract (YE) to induce the fluoroacetate dehalogenase enzyme. Enzyme induction was checked by using the fluoride probe. The cells were then centrifuged again and re-suspended in PBS to be centrifuged again and finally re-suspended in NMS medium. After that, 3 ml of the cells were taken and mixed with another 3 ml from the ZnO photo treated samples. Next, 0.6 ml of 10 g/L of SCA and 0.125 ml of 20 g/L of YE were added to the samples and incubated in a 30 C° dark incubator at 150 rpm for 2 weeks. 0.5 ml was taken by syringe from each sample at times 0, 4 and 14 days of the biological incubation to evaluate if there was some improvement of the defluorination efficiency. The details of the media and most of the calculations followed Kim *et al* publication [11].

3.4 Analysis

3.4.1 Fluoride probe measurements

Fluoride probe model number Orion 9609BNWP, purchased from Thermo Scientific (Waltham, MA), was used for the analysis. The procedure for the measurements starts with taking the 0.5 or 1 ml volume of samples that are in the 2 ml microcentrifuge tubes. A solution of half strength TISAB II with CDTA (Orion 940909), diluted in DI water, was added to the tubes to have a total volume of 2 ml. Then the samples were shaken thoroughly. Samples taken from bacterial culture or non-centrifuged vials were centrifuged before doing the measurements. Fluoride standards were prepared in concentrations of 0.25, 0.1, 0.5, 1 and 2.5 ppm, by diluting a fluoride standard solution of 100 ppm concentration (Orion 940907). The standards were measured first in order to find the standard curve equation and check the probe efficiency. After that, the samples were ready for the probe measurements. The readings were recorded in mV, and they were translated to concentrations after applying the equation of the standard curve. Then, the values were multiplied by 2 or 4 according to the dilutions of the sample by the half strength TISAB II solution.

Results were reported as defluorination efficiency, calculated as follows:

$$\text{Defluorination Efficiency } \% = \frac{\text{free fluoride measured by the probe}}{\text{total theoretical fluorine in solution}} \times 100\%$$

3.4.2 Energy-dispersive x-ray spectroscopy

EDX, or EDS, was used for checking how much fluorine was adsorbed on the ZnO. The purpose of using this test was to have some insights about the adsorption of PFASs on the ZnO. The accelerating voltage was selected to be 15 keV and the current was 10 uA.

3.4.3 X-ray photoelectron spectroscopy

The purpose of using the XPS was to study the functional groups of the fluorinated compounds on the surface of the solid ZnO. The emission current was set to 5 mA with an anode voltage of 15 kV. The pass energy and step size were selected to be 20 eV and -0.05 eV, respectively.

3.4.4 X-ray diffraction

As mentioned in the first chapter, the XRD was used to check if there would be any change or deformation to the chemical structure of the ZnO. The amounts of ZnO used and the samples' volumes were small. Therefore, it was not possible to do a pretreatment to the ZnO after recovering it. As a result, the examination for the reusability of ZnO was indirectly related to the XRD by comparing the spectra of the solid before and after UV exposure. The scan time was selected as 0.4 s, with a step size of 0.03 in a continuous mode.

4. RESULTS AND DISCUSSION

4.1 Introduction

This chapter displays the experimental results along with their discussion. Error bars in figures represent standard deviation.

4.2 Testing ZnO for PFASs Removal

4.2.1 Determining the ability of two types of ZnO (tetrapod and commercial ZnO) to defluorinate selected PFASs.

Figure 2 shows the defluorination efficiencies of the targeted PFASs in 1 g/L ZnO. Results were for samples exposed to UV for 3 days. All fluoride probe measurements for samples sacrificed before UV exposure and for the controls, i.e. without ZnO, were below the level of detection. The highest defluorination efficiencies were obtained for the 5:3 acid with 14.9 % for commercial ZnO and 13.8 % for tetrapod ZnO (Figure 2). For 6:2 FTOH, the powdered ZnO showed a higher defluorination efficiency, about 5%, than the tetrapod ZnO, which was 2.9% (Figure 2). PFOA samples showed only 1.6% and 0.7% defluorination efficiencies with commercial and tetrapod ZnO, respectively. It is important to mention here that defluorination efficiencies of less than 1% are probably not representing accurate values because of the probe characteristics and the selected concentrations. No fluoride detected by the probe for PFHxA and PFBA samples.

6:2 FTOH and PFOA defluorination efficiencies by commercial ZnO were significantly higher than those by the tetrapod one. For the 5:3 acid, the results for the commercial and tetrapod ZnO were not significantly different. It was unexpected to observe that commercial ZnO showed higher defluorination than the tetrapod one. Tetrapod ZnO should have larger surface area than the commercial ZnO. As a result, if adsorption to the catalyst is a key step in defluorination, the tetrapod ZnO will show better defluorination. However, the different geometry and properties of nanoscale

materials, in general, could lead to a different removal mechanism and pathway. We can say that commercial ZnO is better than tetrapod ZnO in defluorinating, i.e. mineralizing, the PFASs. Nevertheless, this does not confirm that commercial ZnO is better than the tetrapod ZnO for the overall degradation, which cannot be assessed without closing the mass balance and analyzing the intermediates produced during the photodegradation.

ZnO settled at the bottom of the vials in spite of their continuous shaking. Therefore, ZnO might have lost surface area available for adsorption. The study of ZnO settlement and aggregation was not within the scope of this work. However, the larger number of particles for the tetrapod ZnO could increase the collision efficiency of the particles and lead to a faster aggregation than the commercial ZnO. Thus, modifying the experimental setup is encouraged to eliminate the settling possibilities. This might include magnetic stirring or continuous purging of oxygen to the reactors.

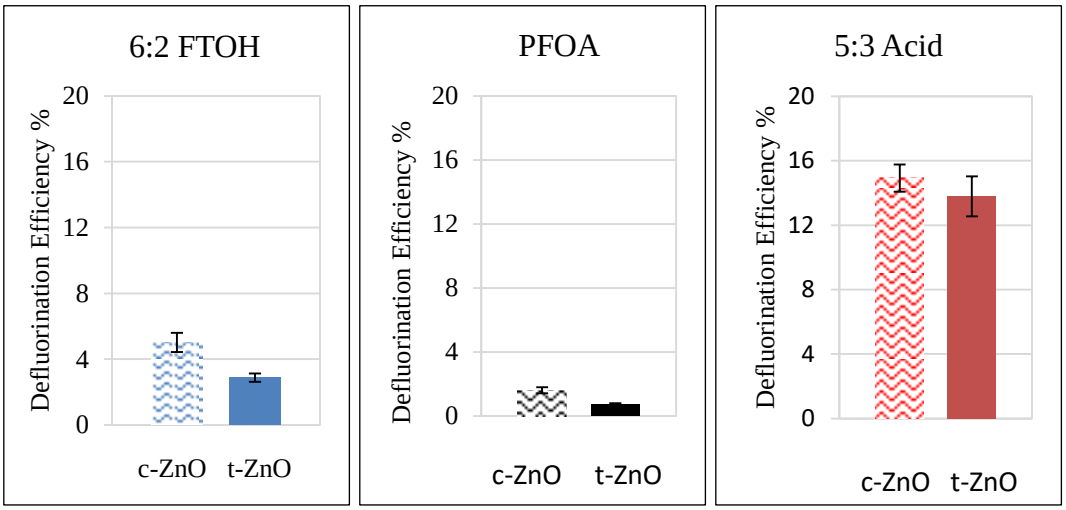

Figure 2 PFASs defluorination efficiencies by tetrapod (t-ZnO) and commercial ZnO (c-ZnO)

PFAAs no defluorination could be attributed to some reasons. First, the types of radicals produced were probably not efficient in breaking the C-F bond and releasing free fluoride. For instance, some of the literature found that •OH was not efficient in

degrading PFOA [16, 40], and •OH is possibly of the main radicals released by ZnO along with the hydrated electrons. Additionally, it is possible that these PFAAs were degraded to some extent, but the degradation was in terms of transformation rather than mineralization. This possibility requires advanced techniques like the LC/MS/MS to measure how much of the parent compound removed in a direct way. Ultimately, PFAAs are soluble in water; therefore, there might be a lower adsorption potential for these compounds than the 5:3 acid and the 6:2 FTOH. The application of semiconductors as photocatalysts requires the targeted contaminants to be at or near the catalyst's surface. Thus, the PFAAs low hydrophobicity might make them not available on or near the ZnO surface to be targeted by the Redox reactions of the radicals.

We can relate the defluorination efficiency to the degradation of the PFASs indirectly as in Figure 4. It is possible to estimate how many F^- molecules removed from the contaminant if the assumption of a step-wise removal of fluorine molecules from the chain is valid. According to this assumption, 5:3 acid is the only PFAS that have more than one F^- molecule removed from the chain. That is why more focus was oriented towards the 5:3 acid among the other PFASs for the rest of the experiments.

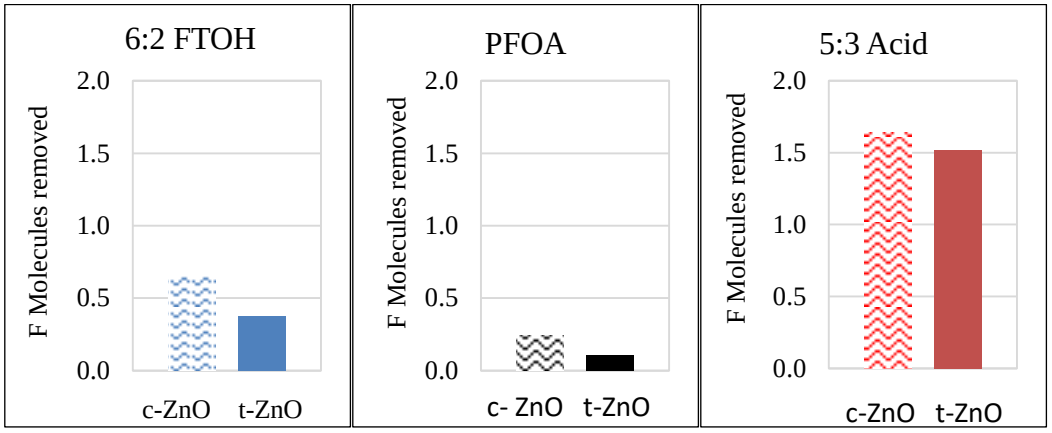

Figure 3 Estimated fluorine molecules removed from the PFASs chain based on calculated defluorination efficiencies

EDX and XPS instruments were unable to detect fluorine on the ZnO for concentrations used for the experiments. Therefore, the results for Figure 4 and Figure 5 were for concentrated samples with a total theoretical fluorine concentration of around 150 ppm. Results showed that for 5:3 acid with tetrapod ZnO, the adsorbed fluorine on the surface after 1 hour of shaking in the dark was about 4 %, on a weight basis, and increased to about 7 % after 36 hours of UV exposure. This might be an indication of having metabolites or intermediates that are more hydrophobic than the parent compound, i.e. the 5:3 acid. Another explanation might be the adsorption kinetics of PFASs, in general, are not quick and the 1 hour shaking in the dark was not enough to reach the equilibrium status.

