

FLORIDA STATE UNIVERISTY  
FAMU-FSU COLLEGE OF ENGINEERING

DEGRADATION OF PERFLUOROOCCTANOIC ACID BY A NON-THERMAL PLASMA  
REACTOR AND BIO-REACTORS

By

MEYSAM FARAHANI

A Thesis submitted to the  
Department of Civil and Environmental Engineering  
in partial fulfillment of the  
requirements for the degree of  
Master of Science

2019

ProQuest Number: 13808275

All rights reserved

INFORMATION TO ALL USERS

The quality of this reproduction is dependent upon the quality of the copy submitted.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if material had to be removed, a note will indicate the deletion.



ProQuest 13808275

Published by ProQuest LLC (2019). Copyright of the Dissertation is held by the Author.

All rights reserved.

This work is protected against unauthorized copying under Title 17, United States Code  
Microform Edition © ProQuest LLC.

ProQuest LLC.  
789 East Eisenhower Parkway  
P.O. Box 1346  
Ann Arbor, MI 48106 – 1346

Meysam Farahani defended this thesis on March 25, 2019.

The members of the supervisory committee were:

Youneng Tang  
Professor Directing Thesis

Bruce R. Locke  
Committee Member

Clayton J. Clark II  
Committee Member

The Graduate School has verified and approved the above-named committee members and certifies that the thesis has been approved in accordance with university requirements.

## ACKNOWLEDGMENTS

First, I express my sincere appreciation to my advisor, Dr. Youneng Tang, whose immense knowledge always aided as a well of motivation for me. His serenity, continuous help, and marvelous ideas made my graduate experience fruitful and inspiring. I believe that I am blessed to have had him as my supervisor.

I would also like to thank my research and supervisory committee members, Dr. Bruce Locke, Dr. Robert Wandell, and Dr. Clayton Clark, for their treasured time and assistance. Their guidance and advice played a significant role in improving my academic skills.

I am grateful to Dr. Rafael Kampmann, who was always supportive whenever I needed him. I was very lucky to be his teaching assistant.

Last but not the least, my infinite gratitude is for my parents for their unbroken care and support during my life. My deepest and endless thanks to my tolerant wife, Sara, who always inspired and reinforced me.

## TABLE OF CONTENTS

LIST OF TABLES .....	vi
LIST OF FIGURES .....	vii
ABSTRACT.....	viii
CHAPTER 1 INTRODUCTION .....	1
1.1 Non-thermal plasma treatment of PFOA in water .....	1
1.1.1 Non-thermal plasma reactor.....	1
1.1.2 PFOA removal by non-thermal plasma reactors.....	3
1.2 Biodegradation of perfluorinated compounds in water .....	5
1.2.1 PFOA, PFOS and other perfluorinated compounds.....	5
1.2.2 Trifluoroacetic acid (TFA).....	6
1.3 Combination of pulsed plasma reactor and bioreactors .....	7
1.4 Research objectives.....	8
CHAPTER 2 MATERIALS AND METHODS .....	9
2.1 Plasma experiments with a wide range of hydraulic retention time .....	10
2.2 Plasma experiments with different carrier gas.....	11
2.3 Plasma experiments with different PFOA concentrations (Argon as the carrier gas) .....	11
2.4 Biodegradation of PFOA and intermediates from plasma degradation of PFOA .....	12
2.5 Sampling and measurement methods for PFOA, intermediates, F <sup>-</sup> and H <sub>2</sub> O <sub>2</sub> .....	14
CHAPTER 3 RESULTS .....	16
3.1 Effect of HRT on F <sup>-</sup> production in plasma reactor .....	16
3.2 Effect of carrier gas (argon and helium) on PFOA degradation and F <sup>-</sup> and intermediates production in plasma reactor.....	17
3.2.1 PFOA measurements .....	17
3.2.2 Fluoride measurements .....	21
3.2.3 Intermediates measurements .....	21
3.2.4 TFA measurements .....	21
3.3 H <sub>2</sub> O <sub>2</sub> production in the plasma reactor .....	27
3.4 Biodegradation of PFOA and its plasma degradation intermediates .....	28
3.4.1 Fluoride (F <sup>-</sup> ) production in the bioreactors .....	28
3.4.2 PFOA degradation in the bioreactors.....	29
CHAPTER 4 DISCUSSION.....	30

4.1 Comparing this study with some other AOPs.....	30
4.2 Mechanism of PFOA degradation in the pulsed plasma reactor.....	32
4.2.1 Degradation pathway .....	32
4.2.2 The role of highly reactive species .....	34
CHAPTER 5 CONCLUSIONS .....	36
REFERENCES .....	37
BIOGRAPHICAL SKETCH .....	42

## LIST OF TABLES

Table 1. The components of one-liter NMS .....	12
Table 2. Average PFOA concentrations in the plasma reactor influent and effluents.....	18
Table 3. Average fluoride concentrations in the plasma reactor influent and effluents .....	22
Table 4. Comparing this study with other AOPs .....	31
Table 5. Comparing this study with Stratton et al. (2017) and Yasouka et al. (2011).....	33

## LIST OF FIGURES

Figure 1. The overall experimental plan for the plasma reactor and bioreactors .....	9
Figure 2. The plasma reactor used in this study.....	10
Figure 3. Schematic of the plasma reactor used in this study.....	11
Figure 4. Experiment configuration for bottles containing effluent from the plasma reactor .....	13
Figure 5. Experiment configuration for bottles containing influent from the plasma reactor .....	14
Figure 6. F <sup>-</sup> Concentrations in effluents with different flow rates (50 ppm of PFOA in DI water as influent of plasma reactor).....	16
Figure 7. Comparing F <sup>-</sup> concentration for effluent of 2, 4 and 10 times recirculation in plasma reactor (50 ppm of PFOA in DI water as influent).....	17
Figure 8. PFOA concentrations in the plasma reactor effluents .....	18
Figure 9. MS-1 peak for PFOA in plasma reactor influent.....	19
Figure 10. MS-2 peak for PFOA in plasma reactor influent.....	20
Figure 11. Fluoride concentrations in the plasma reactor effluents.....	22
Figure 12. Comparing the intensity of the peaks for PFHpA in influent and effluents (HRT = 0.21 s and 0.15 s, respectively) when argon was the carrier gas .....	23
Figure 13. Comparing the intensity of the peaks for PFHpA in influent and effluents (HRT = 0.21 s and 0.15 s, respectively) when helium was the carrier gas .....	24
Figure 14. Comparing the intensity of the peaks for PFHxA in influent and effluents (HRT = 0.21 s and 0.15 s, respectively) when argon was the carrier gas .....	25
Figure 15. Comparing the intensity of the peaks for PFHxA in influent and effluents (HRT = 0.21 s and 0.15 s, respectively) when helium was the carrier gas .....	26
Figure 16. H <sub>2</sub> O <sub>2</sub> concentration in the influent and effluent of the plasma reactor treating DI water containing various PFOA concentrations .....	27
Figure 17. Comparing F <sup>-</sup> production in DI water and synthetic media (NMS) containing 50 ppm of PFOA at flow rate of 1 mL/min (HRT = 0.21s).....	28
Figure 18. Fluoride concentration in bioreactors as a function of time .....	29
Figure 19. Comparing energy yield of this study with other AOPs.....	30