EDX measurements were not duplicated; therefore, the quantification cannot be highly reliable. More research on that aspect is required to confirm these results. However, the most important finding was for a total theoretical fluorine concentration of 150 ppm, only 5:3 acid samples with tetrapod ZnO were fluorine-detectable. With PFOA of a total fluorine concentration of 200 ppm, there was fluorine detected by EDX (results not shown). Unfortunately, there was a difficulty in mapping the commercial ZnO.

5:3 acid concentrated sample after 36 hours of UV light exposure was tested by XPS. Results showed that the ratio of CF3: CF2 functional groups was approximately 1: 2.5, which indicated a removal of about 1.5 CF2 groups from the chain (Figure 5). The defluorination efficiency for this sample was about 3.9 % only. Thus, if we link EDX and XPS measurements, there is a higher removal for the 5:3 acid in terms of transformation rather than complete mineralization.

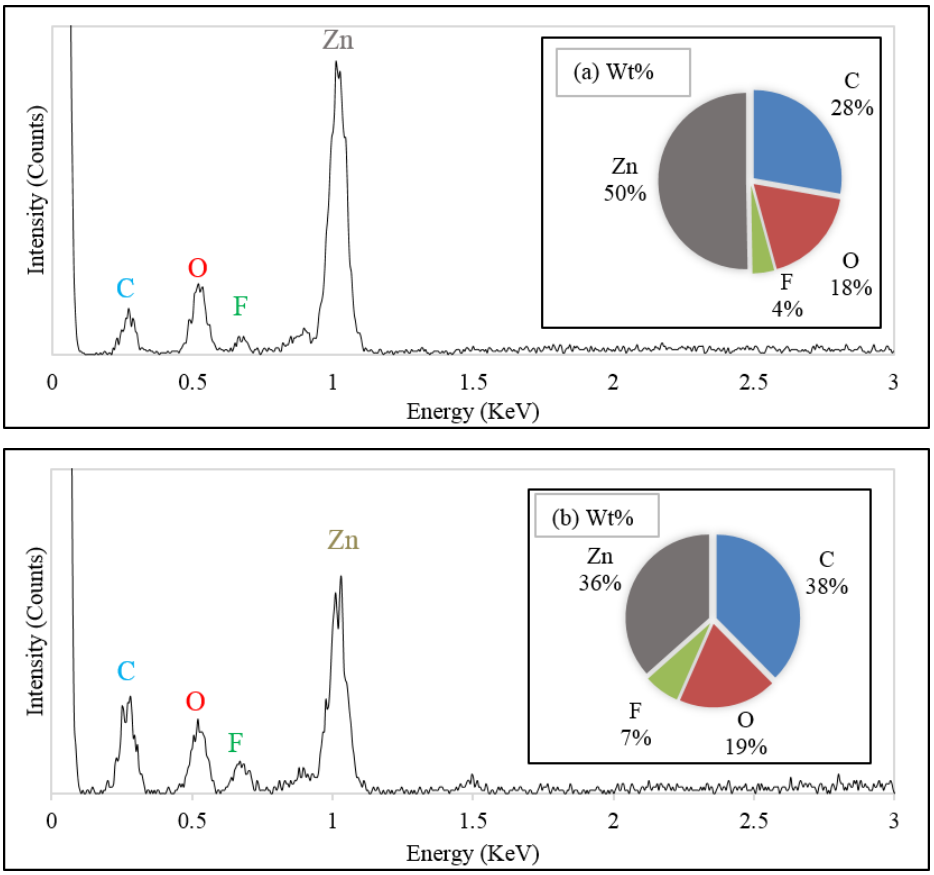

Figure 4 EDX results for 5:3 acid concentrated samples + 1 g/L tetrapod ZnO after (a) 1 hour of shaking in the dark and (b) 36 hours of UV light exposure

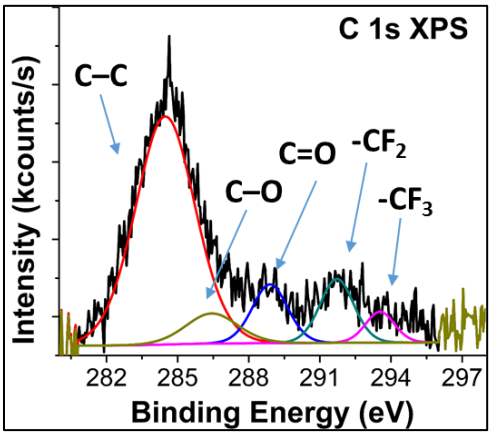

Figure 5 XPS results for 5:3 acid concentrated sample + 1 g/L of tetrapod ZnO after 36 hours of UV exposure

4.2.2 Identifying effects of ZnO dose, pH and addition of persulfate on defluorination of PFASs.

Figure 6 shows the defluorination efficiencies of the 5:3 acid with different ZnO doses at neutral pH. Samples were exposed to UV light for 3 days. The defluorination efficiency increased almost linearly from 3.7% to 13.8% when tetrapod ZnO concentration increased from 0.25 g/L to 1 g/L. Then, defluorination decreased to 12 % when tetrapod ZnO concentration increased to 1.5 g/L. Having tetrapod ZnO concentration higher than 1.0 g/L probably led to having some of the light energy scattered, and ZnO was more prone to aggregation. This was in accordance with some studies of photodegradation by ZnO [19]. The same experiment was repeated with commercial ZnO for the concentrations 0.25-1 g/L. Defluorination efficiency increased with increasing the ZnO concentration. However, the defluorination efficiency increment curve was not linear for the commercial ZnO.

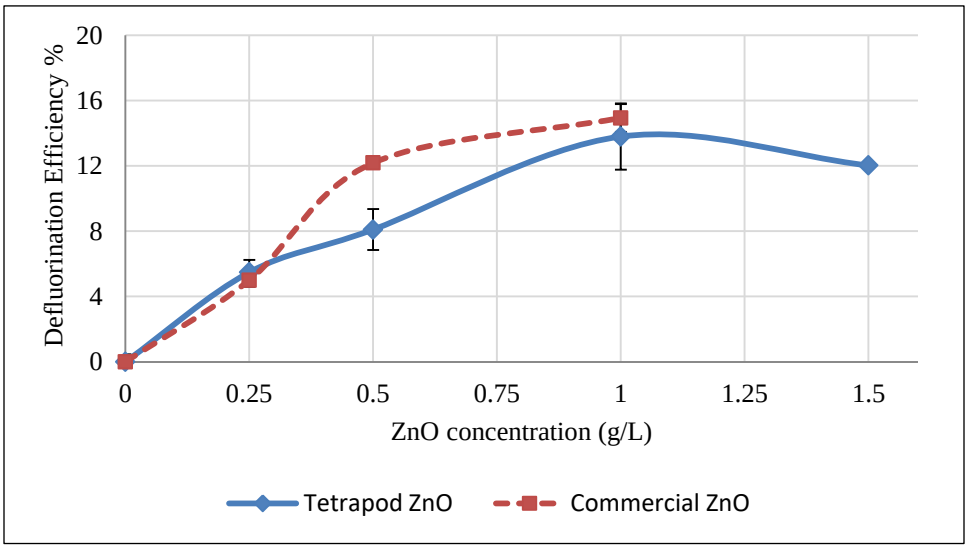

Figure 6 Effects of ZnO concentration on 5:3 acid defluorination efficiency

For the pH effects experiment, the fluoride probe measurements found no fluoride with pH = 3 and pH = 10 (Figure 7). pH is the most crucial factor in all

treatment systems as well as natural environments. On one hand, acidic water will dissolve all the ZnO. When ZnO is dissolved, it may not be capable of absorbing the photons and release the radicals. On the other hand, when pH is raised to 10, there was no defluorination as well. The zeta potentials were not measured for the tetrapod or commercial ZnO. Nevertheless, depending on values given in the literature for ZnO, the surface charge would be negative at pH 10.

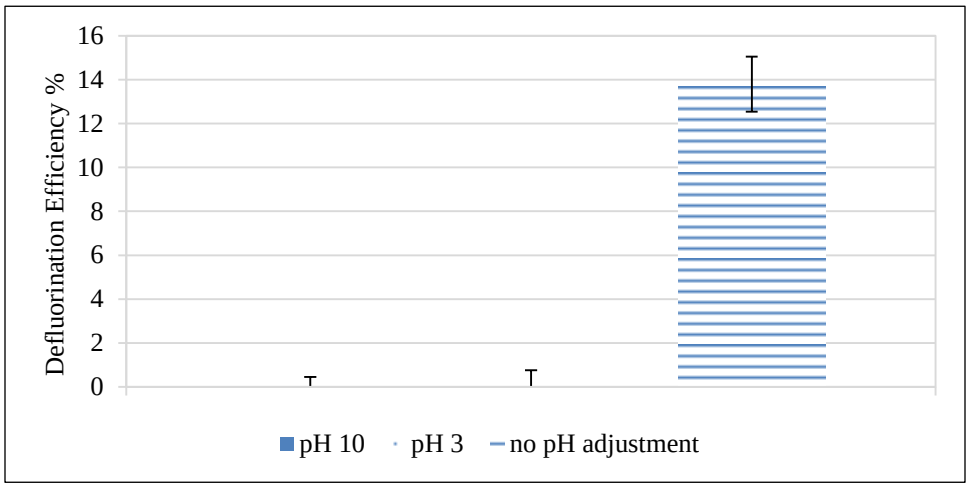

Figure 7 5:3 acid defluorination efficiencies by 1 g/L tetrapod ZnO at acidic, basic and no pH adjustment conditions

There was no fluorine detected by EDX for pH 10 sample after 1 hour of shaking in the dark. However, when the concentrated sample was measured by the fluoride probe after 3 days of UV light exposure, there was about 8.5 % defluorination efficiency. It is possible that when a higher concentration of the 5:3 acid was added, the excess amounts of the 5:3 acid made it more feasible to adsorb within the time and overcome possible repulsion. As a result, it can be hypothesized that both the surface charge and the hydrophobic interactions were the responsible mechanisms for adsorption. However, there is no solid evidence supporting that defluorination necessarily implies adsorption.