## ABSTRACT

Perfluorooctanoic acid (PFOA) is persistent in environment due to its stable structure. It is also toxic to animals and human. The objective of this research is to remove PFOA with a non-thermal plasma reactor, anaerobic and aerobic bio-reactors, and their combination. Mineralization and defluorination (i.e., fluoride production) occurred in the plasma reactor. Neither PFOA removal nor fluoride production was observed in the bioreactors. In the plasma reactor with Argon as the carrier gas, 20  $\mu\text{M}$  of PFOA in deionized (DI) water was removed to 4.22 and 4.04  $\mu\text{M}$ , respectively, when the hydraulic retention time (HRT) was 0.21 s and 0.15 s, respectively. When the carrier gas was changed to Helium, PFOA was removed to 3.85  $\mu\text{M}$  and 3.77  $\mu\text{M}$ , respectively. Therefore, the carrier gas and HRT did not have significant effect on PFOA degradation. However, the carrier gas and HRT strongly affected the defluorination rate: 11% (for HRT = 0.21 s) and 6.5% (for HRT = 0.15) when Argon was the carrier gas, and 22% (for HRT = 0.21 s) and 8.6% (for HRT = 0.15 s) when Helium was the carrier gas. Consequently, a higher energy yield was achieved with Helium as the carrier gas (maximum of  $11.3 \times 10^{-11}$  mole  $\text{F}^-$  production/J) than with Argon as the carrier gas (maximum of  $6.43 \times 10^{-11}$  mole  $\text{F}^-$  production/J). Perfluoroheptanoic acid (PFHpA) and perfluorohexanoic acid (PFHxA) were observed in the effluent of the non-thermal plasma reactor by using liquid chromatography-tandem mass spectrometry (LC/MS/MS). The intermediates production rate was higher when argon was the carrier gas compared with Helium, probably because the degradation mechanisms are different for PFOA and their intermediates.

### **Keywords**

*Bioreactor; Non-thermal plasma reactor; Perfluorooctanoic acid (PFOA); Perfluoroalkyl acids (PFAAs); Perfluoroalkyle substances (PFASs); Perfluorohexanoic acid (PFHxA); Perfluoroheptanoic acid (PFHpA).*

## CHAPTER 1

### INTRODUCTION

Perfluoroalkyle substances (PFASs) are persistent in the environment and toxic to humans and animals. Therefore, they have attracted significant attention recently (Houtz et al., 2013; post et al., 2012; Stahl et al., 2011). Perfluorooctanoic acid (PFOA,  $C_8HF_{15}O_2$ ), a perfluoroalkyl acid (PFAA), is a representative PFAS. The United States Environmental Protection Agency (USEPA) has established a provisional health advisory level of 70 parts per trillion for PFOA ( $C_8HF_{15}O_2$ ) in drinking water (EPA, 2016).

Perfluoroalkyl acids (PFAAs) are not degradable in conventional water treatment plants (Quiñones and Snyder, 2009; Xiao et al., 2013; Appleman et al., 2014). Physicochemical methods such as activated carbon adsorption, reverse osmosis, and advanced oxidation/reduction can remove PFAAs (Appleman et al., 2013; 2014; Yan et al., 2015; Watanabe et al., 2015). However, adsorption through activated carbon and reverse osmosis produce residues that need further treatment or disposal (Appleman et al., 2013; 2014). Advanced oxidation/reduction, such as with sonolysis, activated persulfate, electrolysis, and non-thermal plasma, can destroy these contaminants (Campbell et al., 2009; Liu et al., 2012; Schaefer et al., 2015). Biodegradation of PFAAs are very rare. The objective of this study was to 1) evaluate a liquid-film non-thermal plasma reactor for PFOA degradation and compare it with other advanced oxidation/reduction processes, 2) evaluate the effects of operating conditions, such as the carrier gas and hydraulic retention time (HRT), on PFOA removal, 3) evaluate the biodegradability of PFOA, and 4) evaluate the combined non-thermal plasma reactor and bioreactors for PFOA removal.

### 1.1 Non-thermal plasma treatment of PFOA in water

#### 1.1.1 Non-thermal plasma reactor

To create an electric discharge between electrodes, a non-thermal plasma reactor consisting of two electrodes is connected to a very high voltage power supply. It can provoke materials around the electrical discharge to make ions and radicals. To make plasma, large electric fields are required

to provide the free electrons with sufficient energy for creating ions and dissociating other species. In a non-thermal plasma the temperature or energy of the electrons is much higher than that of the surrounding gases. In the reactor used in the present study the plasma gas temperature was 300 to 750 K. However, the electron energy was in the range of 1 to 4 eV (11,000 to 50,000 K) (Locke et al., 2006; Wang et al., 2018).

Recently, reactors with electrical discharge are studied for water treatment, agriculture, and many other purposes (Locke et al., 2006; Bruggeman and Leys, 2009; Bruggeman et al., 2016). Plasma reactors with many different types of electrodes, and different configurations of reactors, have been tested to obtain the highest efficiency. The main reactive compounds, like free electrons ( $e^-$ ), hydroxyl radicals, ozone and hydrogen peroxide, and hydrogen radicals in different conditions like ultraviolet (UV) light, have been examined as well. Still, there is a need to quantify the effects of them as well as to find and consider other possible reactants. Many data from non-thermal plasma in the gas phase or other AOPs are available to predict reactions in water, but the physical processes and the propagation of electric discharge in the liquid are not well understood (Locke et al., 2006).