For the effects of the PS addition as a co-catalyst, Figure 8 displays the experimental results. 5:3 acid defluorination efficiency was reduced about 27% and 41% with PS addition of 50 µM and 2.6 mM, respectively, while it reduced about 25% and 68% for 6:2 FTOH when 50 µM and 2.1 mM of PS added, respectively. The improvement for PFOA defluorination efficiency was about 41% and 257% with PS addition of 50 µM and 2.1 mM, respectively. For PFHxA and PFBA, no fluoride detected with 50 µM of PS. Nevertheless, when 2.1 mM of PS was added to PFHxA and PFBA, fluoride was detected, but it was with the inaccurate limits of the probe, and therefore values were not quantified nor plotted.

When the 2.1 mM of PS were added to the solution of DI water and PFOA only, the defluorination efficiency was less than 1% (results not plotted). One possible explanation is that the reaction between the sulfate radicals and PFOA took place on or near the ZnO surface. For the polyfluorinated PFASs, i.e. the 5:3 acid and the 6:2 FTOH, there might be some radicals or electrons scavenging between the radicals generated from ZnO and from PS. Sulfate radicals are oxidants; therefore, they can scavenge the reductant radicals generated by ZnO. Studying the defluorination mechanism for PFASs by ZnO is encouraged to determine the redox reactions involved in the defluorination.

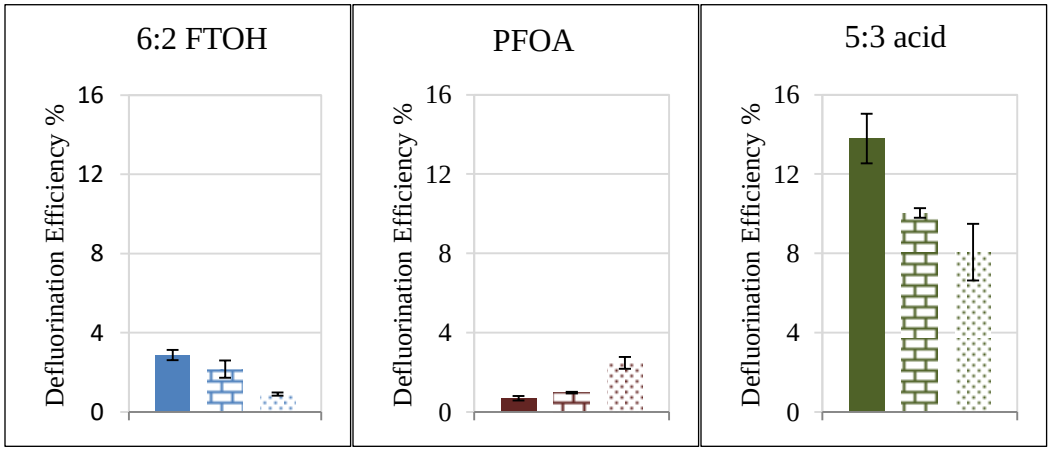

Figure 8 Effects of adding persulfate with 1 g/L of tetrapod ZnO on the PFASs (Solid column: ZnO only, horizontal brick pattern: addition of 50 µM PS and dotted pattern: addition of 2.1 mM persulfate (2.6 mM for 5:3 acid case))

4.2.3 Evaluating the ability of ZnO to remove PFASs mixture

Figure 9 reveals the results of photodegrading a mixture containing 5:3 acid and PFOA in 1 g/L ZnO. The ratios of the mixture components were based on equal molar concentrations. Tetrapod ZnO yielded a defluorination efficiency of 5.9 %; whereas the commercial ZnO defluorination efficiency was about 7 %. This followed the same trend observed previously. If we assume that PFOA component was not defluorinated, then 13.9 % and 16.5 % of the 5:3 acid component was defluorinated by tetrapod and commercial ZnO, respectively. This ratio is similar to the defluorination efficiencies obtained when the 5:3 acid was added to 1 g/L ZnO in task 1a. Accordingly, the existence of PFOA with 5:3 did not inhibit the defluorination of the 5:3 acid. This might be linked to the higher hydrophobicity of the 5:3 acid that made it outcompete PFOA in terms of existing at or near the ZnO surface.

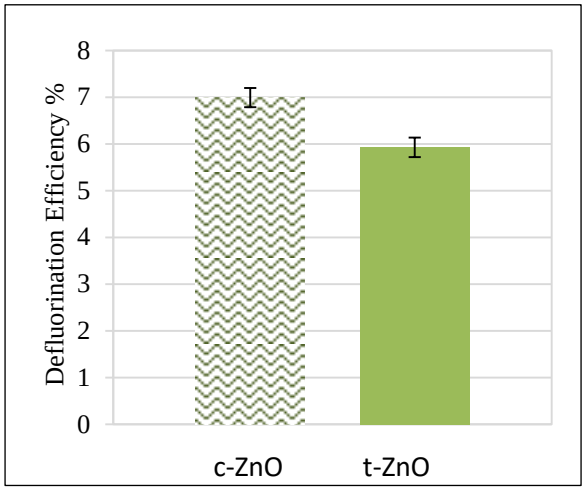

Figure 9 Defluorination efficiencies for a mixture of PFOA and 5:3 acid by 1 g/L ZnO

4.2.4 Determining time-course defluorination of PFASs by tetrapod ZnO

The time-course experiment was conducted for the 5:3 acid in 1 g/L of tetrapod ZnO. The results showed that fluoride release increased during 5 days of UV exposure

(Figure 10). After 5 days, no more fluoride was released. Three possible explanations might be related to stopping further defluorination after 5 days of UV photocatalysis. First, the metabolites and intermediates generating were more persistent and required more energy input to be removed. Second, there is a possibility of having all the ZnO been used up. Finally, the oxygen in the vials could be depleted, and that might change the redox reactions.

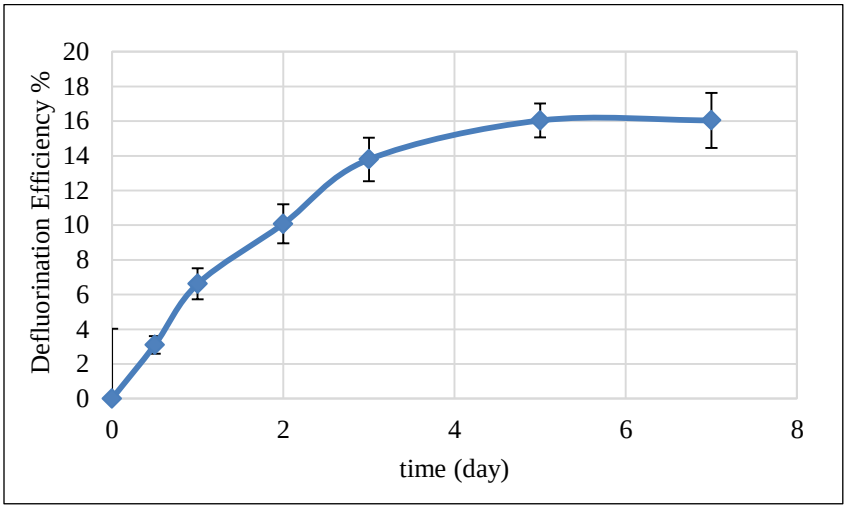

Figure 10 Change of defluorination efficiency with time for the 5:3 acid in 1 g/L tetrapod ZnO

For the time-course experiments of PFAAs with tetrapod ZnO, 27 mM of PS was added. ZnO was not dissolved immediately after adding PS. However, after about 1 day of UV light exposure, most of the ZnO dissolved (pictures available in the appendix). This is an indication of the sulfate radicals' generation and reduction of pH. The pH of the samples dropped after adding PS from about 7.5 to near 6. For PFOA defluorination, the efficiency increased from less than 1% without PS to about 4.4% (Figure 11). The curve of defluorination efficiency for PFOA was different from the 5:3 experiment. This is probably because PS performs better with lower pH; therefore, as pH goes down, more defluorination could be observed.

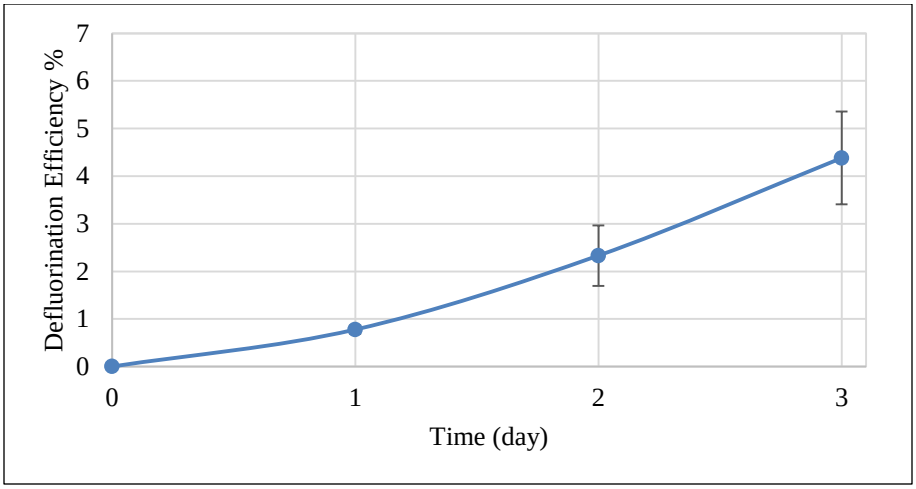

Figure 11 Change of defluorination efficiency with time for PFOA in 1 g/L tetrapod ZnO + 27 mM PS