Due to discharging of high voltage electricity in water, some of the products of non-thermal pulsed plasma reactors are hydrogen peroxide ( $H_2O_2$ ) and hydroxyl radicals ( $\cdot OH$ ), Hydroperoxyl, and other radicals (Davies and Hickling, 1952; Sato et al., 1996; Joshi et al., 1995; Sunka et al., 1999; Hickling, 1971; Stara and Krcma, 2004; Locke and Shih, 2011). These products and other reactive compounds produced by plasma reactors and high-energy pulses can remove many types of organic compounds (Locke et al., 2006). Some research has indicated that electrical discharge plasma with lower energy is more useful for lower concentrations of contaminants, but for organic contaminants in higher concentrations, plasma with higher energy in a more powerful pulsed-arc process (thermal plasma) may be more effective. Hybrid gas-liquid systems are effective for the decomposition of contaminants in gas and liquid phase at the same time. More research in laboratories and at the pilot scale is needed for better understanding and measurement of the effect of non-thermal plasma on the degradation of contaminants from water. Studies need to be conducted with different contaminant concentrations, different pH levels, different conductivities, wide ranges of retention time, and different densities of energy (Locke et al., 2006).

One of the reasons that non-thermal pulsed plasma can be used for water purification purposes is that they can produce species like hydroxyl radicals ( $\cdot\text{OH}$ ), which is a strong oxidant able to eliminate many contaminants. To measure the potential of the plasma reactor in the production of  $\cdot\text{OH}$ , researchers mostly measure  $\text{H}_2\text{O}_2$ , which has more stable structure. Also,  $\text{H}_2\text{O}_2$  is mostly produced by  $\cdot\text{OH}$  (Locke and Shih, 2011). The efficiency of the plasma reactor in water purification, and the rate of production of  $\text{H}_2\text{O}_2$  in the reactor, are related to conditions of operation such as the flow rates of gas and liquid and input power (Wang et al., 2018). Increasing the voltage of the plasma discharge in the non-thermal pulsed plasma reactor while argon is the carrier gas increases the production rate of  $\text{H}_2\text{O}_2$ , but the energy yield decreases with the increased voltage. (Wandell et al., 2018). The generation of  $\text{H}_2\text{O}_2$  occurs mostly inside and close to where liquid interacts with the plasma (Hsieh et al., 2017). Further, hydrogen peroxide decomposition happens very fast when increasing the temperature. Therefore, amplification of the density of the energy in the interface does not add to the  $\text{H}_2\text{O}_2$  production rate (Wang et al., 2018). The generation of  $\text{H}_2\text{O}_2$  depends on the carrier gas. Wang et al. (2018) studied the effect of different carrier gasses (argon and helium) on plasma properties and  $\text{H}_2\text{O}_2$  production in a non-thermal pulsed plasma reactor. Current work also compared the effect of different carrier gases (argon and helium) on the degradation of PFOA,  $\text{F}^-$  production, and  $\text{H}_2\text{O}_2$  production in a pulsed plasma reactor while the influent had 8.28 ppm (20  $\mu\text{M}$ ) of PFOA in DI water.

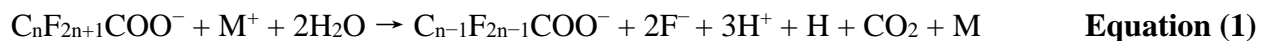
### 1.1.2 PFOA removal by non-thermal plasma reactors

Stratton et al. (2017) used a non-thermal plasma discharge reactor to remove PFOA from water (a reactor similar to that in the current work). Two different experiments were conducted to achieve a high removal rate and high removal efficiency. 1.4 L of 20  $\mu\text{M}$  (8.28 ppm) PFOA (the same as the concentration of PFOA in the current work) in water was used and the duration of the treatment was 30 minutes (batch reactors). For the high removal rate (90%), the input power was 76.5 W, and for the high efficiency the input power was 4.1 W, and the PFOA removal was 25%. The energy yield was  $18 \times 10^{-11}$  mole/J for the high removal rate and  $95 \times 10^{-11}$  mole/J for the high efficiency rate. The defluorination rate was 5% in high efficiency and 22% for the high removal rate. Stratton et al. (2017) proposes that the main reactants in PFOA removal are  $e^-_{\text{aq}}$  (responsible for 90% of PFOA removal) and  $\text{Ar}^+$  (responsible for 10% of PFOA removal) (aqueous electrons

and Argon Ions), and  $\cdot\text{OH}$  has no significant effect on PFOA removal. The effect of other perfluorinated compounds on PFOA removal was insignificant (Stratton et al., 2017).

They suggested that the degradation of PFOA in a non-thermal plasma reactor was reduction-based and that  $e^-_{\text{aq}}$  was the primary reactant. Negative polarity discharges can produce a lot of  $e^-_{\text{aq}}$ . Their research group examined both electrode polarities (negative and positive) to determine the role of  $e^-_{\text{aq}}$ . The rate constant in the negative polarity was much higher than in the positive. This demonstrated the importance of aqueous electrons ( $e^-_{\text{aq}}$ ) in PFOA degradation. The researchers used 10 mM of  $\text{NaNO}_3$  (an  $e^-_{\text{aq}}$  scavenger) in a liquid discharge reactor (LDR) to double check the effect of  $e^-_{\text{aq}}$ . The degradation of PFOA completely stopped after that. They thought that this was another proof of the significant effect of  $e^-_{\text{aq}}$  on the degradation of PFOA. The research group proposed that  $\cdot\text{H}$ ,  $\cdot\text{OH}$ , and other oxidants generated in this plasma reactor have no important effects on the degradation of PFOA because both positive and negative polarities generate oxidants and positive polarity can produce more oxidants. In gas discharged with bubbling (GDB) reactors,  $\text{NaNO}_3$  as an  $e^-_{\text{aq}}$  scavenger stopped 90% of PFOA degradation but not 100%, so they proposed that another agent was responsible for PFOA degradation in the gas phase. There were numerous free electron and argon ions in GDB. They calculated that the ionization potential for argon ( $\sim 15.7$  eV) was a lot bigger than the PFOA ionization potential ( $\sim 11$  eV), which, in a charge transfer, gave a lot of energy to PFOA and helped to break it. Free electrons cause excitation or ionization and argon ions may initiate a reaction there. In addition, the thermal decomposition of PFOA is possible (it happens in  $300 - 350^\circ\text{C}$ ) (Stratton et al., 2017).