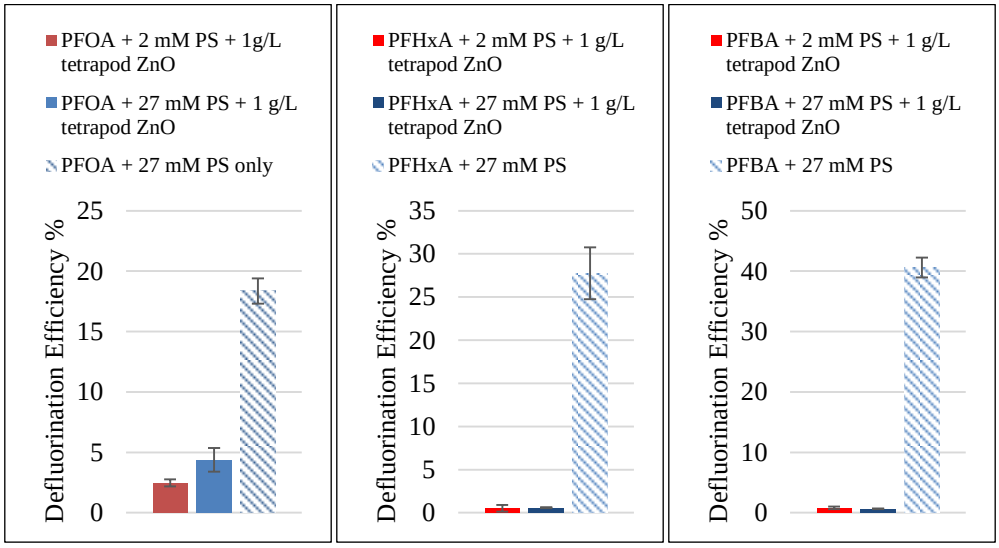

Figure 12 Comparisons of PFASs defluorination between adding 27 mM of PS alone and adding PS with tetrapod ZnO

Adding 2 mM of PS as the sole catalyst showed lower defluorination than when it was added with ZnO as mentioned before. However, it was quite interesting that when PS concentration increased to 27 mM, the defluorination with PS alone showed very

high defluorination efficiency (Figure 12). The defluorination efficiency increased with decreasing the PFAAs chain and reached 40% with PFBA. We hypothesized here that when PS concentration increased, PS: PFASs was in the range of 700:1 for PFBA and 1400:1 for PFOA, based on molar calculations, there was excess PS available to treat these contaminants without the need of ZnO.

Consequently, the photodegradation process can be divided into two sub-steps. First, the contaminants need to be treated with ZnO. Second, the supernatant can be taken for PS degradation. Accordingly, 3 ml was taken from the tetrapod ZnO-treated mixture (Figure 9), and 27 mM PS was added to the sample. Results showed that the efficiency increased after 2 additional days of UV exposure (total of 5 days, Figure 13) from 5.9% to 8.6%. If we assume that 5:3 acid component was only defluorinated during the ZnO photodegradation step, the defluorination of PFOA for the PS only stage is about 4.65%. This value is lower than the value obtained when PS was used with PFOA only in the sample (around 18.4 %, Figure 11). However, for PFOA+PS experiment, samples were exposed to UV for 3 days while for mixtures experiments; the extended UV exposure time for PS only part was 2 days only. It is probably that remaining 5:3 acid was competing with PFOA for sulfate radicals. Thus, the PFOA defluorination in the mixture was not as much as when it was added alone to the DI water + PS.

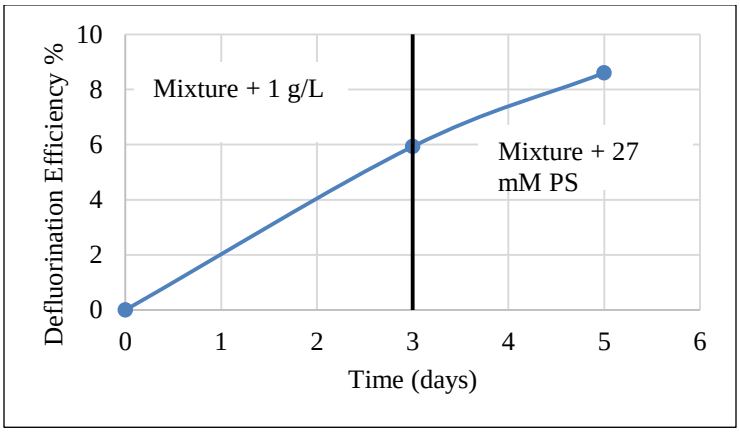

Figure 13 Separating tetrapod ZnO and PS treatments for the mixture of 5:3 acid and PFOA

4.2.5 Evaluating the structural stability of ZnO.

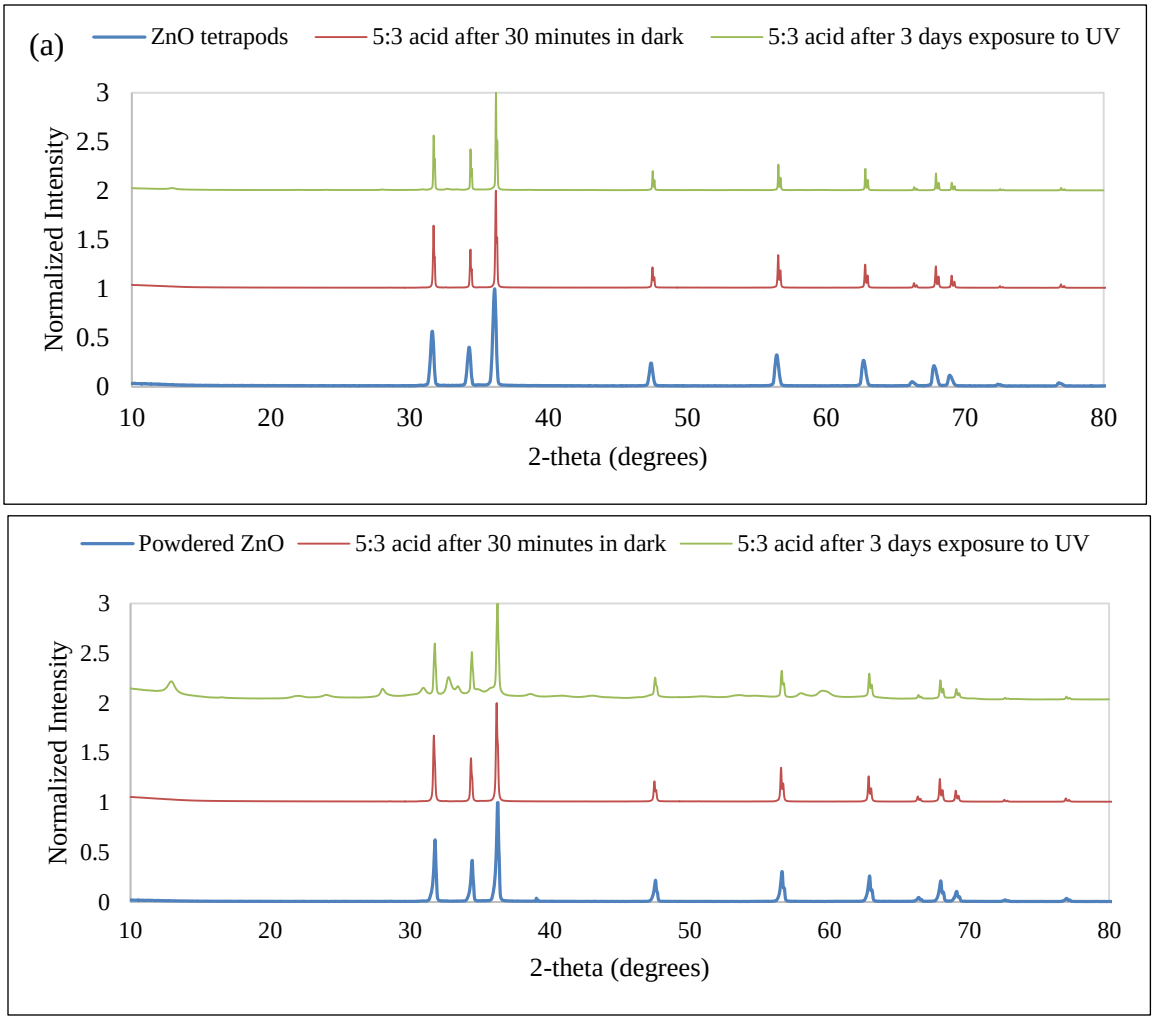

Figure 14 XRD Analysis for 5:3 acid samples with both (a) tetrapod and (b) commercial ZnO

Figure 14 shows the XRD spectra for 5:3 acid samples with both powdered and tetrapod ZnO. For both types of ZnO, there were no significant changes or shifts in the peaks of the curves after 30 minutes of shaking in the dark. However, after 3 days of UV light exposure, the commercial ZnO curve was not as smooth as for the fresh ZnO.

These findings were similar for 6:2 FTOH (Figure 20 in the appendix) with fewer changes for the commercial ZnO curve. Therefore, XRD analysis showed that the tetrapod ZnO was more structurally stable than the commercial ZnO. While the recyclability of ZnO could not be checked because the collected catalyst was not enough to be filtered and washed well, the XRD results can reflect that the commercial ZnO is more prone to deformations than the tetrapod one. One of the issues need to be studied in the future is how the age of the ZnO will affect the structural stability of the solid. Tetrapod ZnO was used for experiments after few weeks of its synthesis, whereas the commercial ZnO was purchased and it is not known accurately for how long it was stored before its usage.

4.3 Evaluating the Extent of PFASs Removal Using a Combination of Tetrapod ZnO-Assisted Photodegradation and FTOH-Degrading Bacteria

4.3.1 Determining the effects of growth medium on PFASs defluorination by tetrapod ZnO.

5:3 acid defluorination was highly inhibited when ZnO was added to a growth medium or buffer solution instead of DI water (Figure 15). This was in agreement with other photocatalysts when Indium oxide was added to water from effluents of secondary treatment systems to degrade PFOA [39]. It is not expected that the existence of many ions in the water inhibited the UV transmittance to the ZnO, as explained in the appendix. There are many positively and negatively charged ions in the bacterial growth media, as per the recipe of these media in the appendix, and they could sorb on the ZnO more quickly than the PFASs. Moreover, the water chemistry changed itself, and the types of radicals generated probably differed significantly. There were other trials for diluting the growth media, and observations showed that, for instance, even diluting the medium 100 times did not increase the defluorination efficiency.

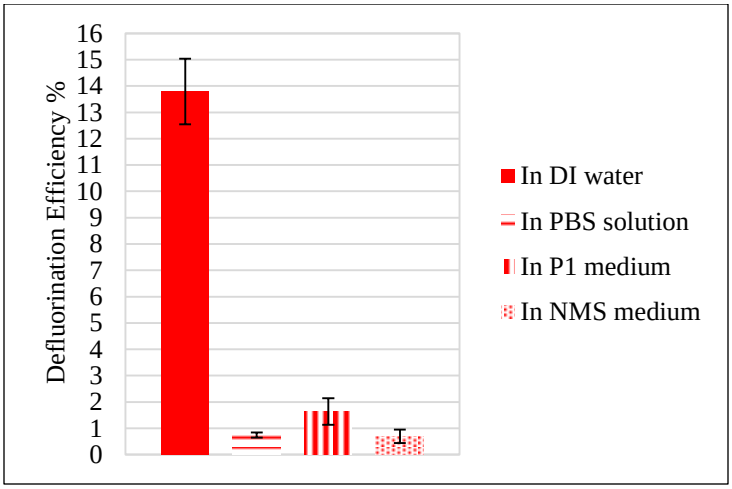

Figure 15 5:3 acid defluorination efficiencies in different growth media (pattern) Vs. in DI water (solid color) (samples were duplicated only).

4.3.2 Examining biodegradation potential of the metabolites generated from tetrapod ZnO-assisted photodegradation of PFASs.

There was a very slight improvement for the photo-treated 5:3 acid after 14 days of the biological incubation (Figure 16). The increment of defluorination was about 1 % only (from 11.8 % to 12.8%). It is not known whether that increment in the defluorination efficiency was an actual improvement or it was within the margin of error. However, each individual sample showed a slight release of the free fluoride with the time. For two out of three samples, there was only 0.01 ppm increased over the entire biological incubation time. For the third sample, there was 0.06 ppm increment. According to Kim *et al* paper, when 5:3 was tested by *P. fluorescens* DSM 8341, the only metabolite detected after 14 days of the experiment was the 5:3 Uacid (about 3% only on a molar basis); in addition, there were no free fluoride measurements [11]. Finally, based on the theoretical calculations after diluting the samples, the amounts of fluoride released at the end of the photodegradation step was a little less than what was measured at time 0 for the biodegradation step. Therefore, without going for advanced analysis of the samples using LC/MS/MS instruments, we cannot confirm the feasibility of the photo-bio treatment train.

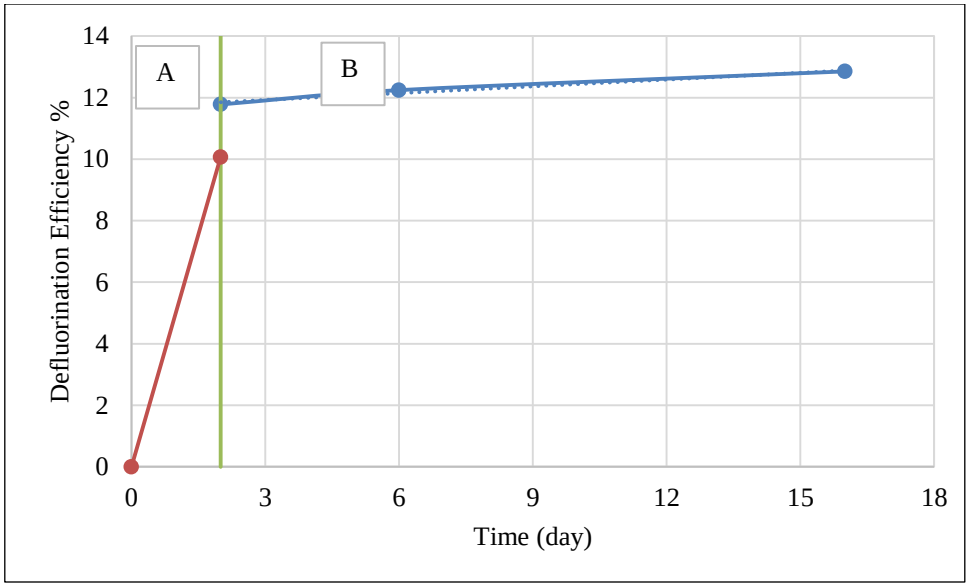

Figure 16 Photo (A) and bio (B) degradation treatment train for 5:3 acid

4.4 Applications to Treatment Systems

Outcomes of this research showed that there is a potential to treat some polyfluorinated acids by ZnO. In addition, the PFAAs defluorination might be enhanced by adding persulfate. However, all the successful defluorination experiments were conducted in DI water. Thus, applying this technology directly to the effluents from treatment systems will not be effective. Before scaling up the experiments, isolating the PFASs among other contaminants, ions and natural organic matters is strongly recommended. Although there is no strong experimental evidence supporting that, the contaminants have to be on or near the photocatalyst's surface in order to be treated. Therefore, working on enhancing the adsorption capacities and potentials for ZnO may also optimize the degradation. Coating the ZnO or mixing it with other catalysts are possible solutions worthy of further studies.

The UV lamps used were of 4 W and long wave range. The lamps were placed below the vials. Therefore, the vials got the UV light from the bottom only. The positioning of vials and lamps were selected for two main experimental reasons. The first reason is to restrict any interaction between the solution and the PTFE septa caps.

The other reason related to the fact that placing the lamp other than below the vials will limit the number of samples being exposed to the UV lamp. According to the manufacturer, the UV light intensity is about 13 W/m^2 when samples are placed at a distance of 3 inches, whereas the natural sunlight intensity is about 3.8 W/m^2 near the sea level [35]. Therefore, on one hand, we are using higher light intensity than the sunlight. On the other hand, we did not expose the entire sample to the UV light. Some preliminary experiments were done by exposing the samples to sunlight. The results after 7 days of sunlight exposure were similar to the obtained results. However, the results will obviously vary with seasonal changes. To sum up, more research is required to check the feasibility of ZnO to be applied on the large scale treatment. It is important to re-mention that one of the advantages of ZnO is its inexpensive cost as compared to some other photocatalysts like titanium and indium oxides. Another advantage of ZnO is the high possibility of recovery so that it can be reused again.

5. CONCLUSIONS AND RECOMMENDATIONS

5.1 Introduction

This short chapter is divided into two main parts. The first part lists the conclusions found in this study, whereas the second part presents recommendations for future work.

5.2 Conclusions

The main conclusions can be summarized in the following points:

- Powdered commercial ZnO showed better defluorination than the tetrapod ZnO for all of the selected PFASs when the concentration of 1g/L of ZnO was used. However, the overall degradation and removal of the parent compounds needs to be investigated.
- ZnO, in general, showed a good potential to defluorinate the 5:3 polyfluorinated acid in natural pH.
- The 6:2 FTOH biodefluorination is better than photodefluorination by ZnO.
- PFAAs, like PFOA, PFHxA and PFBA can be better removed with the addition of small amounts of persulfate to ZnO.
- Adding PS only to DI water and PFAAs could defluorinate PFAAs to a high extent with exposure to 365 nm UV at room temperature conditions. The pH of the solution will be reduced to around 4.
- Kinetics showed that the ZnO will increase the rate of 5:3 acid defluorination gradually during the first 3 days of UV exposure. No further defluorination could be observed after 5 days.
- The existence of ions needed for bacterial growth hindered the defluorination of the 5:3 acid.
- It might be possible to biodegrade the photodegraded samples. However, more studies are required to confirm this finding.

5.3 Recommendations

This is the first report studying the PFASs removal with ZnO. Therefore, many issues need to be further verified and studied:

- There is a necessity to investigate the intermediates produced through the photodegradation processes. This type of analysis requires advanced instruments like LCMS. The results of this analysis will answer many of the questions raised in the discussion of this project. The advanced instruments will enable conducting experiments at lower concentrations similar to the current concentrations of PFASs in the environment.
- More detailed solid analysis is required to better understand the speciation of the fluorine on the solid ZnO. This will enable closing the mass balance and will give more ideas about what is actually happening on the solid itself.
- It is vital to improve the experimental setup. This can be achieved by having reactors designed specifically for these experiments. In addition, purging oxygen might be required to keep the aerobic conditions efficient and also avoid ZnO settlement and aggregation.
- Examining more PFASs is valuable. For instance, other sub-groups like the sulfonated PFASs need to be studied due to their importance and distribution.
- There is a need to address the challenges and find solutions for optimizing a treatment train.
- It is worthy to study either coating the ZnO with some materials or mixing it with other photocatalysts.

REFERENCES

1. Kim, M., L.Y. Li, J.R. Grace, and C. Yue, *Selecting reliable physicochemical properties of perfluoroalkyl and polyfluoroalkyl substances (PFASs) based on molecular descriptors.* Environmental Pollution, 2015. **196**: p. 462-472.
2. Key, B.D. and R.D. Howell, *Fluorinated organics in the biosphere.* Environmental Science and Technology, 1997. **31**(9): p. 2445-2454.
3. Arias Espana, V.A., M. Mallavarapu, and R. Naidu, *Treatment technologies for aqueous perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA): A critical review with an emphasis on field testing.* Environmental Technology and Innovation, 2015. **4**: p. 168-181.
4. Bao, Y., J. Niu, Z. Xu, D. Gao, J. Shi, *et al.*, *Removal of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) from water by coagulation: mechanisms and influencing factors.* Journal of Colloid and Interface Science, 2014. **434**: p. 59-64.
5. Liu, D., Z. Xiu, F. Liu, G. Wu, D. Adamson, *et al.*, *Perfluorooctanoic acid degradation in the presence of Fe(III) under natural sunlight.* Journal of Hazardous Materials, 2013. **262**: p. 456-463.
6. Wu, Y.X. and V.W.C. Chang, *The effect of surface adsorption and molecular geometry on the determination of henry's law constants for fluorotelomer alcohols.* Journal of Chemical and Engineering Data, 2011. **56**(8): p. 3442-3448.
7. Arvaniti, O.S., Y. Hwang, H.R. Andersen, A.S. Stasinakis, N.S. Thomaidis, *et al., Reductive degradation of perfluorinated compounds in water using Mg-aminoclay coated nanoscale zero valent iron.* Chemical Engineering Journal, 2015. **262**: p. 133-139.
8. Houtz, E.F. and D.L. Sedlak, *Oxidative conversion as a means of detecting precursors to perfluoroalkyl pcids in urban runoff.* Environmental Science and Technology, 2012. **46**: p. 9342-9349.