Yasouka et al. (2011) studied the degradation (decomposition) of perfluorooctanoic acid (PFOA) with a dc plasma reactor that works with tiny gas bubbles in the contaminated water. They investigated plasma characteristics such as discharge voltage with different gasses. The energy yield, efficiency, and rate of decomposition were measured by the concentrations of fluoride and sulfate in the effluent. A PFOA defluorination of 30% was achieved. Scavengers of  $\cdot\text{OH}$  and  $e^-_{\text{aq}}$  could not significantly decrease the efficiency. The researchers suggested that species with positive charge were responsible for the degradation of PFOA. Equation 1 shows the overall degradation pathway for PFOA and its intermediates (Yasouka et al., 2011).



## 1.2 Biodegradation of perfluorinated compounds in water

### 1.2.1 PFOA, PFOS and other perfluorinated compounds

Since the number of studies on the biodegradability of PFOA is small and most researchers study PFOA and other fluorinated compounds at the same time, the review in this section also include other fluorinated compounds. These studies are reviewed below in the chronological order. In summary, there are very limited reports showing the biological removal of PFOA, and no report on bio-mineralization (de-fluorination) of PFOA. This is because the C–F bond is very stable (Parsons et al., 2008; Vecitis et al., 2009). A decrease in PFOA concentrations in bioreactors may be due to the adsorption of PFOA onto the bacteria (Vecitis et al., 2009; Sinclair and Kannan, 2006; Schultz et al., 2006; Hollingsworth et al., 2005; Key et al., 1998; Office of Pollution Prevention & Toxics, 1978; 1994). Some of the studies are based on co-metabolism, the transformation of a non-growth substrate in the obligate presence of a growth substrate or another transformable compound (Hazen, 2010).

One of the first reported studies was about the biodegradability of three fluorinated surfactants under aerobic and anaerobic reactors (Remde and Debus, 1996). Two fluorinated surfactants were consumed in aerobic reactors and the last one was remediated in an anaerobic condition. Degradation of the first compound was high enough to classify it as a biodegradable surfactant, but there was no  $F^-$  production. For perfluorooctanesulfonic acid (PFOS), neither aerobic nor anaerobic showed biodegradation (Remde and Debus, 1996).

Schröder (2003) did research on the biodegradation of perfluorinated compounds (PFCs) using wastewater contaminated with some perfluorinated compounds (PFOA, PFOS, and nonionic surfactants, including partially fluorinated alkyl ethoxylates, perfluorooctanesulfonyl-amidopolyethoxylate, and perfluorooctanesulfonyl-amido-polyethoxylate methyl ether) in aerobic and anaerobic reactors. The removal of PFOS was fast (two days) in the anaerobic reactor and the removal of PFOA was slower. For non-ionic surfactants, only the sulfonyl compounds were degraded. There were neither metabolites nor  $F^-$  production in the anaerobic reactors (Schröder, 2003).

Meesters and Schröder (2004) did another study on the bioremediation of PFOA and PFOS containing sludge from a wastewater treatment plant in Germany. There was no biodegradation in

the aerobic reactors, but in anaerobic reactors, the contaminant concentrations (both PFOS and PFOA) were under detection limit after 26 days. No metabolites or  $F^-$  detection was reported.

In the studies of Liou et al. (2010) on the degradation of PFOA, the researchers mostly concentrated on anaerobic conditions with five different microbial communities, examining 259 days of retention time with acetate, lactate and ethanol, and hydrogen as the substrates. They assumed that PFOA is the electron acceptor and hydrogen is the electron donor. Co-metabolism of PFOA also was examined with trichloroethylene (TCE). They detected the degradation of PFOA in the co-metabolism study with an influent concentration of 100 ppb for PFOA in 65 days. However, they could not find any products of PFOA in the effluent (Liou et al., 2010).

The research group of Kwon et al. (2014) tried to degrade PFOS using *Pseudomonas aeruginosa* strain HJ4, which is 99% similar to the mesophilic rod type bacteria, in 30 to 37 degree Celsius environments. At pH of 7-9 and aerobic condition, 67% of PFOS, which had a concentration of 1400 to 1800  $\mu\text{g/L}$  in the influent, was degraded in only 48 hours. However, no fluoride ion was detected in the effluent.

Horneman et al. (2017) investigated the biodegradation of PFOA, perfluoroheptanoic acid (PFHpA,  $\text{C}_7\text{HF}_{13}\text{O}_2$ ), perfluorohexanoic acid (PFHxA,  $\text{C}_6\text{HF}_{11}\text{O}_2$ ), perfluoropentanoic acid (PFPeA,  $\text{C}_5\text{HF}_9\text{O}_2$ ), and perfluorobutanoic acid (PFBA,  $\text{C}_4\text{HF}_7\text{O}_2$ ) in a water treatment plant (aerobic biodegradation) and found no biodegradation of PFOA, PFHpA, PFHxA, PFPeA, and PFBA in their bioreactor.

### 1.2.2 Trifluoroacetic acid (TFA)

Trifluoroacetic acid (TFA) have been studied by a few researchers since it has the shortest chain. Visscher et al. (1994) showed that TFA remediation can happen in both oxic (aerobic) and anoxic (anaerobic) microbial communities. In anoxic reactors, the products are  $\text{CH}_4$  and  $\text{CO}_2$ , which are not harmful, but under aerobic condition, a bioreactor can produce  $\text{CHF}_3$ , which is a gas that can cause problems for the environment and the ozone layer. Consequently, the research group decided to use anoxic microbial communities (anaerobic bio-reactor). Anoxic sediments were from a San Francisco Bay salt marsh and from a lake with fresh water. Their conclusion was that the factor of



degradation was the microbial communities and not the chemical reactions. The production of  $^{14}\text{CH}_4$  shows that THF degradation also can happen in other types of sediments. In acetolactic methanogenesis, TFA biodegradation could lead to the production of  $\text{CO}_2$ . Radio-labeled TFA (2- $^{14}\text{C}$ -TFA) was used in the work to yield much lower concentrations (0.185  $\mu\text{M}$ ). The highest degradation rate was in the lowest concentrations. In addition, there was more conversion of TFA to  $\text{CO}_2$  in lower concentrations.  $\text{CHF}_3$  was detected only for concentrations above 0.463  $\mu\text{M}$ .