9. Schröder, H.F. and R.J.W. Meesters, *Stability of fluorinated surfactants in advanced oxidation processes—A follow up of degradation products using flow injection–mass spectrometry, liquid chromatography–mass spectrometry and liquid chromatography–multiple stage mass spectrometry.* Journal of Chromatography A, 2005. **1082**: p. 110-119.
10. Kim, M.H., N. Wang, T. McDonald, and K.H. Chu, *Biodefluorination and biotransformation of fluorotelomer alcohols by two alkane-degrading Pseudomonas strains.* Biotechnology and Bioengineering, 2012. **109**(12): p. 3041-3048.
11. Kim, M.H., N. Wang, and K.H. Chu, *6:2 Fluorotelomer alcohol (6:2 FTOH) biodegradation by multiple microbial species under different physiological conditions.* Applied Microbiology and Biotechnology, 2014. **98**(4): p. 1831-1840.
12. Trautmann, A.M., H. Schell, K.R. Schmidt, K.M. Mangold, and A. Tiehm, *Electrochemical degradation of perfluoroalkyl and polyfluoroalkyl substances (PFASs) in groundwater.* Water Science and Technology, 2015. **71**(10): p. 1569-1575.
13. Akhmal Saadon, S., P. Sathishkumar, A.R. Mohd Yusoff, M.D. Hakim Wirzal, M.T. Rahmalan, *et al.*, *Photocatalytic activity and reusability of ZnO layer synthesised by electrolysis, hydrogen peroxide and heat treatment.* Environmental Technology (United Kingdom), 2016. **37**(15): p. 1875-1882.
14. Vellanki, B.P., B. Batchelor, and A. Abdel-Wahab, *Advanced reduction processes: A new class of treatment processes.* Environmental Engineering Science, 2013. **30**(5): p. 264-271.
15. Xiaobo, W., Q. Yanlei, Z. Lihua, and T. Heqing, *Nitrogen-doped reduced graphene oxide as a bifunctional material for removing bisphenols: synergistic effect between adsorption and catalysis.* Environmental Science and Technology, 2015. **49**(11): p. 6855-6864.

16. Lee, Y.-C., S.-L.s.n.t. Lo, J. Kuo, and C.-P. Huang, *Promoted degradation of perfluorooctanic acid by persulfate when adding activated carbon.* Journal of Hazardous Materials, 2013. **261**: p. 463-469.
17. Esplugas, S., J. Giménez, S. Contreras, E. Pascual, and M. Rodríguez, *Comparison of different advanced oxidation processes for phenol degradation.* Water Research, 2002. **36**(4): p. 1034-1042.
18. Michael R. Hoffmann, Scot T. Martin, a. Wonyong Choi, and D.W. Bahnemannt, *Environmental applications of semiconductor photocatalysis.* Chemical reviews, 1995. **95**(1): p. 69-96.
19. Mai, F.D., C.C. Chen, J.L. Chen, and S.C. Liu, *Photodegradation of methyl green using visible irradiation in ZnO suspensions: determination of the reaction pathway and identification of intermediates by a high-performance liquid chromatography-photodiode array-electrospray ionization-mass spectrometry method.* Journal of Chromatography A, 2008. **1189**(1-2): p. 355-365.
20. Montazerozohori, M. and S.A. Hosseini Pour, *Phototocatalytic decolorization of 5-[4-(dimethylamino) phenylmethylene]-2-thioxo-4-thiazolidinone using nano-powder zinc oxide at various basic buffer pHs.* Desalination and Water Treatment, 2013. **52**(40-42): p. 7993-7998.
21. Bak, S.-A., M.-S. Song, I.-T. Nam, and W.-G. Lee, *Photocatalytic oxidation of trichloroethylene in water using a porous ball of nano-ZnO and nanoclay composite.* Journal of Nanomaterials, 2015. **2015**: p. 1-8.
22. Liu, J., N. Wang, B. Szostek, R.C. Buck, P.K. Panciroli, *et al.*, *6-2 fluorotelomer alcohol aerobic biodegradation in soil and mixed bacterial culture.* Chemosphere, 2010. **78**: p. 437-444.
23. (EPA), U.S.E.P.A. *Fact sheet PFOA & PFOS drinking water health advisories*. 2016; Available from: https://www.epa.gov/sites/production/files/2016-06/documents/drinkingwaterhealthadvisories_pfoa_pfos_updated_5.31.16.pdf.
24. Zhang, S., B. Szostek, P.K. McCausland, B.W. Wolstenholme, X. Lu, *et al.*, *6:2 and 8:2 fluorotelomer alcohol anaerobic biotransformation in digester sludge*

from a WWTP under methanogenic conditions. Environmental Science and Technology, 2013. **47**(9): p. 4227-4235.

25. Takagi, S., F. Adachi, K. Miyano, Y. Koizumi, H. Tanaka, *et al., Fate of perfluorooctanesulfonate and perfluorooctanoate in drinking water treatment processes.* Water Research, 2011. **45**(13): p. 3925-3932.
26. Gregg, K., B. Hamdorf, K. Henderson, J. Kopecny, and C. Wong, *Genetically modified ruminal bacteria protect sheep from fluoroacetate poisoning.* Applied and Environmental Microbiology, 1998. **64**(9): p. 3496-3498.
27. Guo, R., W.-J. Sim, E.-S. Lee, J.-H. Lee, and J.-E. Oh, *Evaluation of the fate of perfluoroalkyl compounds in wastewater treatment plants.* Water Research, 2010. **44**: p. 3476-3486.
28. Allred, B.M., J.R. Lang, M.A. Barlaz, and J.A. Field, *Physical and biological release of poly- and perfluoroalkyl substances (PFASs) from municipal solid waste in anaerobic model landfill reactors.* Environmental Science and Technology, 2015. **49**(13): p. 7648-7656.
29. Backe, W.J., T.C. Day, and J.A. Field, *Zwitterionic, cationic, and anionic fluorinated chemicals in aqueous film forming foam formulations and groundwater from U.S. military bases by nonaqueous large-volume injection HPLC-MS/MS.* Environmental Science and Technology, 2013. **47**(10): p. 5226-5234.
30. Place, B.J. and J.A. Field, *Identification of novel fluorochemicals in aqueous film-forming foams used by the US military.* Environmental Science and Technology, 2012. **46**(13): p. 7120-7127.
31. Park, S., L.S. Lee, A. Zull, V.F. Medina, and S. Waisner, *Heat-activated persulfate oxidation of PFOA, 6:2 fluorotelomer sulfonate, and PFOS under conditions suitable for in-situ groundwater remediation.* Chemosphere, 2016. **145**: p. 376-383.
32. Stock, N.L., D.C.G. Muir, and S. Mabury, *Perfluoroalkyl Compounds*, in *Persistent Organic Pollutants*. 2009, John Wiley & Sons, Ltd. p. 25-69.

33. Lee, Y.-C., S.-L. Lo, P.-T. Chiueh, Y.-H. Liou, and M.-L. Chen, *Microwave-hydrothermal decomposition of perfluorooctanoic acid in water by iron-activated persulfate oxidation.* Water Research, 2010. **44**: p. 886-892.

34. (EPA), U.S.E.P.A. *Emerging contaminants – perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA)*. 2013; Available from: https://nepis.epa.gov/Exe/ZyNET.exe/P100LTG6.TXT?ZyActionD=ZyDocument&Client=EPA&Index=2011+Thru+2015&Docs=&Query=&Time=&EndTime=&SearchMethod=1&TocRestrict=n&Toc=&TocEntry=&QField=&QFieldYear=&QFieldMonth=&QFieldDay=&IntQFieldOp=0&ExtQFieldOp=0&XmlQuery=&File=D%3A%5Czyfiles%5CIndex%20Data%5C11thru15%5CTxt%5C00000014%5CP100LTG6.txt&User=ANONYMOUS&Password=anonymous&SortMethod=h%7C-&MaximumDocuments=1&FuzzyDegree=0&ImageQuality=r75g8/r75g8/x150y150g16/i425&Display=hpfr&DefSeekPage=x&SearchBack=ZyActionL&Back=ZyActionS&BackDesc=Results%20page&MaximumPages=1&ZyEntry=1&SeekPage=x&ZyPURL.

35. Taniyasu, S., N. Yamashita, E. Yamazaki, G. Petrick, and K. Kannan, *The environmental photolysis of perfluorooctanesulfonate, perfluorooctanoate, and related fluorochemicals.* Chemosphere, 2013. **90**(5): p. 1686-1692.

36. Wang, Y., J. Niu, Y. Li, T. Zheng, Y. Xu, *et al.*, *Performance and mechanisms for removal of perfluorooctanoate (PFOA) from aqueous solution by activated carbon fiber.* RSC Adv., 2015. **5**(106): p. 86927-86933.

37. Prevedouros, K., I.T. Cousins, R.C. Buck, and S.H. Korzeniowski, *Sources, fate and transport of perfluorocarboxylates.* Environmental Science and Technology, 2006. **40**(1): p. 32-44.

38. Wang, N., R.C. Buck, B. Szostek, L.M. Sulecki, and B.W. Wolstenholme, *5:3 Polyfluorinated acid aerobic biotransformation in activated sludge via novel "one-carbon removal pathways".* Chemosphere, 2012. **87**: p. 527-534.

39. Li, X., P. Zhang, L. Jin, T. Shao, Z. Li, *et al.*, *Efficient photocatalytic decomposition of perfluorooctanoic acid by indium oxide and its mechanism.* Environmental Science and Technology, 2012. **46**(10): p. 5528-5534.
40. Fr. Schröder, H., W. Gebhardt, J. Pinnekamp, H.J. José, and R.F.P.M. Moreira, *Biological wastewater treatment followed by physicochemical treatment for the removal of fluorinated surfactants.* Water Science and Technology, 2010. **61**(12): p. 3208-3215.
41. Murphy, C.D., *Biodegradation and biotransformation of organofluorine compounds.* Biotechnol Letters, 2010. **32**(3): p. 351-359.
42. Kwon, B.G., H.J. Lim, S.H. Na, B.I. Choi, D.S. Shin, *et al.*, *Biodegradation of perfluorooctanesulfonate (PFOS) as an emerging contaminant.* Chemosphere, 2014. **109**: p. 221-225.
43. Eschauzier, C., E. Beerendonk, P. Scholte-Veenendaal, and P. De Voogt, *Impact of treatment processes on the removal of perfluoroalkyl acids from the drinking water production chain.* Environmental Science and Technology, 2012. **46**(3): p. 1708-1715.
44. Xiao, F., M.F. Simcik, and J.S. Gulliver, *Mechanisms for removal of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) from drinking water by conventional and enhanced coagulation.* Water Research, 2013. **47**: p. 49-56.
45. Lin, H., Y. Wang, J. Niu, Z. Yue, and Q. Huang, *Efficient sorption and removal of perfluoroalkyl acids (PFAAs) from aqueous solution by metal hydroxides generated in situ by electrocoagulation.* Environmental Science and Technology, 2015. **49**(17): p. 10562-10569.
46. Koda, Y., T. Terashima, and M. Sawamoto, *Fluorous microgel star polymers: selective recognition and separation of polyfluorinated surfactants and compounds in water*. Journal of the American Chemical Society, 2014. **136**(44): p. 15742-15748.

47. Zhang, C., Y. Peng, K. Ning, X. Niu, S. Tan, *et al.*, *Remediation of perfluoroalkyl substances in landfill leachates by electrocoagulation.* Clean - Soil, Air, Water, 2014. **42**(12): p. 1740-1743.
48. Colosi, L.M., R.A. Pinto, H. Qingguo, and J.W.J. Weber, *Peroxidase-mediated degradation of perfluorooctanoic acid.* Environmental Toxicology and Chemistry, 2009. **28**(2): p. 264-271.
49. Qu, Y., C.-J. Zhang, P. Chen, Q. Zhou, and W.-X. Zhang, *Effect of initial solution pH on photo-induced reductive decomposition of perfluorooctanoic acid.* Chemosphere, 2014. **107**: p. 218-223.
50. Song, Z., H. Tang, N. Wang, and L. Zhu, *Reductive defluorination of perfluorooctanoic acid by hydrated electrons in a sulfite-mediated UV photochemical system.* Journal of Hazardous Materials, 2013. **262**: p. 332-338.
51. Sun, X.W. and Y. Yang, *ZnO nanostructures and their applications.* 2012: Singapore : Pan Stanford Pub., [2012].
52. Gholami, M., H.R. Nassehinia, A. Jonidi-Jafari, S. Nasseri, and A. Esrafili, *Comparison of Benzene & Toluene removal from synthetic polluted air with use of nano photocatalyticTiO2/ ZnO process.* Journal of Environmental Health Science and Engineering, 2014. **12**: p. 1-8.

APPENDIX

1- Measuring the efficiency of vials in terms of light absorbance

A simple experiment was conducted to test the efficiency of the vials for UV light absorbance. The borosilicate glass vials were placed between the sender and the receiver of the UV light of a spectrophotometer. The vials were cleaned carefully before being placed. Then, 365 nm wavelength was selected and transmittance was chosen as the type of measurements. The light absorbance was calculated according to Beer-Lambert's law as follows:

$$Absorbance\ Units\ (Au) = {-\log_{10}^{\left(Transmittance\ \%/_{100}\right)}}/_{2}$$

The reason why values were divided by 2 because the light passed through two layers of glass as the vials were placed vertically, whereas this project's experiments were conducted in a way that the UV light passes through the base of the vial (one layer of glass). The thickness of the glass of the vials was 1.3 mm in all sides according to the manufacturer. However, the vials were cylindrical, and that may cause some scattering of the light. Results showed that the absorbance of the empty vial was less than 0.1 Au for wavelengths in the range of 330-400 nm. The absorbance was slightly higher when vials where filled with DI water (Figure 17). Moreover, some clear growth medium like P1 medium showed similar absorbance as DI water, indicating that the existence of ions in the medium did not affect the absorbance significantly.

2- Absorbance of samples with tetrapod and powdered ZnO

The purpose of this experiment was to estimate to which depth the UV light will penetrate the samples that include ZnO. The empty cuvettes were used as blanks to show 100% transmittance. After that, solutions of 1 g/L of ZnO were prepared and shaken. The solutions needed to be shaken immediately before adding them to the cuvettes to avoid settlement of ZnO particles. 1 ml of the solution transferred to the cuvettes, and

measured directly for transmittance. For these measurements, absorbance was calculated as follows:

$$Absorbance\ Units\ (Au) = -log_{10}^{\left(Transmittance\ \%/_{100}\right)}$$

Results showed that both of tetrapod and powdered ZnO absorbed most of the light within depth of 0.45 cm (Figure 18). Based on measurements of glass vials and samples absorbance, we can conclude that within 0.5 cm of sample depth from the base of the vial, almost all UV photons were absorbed. This finding supported the necessity of shaking the samples well in order to let most of the samples get photons from the UV light. It is worthy to mention that the outcomes for parts 1 and 2 in the appendix are not necessarily accurate due to many variations related to the shapes of the vials and possible settlement of ZnO.

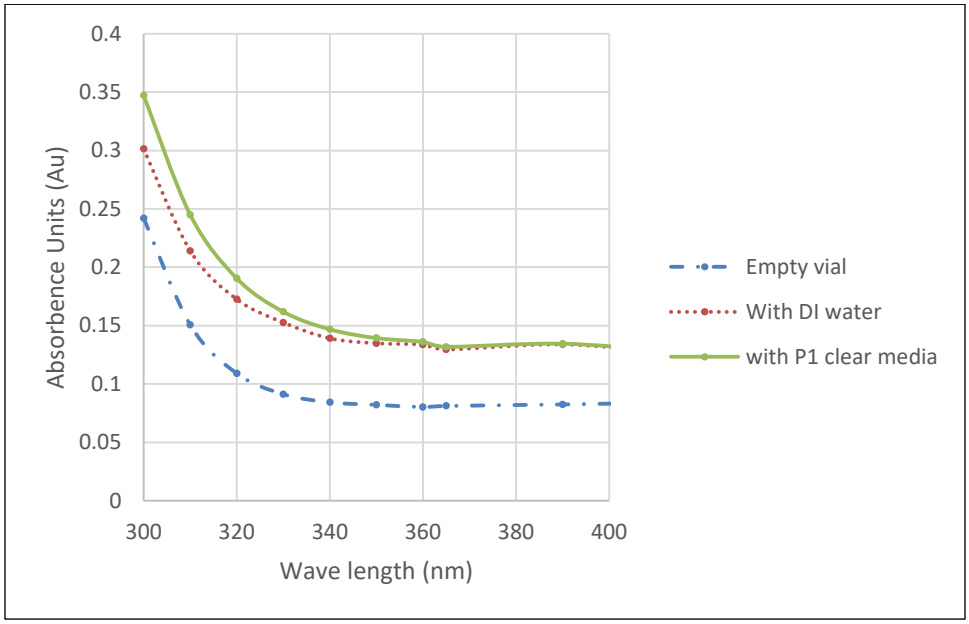

Figure 17 Light absorbance of borosilicate glass vials with different wave lengths

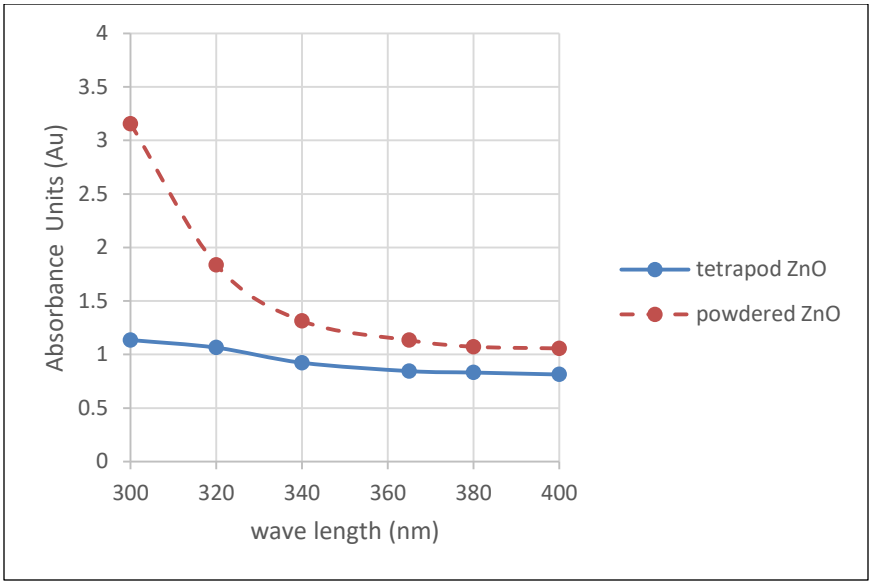

Figure 18 Light absorbance of 0.45 cm samples length of 1 g/L ZnO

3- Effects of PS on the solubility of tetrapod ZnO

Figure 19 shows how the ZnO before PS addition of 27 mM (a) will dissolve after the exposure to the UV lamp for 1-3 days.

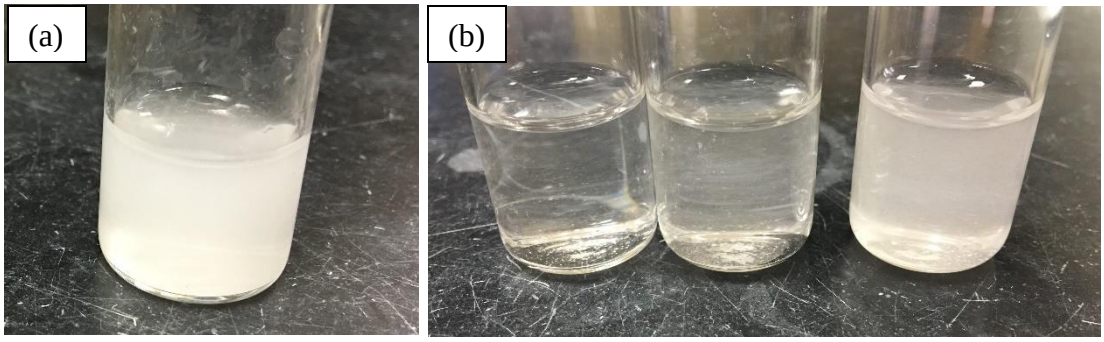

Figure 19 1 g/L of tetrapod ZnO with 27 mM PS (a) before UV exposure (b) after 1, 2 and 3 days of UV exposure (from right to left)

4- XRD results for 6:2 FTOH

Following the results of task 1e, the 6:2 FTOH was tested by XRD as well. The results (Figure 20) showed a similar trend to the obtained results with 5:3 acid samples but with less deformation for samples of powdered ZnO.