The research team of Kim et al. (2000) wanted to answer the important question of whether TFA is biodegradable. This research group claimed that they were able to degrade TFA with an anaerobic microbial community. As TFA and TCA (trichloroacetic acid) are chemically very similar, TCA was used to co-metabolize TFA. Fluoride ( $\text{F}^-$ ) and chloride ( $\text{Cl}^-$ ) concentrations were measured in the effluent, and these were found to be increasing over time. Then, they concluded that the effect was from the degradation of TFA and TCA and not adsorption to the body of bacteria.

Alexandrino et al. (2017) studied the biodegradation of TFA and found that monofluoroacetate acid (MFA) was degraded by many aerobic microbial communities but difluoroacetate acid (DFA) and trifluoroacetate acid (TFA) in aerobic microbial communities were recalcitrant.

### **1.3 Combination of pulsed plasma reactor and bioreactors**

On the one hand, pulsed plasma reactors are very effective in the degradation of contaminants in water treatment; on the other hand, using plasma reactors for the purpose of water treatment and the degradation of PFOA is very expensive due to the very large energy consumption required and the need for expensive equipment (Locke et al., 2006). Bioreactors are very cost effective, but sometimes they are too slow in water treatment (Parsons et al., 2008). Thus, one of the objectives of this research was to combine the pulsed plasma reactor and bioreactors to save both energy (money) and time. The method applied in current work, was to use the effluent of the plasma reactor as the influent of both the aerobic and anaerobic bioreactors.



#### **1.4 Research objectives**

The first objective of this research is to evaluate how hydraulic retention time (through recirculation or flow rate change) affects the PFOA removal and intermediates and fluoride production in the plasma reactor.

The second objective of this research is to evaluate how different carrier gases affect the PFOA removal and intermediates and fluoride production in the plasma reactor. As reviewed in Section 1.1.1, helium and argon lead to different plasma properties.

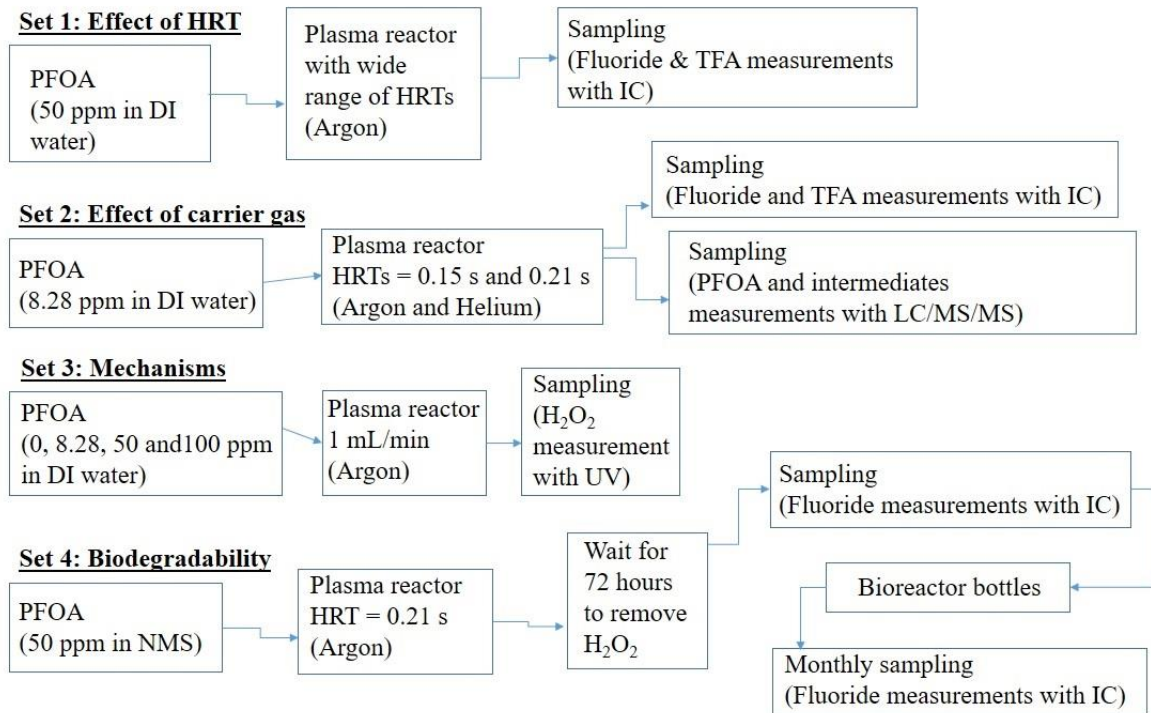
The third objective of this research is to study the PFOA degradation mechanisms in the plasma reactor.

The fourth objective of this research is to evaluate if PFOA and its plasma degradation daughter products can be degraded under aerobic and anaerobic conditions when an activated sludge is used as the inoculum.

## CHAPTER 2

### MATERIALS AND METHODS

To achieve the four research objectives, four sets of experiments were set up following Figure 1 and elaborated in Sections 2.1, 2.2, 2.3 and 2.4, respectively. The first set (Section 2.1) were preliminary experiments to evaluate the effects of a wide range of hydraulic retention time (HRT = 0.12 s – 1.65 s) on PFOA degradation in the plasma reactor. The second set (Section 2.2) focused on the effect of carrier gas on PFOA degradation in the plasma reactor, and were based on only two HRTs (0.15 s and 0.21 s). The third set (Section 2.3) focused on H<sub>2</sub>O<sub>2</sub> measurements with different PFOA concentrations to find a clue for the pathway of degradation. The fourth set (Section 2.4) focused on the biodegradation of PFOA and its daughter products (intermediates) from the plasma reactor. The sampling and analysis are summarized in Section 2.5.