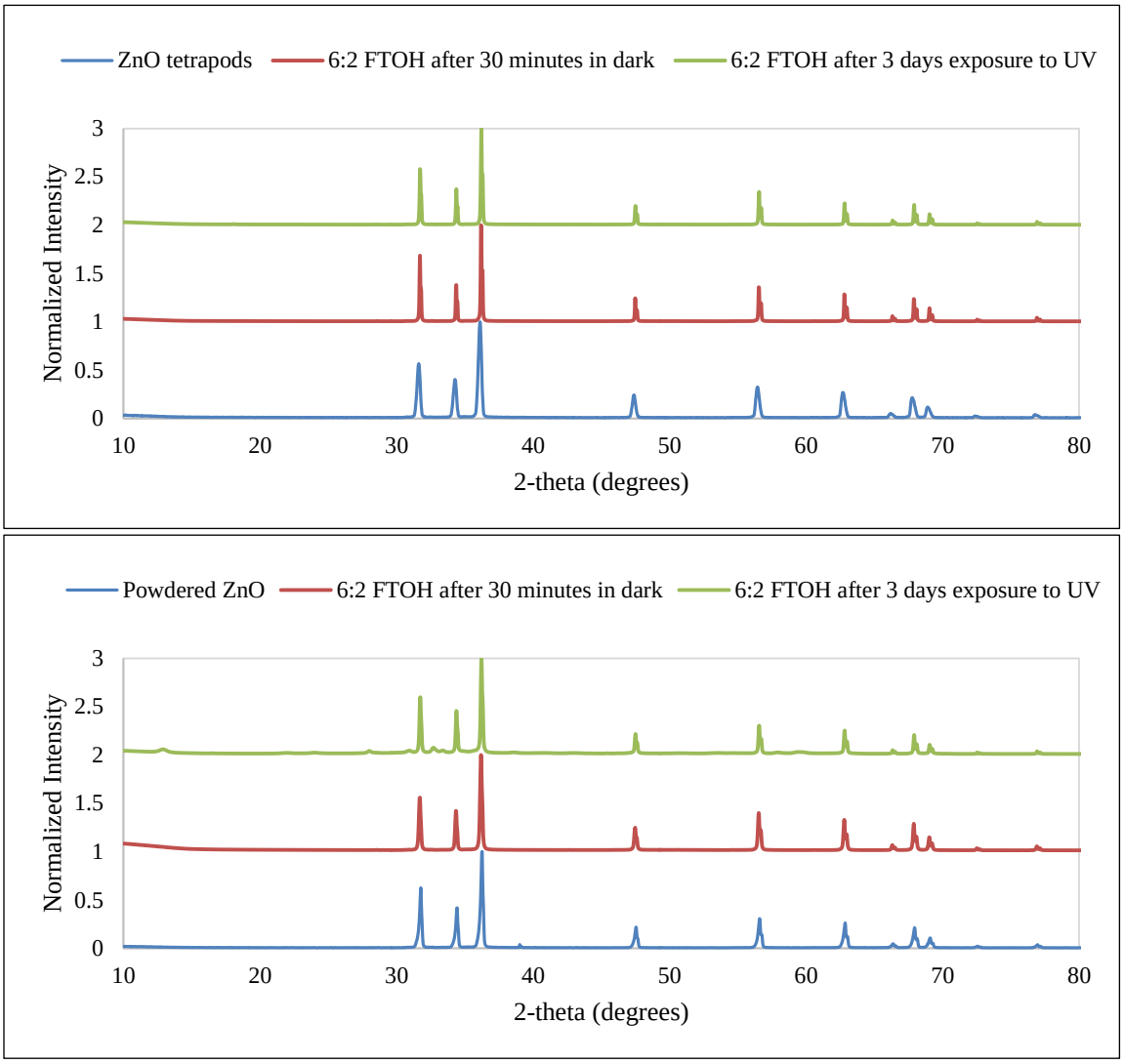

Figure 20 XRD analysis results for samples with 6:2 FTOH

5- Stock solutions preparations

Stock solutions are prepared as follows (for all tasks, except task 1c and some samples for EDX/XPS measurements):

1- 6:2 FTOH: available as liquid. Prepare a 25 ml vial. Add 25 ml 50% ethanol (v/v) and close the vials tightly. Then add 62 ul of 6:2 FTOH to have a stock solution of 4.125 g/L solution.
2- 5:3 acid: available as powder. Dissolve 0.035 g in 10 ml 33% ethanol (v/v) to have a stock solution of 3.5 g/L solution.
3- PFOA: Available as powder. Dissolve 25 mg in 10 ml of DI water to have a stock solution of 2.5 g/L.
4- PFHxA: Available as liquid. Add 25 ul of PFHxA to 10 ml of DI water to have a stock solution of 4.39 g/L.
5- PFBA: Available as liquid. Add 20 ul of PFBA to 10 ml of DI water to have a stock solution of 3.28 g/L.

5- Tables showing the calculations used for the experiments

Targeted F^- Concentration (ppm)	DI water added (ml)	ppm concentration of solution chosen to add F^- from	Amount added (ml)
2.5	2.925	100	0.075
1	1.2	2.5	0.8
0.5	1.6	2.5	0.4
0.1	1.8	1	0.2
0.025	1.5	0.1	0.5

Table 2 Calculations for fluoride standard curve preparation

PFAS	Stock solution concentration (g/L)	Molecular weight (g/mole)	Added volume from stock solution (ul)	Amount of the compound added into vial (ug)	Concentration of the compound in a vial containing 6 mL liquid (uM)	Theoretical F^- released, if complete defluorinated, uM	Theoretical F^- released, if complete defluorinated, mg/L	Calculated Concentration (mg/L)
6:2 FTOH*	4.13	364.10	30.00	47.40	21.70	282.07	5.36	7.90
PFOA	2.50	414.07	20.00	50.00	20.06	300.88	5.72	8.31
5:3 Acid	3.50	342.11	15.00	52.50	25.51	280.64	5.33	8.73
PFHxA	4.39	314.05	12.00	52.68	27.90	306.92	5.83	8.76
PFBA	3.28	214.04	15.00	49.20	38.22	267.51	5.08	8.18
*** The amount of 6:2 FTOH added was based on having at least 5 pp of total fluorine in liquid when considering Henry's constant**								

Table 3 Calculations of the final concentrations and theoretical F^- contents for task 1 (except for task 1c and samples with persulfate for tasks 1b and 1e)

Compound	Stock solution concentration (g/L)	Added volume from stock solution (ul)	Concentration of the compound in a vial containing 6 mL liquid (uM)	Theoretical F^- released, if complete defluorinated, uM	Theoretical F^- released, if complete defluorinated, mg/L	Calculated Concentration (mg/L)	Persulfate added (ul)	mM Persulfate	Molar PS:PFAS ratio
sodium persulfate	4.8	15	50.29			11.97			
6:2 FTOH	4.125	30	56.22	730.92	13.89	20.47	15	0.05	0.89
PFOA	2.5	20	20.01	300.13	5.70	8.29	15	0.05	2.50
5:3 Acid	3.5	15	25.45	279.94	5.32	8.71	15	0.05	1.96
PFHxA	4.39	12	27.90	306.92	5.83	8.76	15	0.05	1.79
PFBA	3.28	15	38.22	267.51	5.08	8.18	15	0.05	1.31
sodium persulfate	150	20	2093.60			498.34			
6:2 FTOH	4.125	30	56.18	730.32	13.88	20.45	20	2.09	37.26
PFOA	2.5	20	19.99	299.88	5.70	8.28	20	2.09	104.69
5:3 Acid	3.5	15	25.41	279.48	5.31	8.69	25	2.09	82.38
PFHxA	4.39	12	27.90	306.92	5.83	8.76	20	2.61	93.69
PFBA	3.28	15	38.22	267.51	5.08	8.18	20	2.09	54.77

Table 4 Calculations of the final concentrations and theoretical F^- contents when persulfate is added to have a final PS concentration of 50 uM and 2 mM.

	Volume of the 30% ethanol in vial (ml)	Amount of PFAS added (mg)	Concentration in stock solution (mg/mL)	molecular weight(g/ mole)	Molar Concentration of the stock solution (mM)
5:3 Acid	5	10	2.00	342.11	5.85
PFOA	5	12	2.40	414.07	5.80

Table 5 Stock solution concentration of the mixture to be used in task 1c.

PFAS	Stock solution concentration (g/L)	Molecular weight (g/mole)	Added volume from stock solution (ul)	Amount of the compound added into vial (ug)	Concentration of the compound in a vial containing 6 mL liquid (uM)	Theoretical F^- released, if complete defluorinated, uM	Theoretical F^- released, if complete defluorinated, mg/L	Calculated Concentration (mg/L)
PFOA	2.40	414.07	12.00	28.80	11.57	173.54	3.30	4.79
5:3 Acid	2.00	342.11	12.00	24.00	11.67	128.36	2.44	3.99
					Total:	***301.89***	***5.74***	

Table 6 Calculations of the Final concentrations and theoretical F^- contents for tasks 1c

NMS medium		**P1 mineral salts medium**		**PBS solution**	
Ingredients	concentration (mM)	Ingredients	concentration (mM)	Ingredients	concentration (mM)
$NaNO_3$	11.7602	$(NH_4)2HPO_4$	75.72	NaCl	137
Na_2HPO_4	6.1003	K_2HPO_4	28.71	KCl	2.7
K_2SO_4	0.9801	Na_2SO_4	3.52	Na_2HPO_4	10
$MgSO_4$•7H2O	0.1502			KH_2PO_4	1.8
$CaSO_4$• $2H_2O$	0.0703				
$FeSO_4$•7 H_2O	0.0799				
KI	0.0012				
$ZnSO_4$•$7H_2O$	0.0021				
$MnSO_4$	0.0020				
H_3BO_3	0.0016				

Table 7 Recipes for some of the media that were used in task 2 experiments