**Figure 1. The overall experimental plan for the plasma reactor and bioreactors**

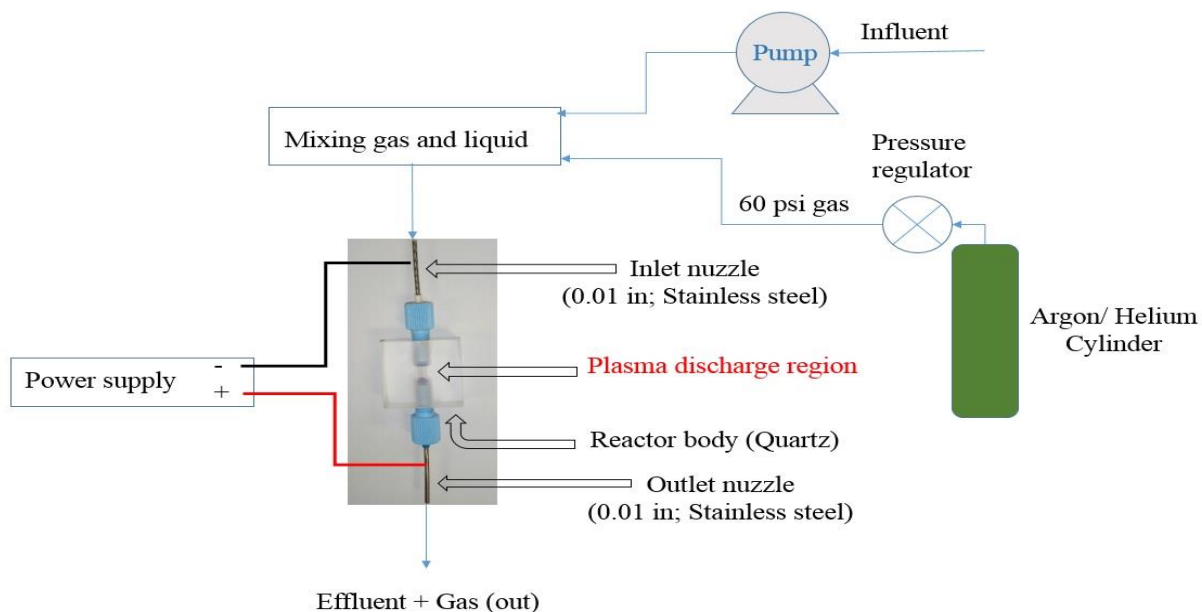
Note: PFOA, IC, DI, LC/MS/MS, HRT and UV are abbreviations for perfluorooctanoic acid, ion chromatography, liquid chromatography-tandem mass spectrometry, hydraulic retention time and ultraviolet-visible spectroscopy respectively.

## 2.1 Plasma experiments with a wide range of hydraulic retention time

16 KV, 10 KHz, 40 ns, and 1.15 mJ/pulse were the operation conditions of the power supply of the non-thermal plasma reactor used in this study. Power consumption was 11.5 J/s (W). The carrier gas was argon, the gas pressure was 60 psi, and the inlet nuzzle was 0.01 inch. Different flow rates (0.5 mL/min (HRT= 0.25 s), 1 mL/min (HRT= 0.21 s), 2 mL/min (HRT= 0.15 s) and 4 mL/min (HRT= 0.12 s)) and different recirculation (2, 4 and 10 times recirculation (TR)) with a flow rate of 2 mL/min (2TR (HRT= 0.45 s), 4TR (HRT= 0.75) and 10 TR (HRT= 1.65 s)) were used in the experiments. The experiment with recirculation was used to obtain a longer retention time since a flow rate < 1 mL/min could not produce a continuous liquid film. Figures 2 and 3 show the plasma reactor used in this study. Each HRT experiment was conducted in triplicate (Wang et al., 2018). 120  $\mu$ M (50 ppm) of PFOA in deionized (DI) water was used as the reactor influent. TFA and F<sup>-</sup> measurements were done for this part.



Figure 2. The plasma reactor used in this study



**Figure 3. Schematic of the plasma reactor used in this study**

## 2.2 Plasma experiments with different carrier gas

The operating conditions of the non-thermal plasma reactor used in this study were the same as given Section 2.1. However, two carrier gases (argon and helium) were compared at two different flow rates (1 mL/min (HRT= 0.21 s) and 2 mL/min (HRT= 0.15 s)). Each experiment was conducted in triplicate. The total influent for this part of experiment was ~225 mL. 20  $\mu$ M (8.28 ppm) of PFOA in DI water was used as the reactor influent. PFOA,  $F^-$ , TFA and intermediates measurements were done for this set of experiments.

## 2.3 Plasma experiments with different PFOA concentrations (Argon as the carrier gas)

This part of experiment was conducted with different PFOA concentrations (0 ppm (0  $\mu$ M), 8.28 ppm (20  $\mu$ M), 50 ppm (120  $\mu$ M) and 100 ppm (240  $\mu$ M)) in DI water. The carrier gas was argon and the flow rate was 1 mL/min. Only  $H_2O_2$  measurement was done in this part of experiment. We did these experiments to develop better understanding of mechanism of PFOA degradation.

## 2.4 Biodegradation of PFOA and intermediates from plasma degradation of PFOA

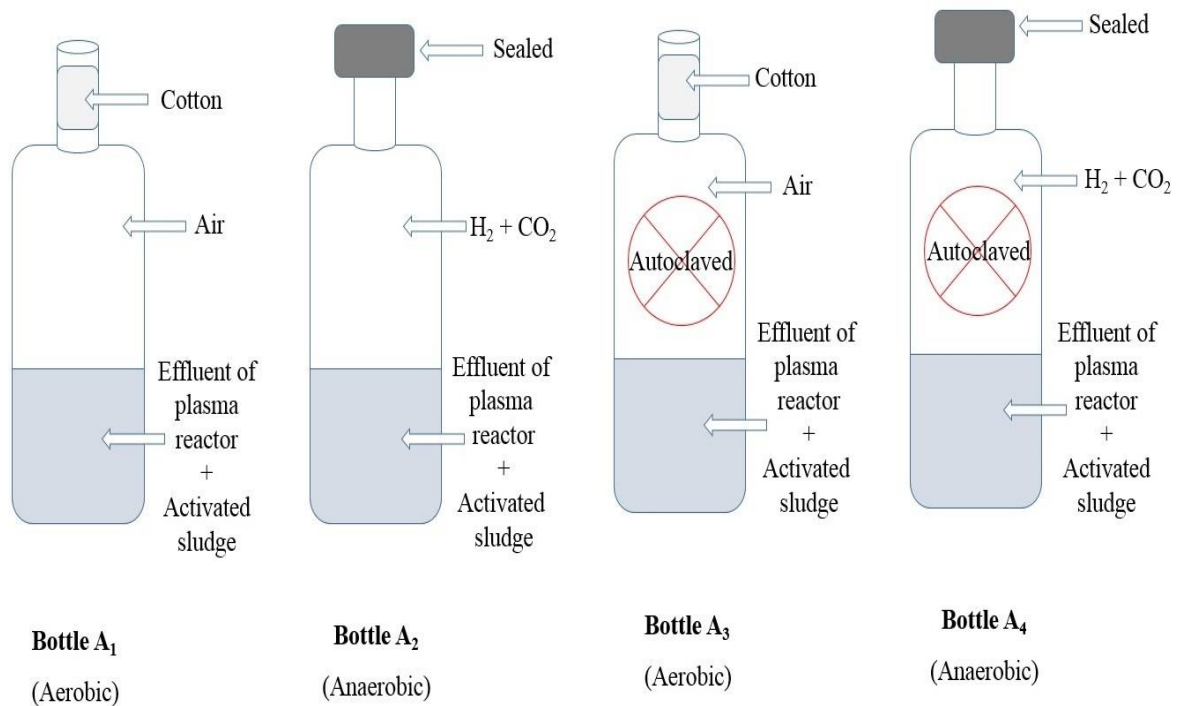
For these experiments, the plasma reactor conditions were the same as those given in Section 2.1, but the influent was a modified nitrate mineral solution (NMS, See Table 1 for composition, based on Mahindra and Alvarez-Cohen (2006) and Sei et al. (2013)) containing 120  $\mu\text{M}$  (50 ppm) PFOA, and the flow rate of the pulsed plasma reactor was 1 mL/min (HRT= 0.15 s). The plasma-treated water was introduced into the biological reactors 72 hours after the plasma treatment for removing  $\text{H}_2\text{O}_2$ , which could kill bacteria.

**Table 1. The components of one-liter NMS**

Chemicals in NMS	Concentrations (mM)
$\text{NaNO}_3$	11.76
$\text{Na}_2\text{SO}_4$	1.28
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	0.15
$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	0.07
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	0.08
$\text{KH}_2\text{PO}_4$	3.9
$\text{K}_2\text{HPO}_4$	6.1
$\text{ZnCl}_2$	0.002
$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	0.002
$\text{H}_3\text{BO}_3$	0.002
$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	0.004
$\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$	0.004
$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	0.001
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	0.001
$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$	0.001
$\text{Na}_2\text{SeO}_4$	0.001
KI	0.001

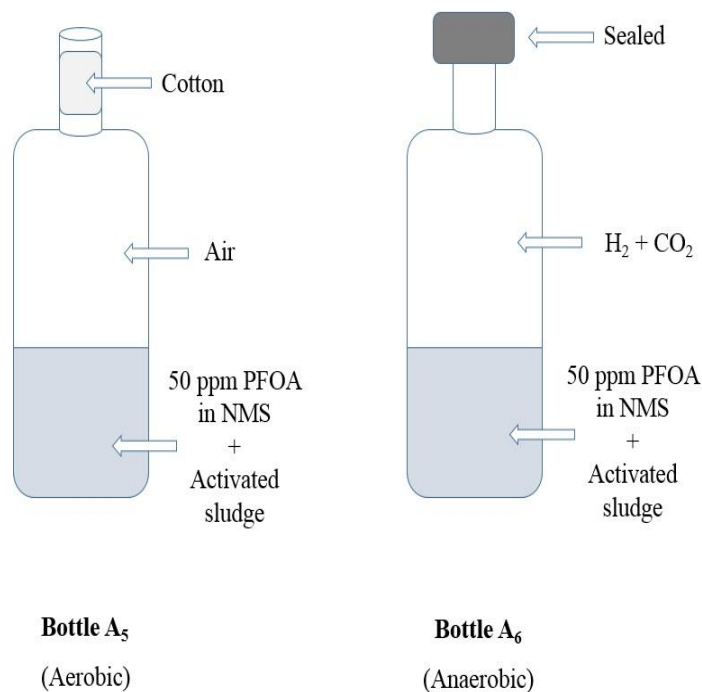
The inoculum was a mixture of 20 mL activated sludge from Graceville Wastewater Treatment Facility and 40 mL activated sludge from a denitrification reactor from Thomas P. Smith Water Reclamation Facility. To remove chemicals in the wastewater, the activated sludge mixture were centrifuged and then re-suspended in the NMS media for three times.

Six bottles labeled A<sub>1</sub>, A<sub>2</sub>, A<sub>3</sub>, A<sub>4</sub>, A<sub>5</sub>, and A<sub>6</sub> (500 mL glass bottles containing 200 mL liquid and 300 mL gas) were set up as shown in Figures 4 and 5. Bottles A<sub>3</sub> and A<sub>4</sub> were autoclaved under 120 degrees Celsius for 60 minutes as controls of Bottles A<sub>1</sub> and A<sub>2</sub>, respectively. Nitrogen and CO<sub>2</sub> gas were bubbled into bottles A<sub>2</sub>, A<sub>4</sub>, and A<sub>6</sub> for a half an hour to make them anaerobic and to keep their pH levels at 7. Then, H<sub>2</sub> gas was bubbled into these three bottles for three minutes. These bottles were capped with rubber stoppers and aluminum caps. The bottles were put on the shaker. To reduce volatilization and contamination, cotton was used to seal bottles A<sub>1</sub>, A<sub>3</sub>, and A<sub>5</sub> that were aerobic bottles (air was the only gas in A<sub>1</sub>, A<sub>3</sub> and A<sub>5</sub>).



**Figure 4. Experiment configuration for bottles containing effluent from the plasma reactor**

Note: Plasma reactor flow rate was 1 mL/min (HRT= 0.15)



**Figure 5. Experiment configuration for bottles containing influent from the plasma reactor**

### 2.5 Sampling and measurement methods for PFOA, intermediates, F<sup>-</sup> and H<sub>2</sub>O<sub>2</sub>

Samples for H<sub>2</sub>O<sub>2</sub> measurement were collected immediately after the experiments. Delay in H<sub>2</sub>O<sub>2</sub> sampling and measurements could lead to decreases in H<sub>2</sub>O<sub>2</sub> due to post-plasma reactions. For the purpose of H<sub>2</sub>O<sub>2</sub> measurements we used 1 mL per sample. For TFA and F<sup>-</sup> measurements, we needed 5 mL per sample. For the PFOA and intermediates measurements, we used 1 mL per sample. Sampling from bioreactors for the purpose of F<sup>-</sup> and PFOA measurement was conducted monthly.

H<sub>2</sub>O<sub>2</sub> was measured with a UV/VIS spectrometer (Lambda 35, PerkinElmer) immediately after sampling. 2 mL liquid sample was mixed with 1 mL of titanium oxysulfate sulfuric acid complex solution (TiOSO<sub>4</sub>). A yellowish transparent liquid was formed. The absorbance of that yellowish liquid was measured with a UV/VIS spectrometer at a wavelength of 410 nm. The wavelength was converted to H<sub>2</sub>O<sub>2</sub> concentration by a calibration curve generated with stock solutions of H<sub>2</sub>O<sub>2</sub> (Wandell et al., 2018).

To measure F<sup>-</sup> and TFA, ion chromatography (IC) with an anion column was used (Thermo Scientific with Dionex IonPac™ AS12A column and a Dionex AERS 500 Carbonate 4 mm suppressor).

PFOA was measured using nLC-MS/MS Orbitrap (Easy Nano LC II system, Thermo Scientific) with a 100 µm × 2 cm trap column (easy column, catalog no. SC001, Thermo Scientific), a 75 µm × 10 cm C18AQ analytical column (Thermo Scientific), and a Velos LTQ-Orbitrap Mass Spectrometer (Thermo Scientific) in the college of medicine translational science laboratory. The area under the curve (AUC) of the precursor ions PFOA vs. the internal standard (<sup>13</sup>C8 isotopes of PFOA, 50 µg/mL in methanol from Cambridge Isotope Laboratories, Inc.) was calculated in XCalibur (Thermo Scientific vendor software) and quantification was based on the calibration curve of the readouts (Xiao et al., 2012). A dilution factor of 100 was used for the plasma treated water and a dilution factor of 1000 was used for the influents.

For identification of the intermediates, the collected data were initially analyzed with open-access software (XCMS). Identification of intermediates was carried out by searching against the Metlin database.



## CHAPTER 3

### RESULTS

#### 3.1 Effect of HRT on F<sup>-</sup> production in plasma reactor

For 50 ppm of PFOA in the DI water treated by the plasma reactor, the highest concentration of F<sup>-</sup> resulted from the flow rate of 0.5 mL/min (HRT= 0.24 s), that was 4.2 ppm. Figure 6 shows the F<sup>-</sup> concentration in the effluent of the plasma reactor with different flow rates (different HRTs). Figure 7 shows the F<sup>-</sup> concentration in the effluent of the plasma reactor at an influent flow rate of 2 mL/min and a recirculation flow rate of 2 (HRT= 0.45 s), 4 (HRT= 0.75 s), and 10 times (HRT= 1.65 s). The fluoride concentration increased as the HRT increased.

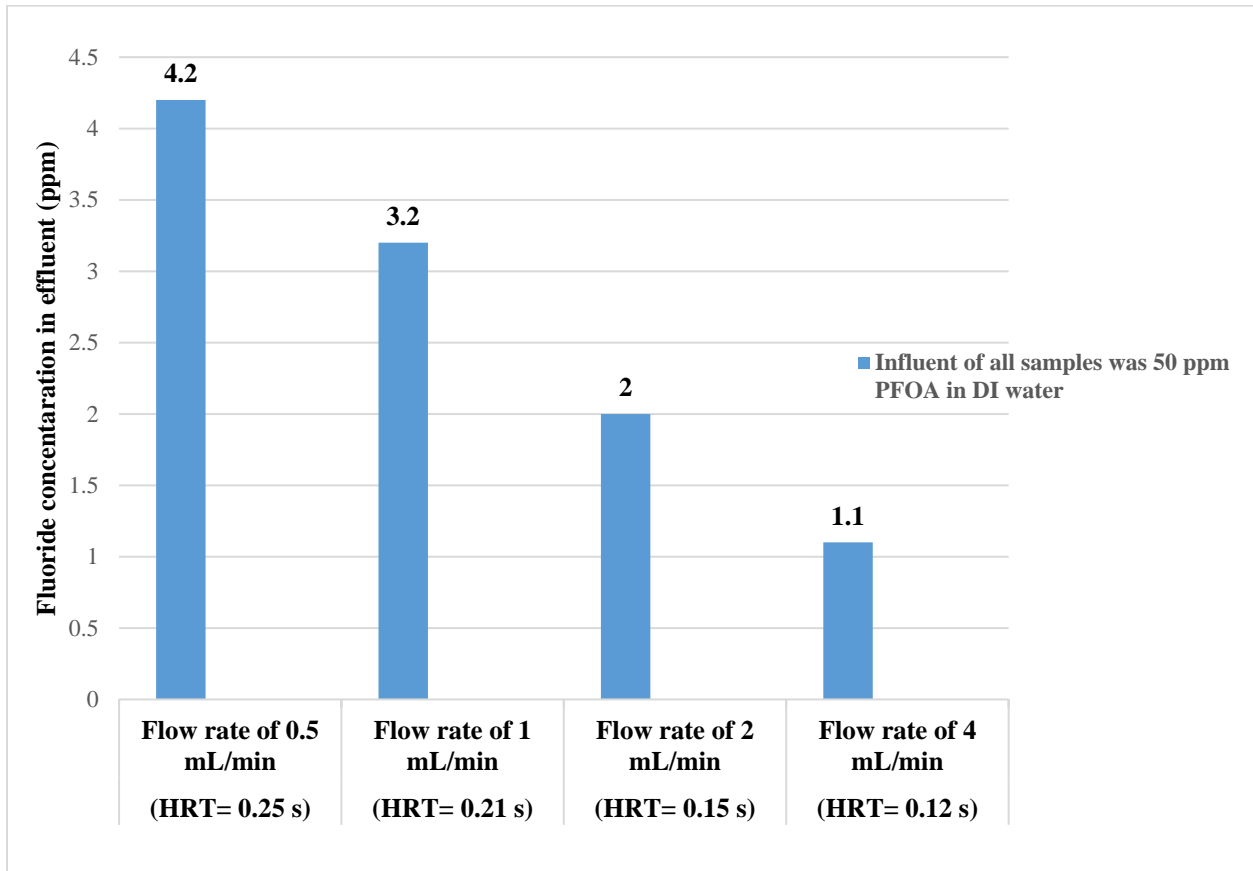
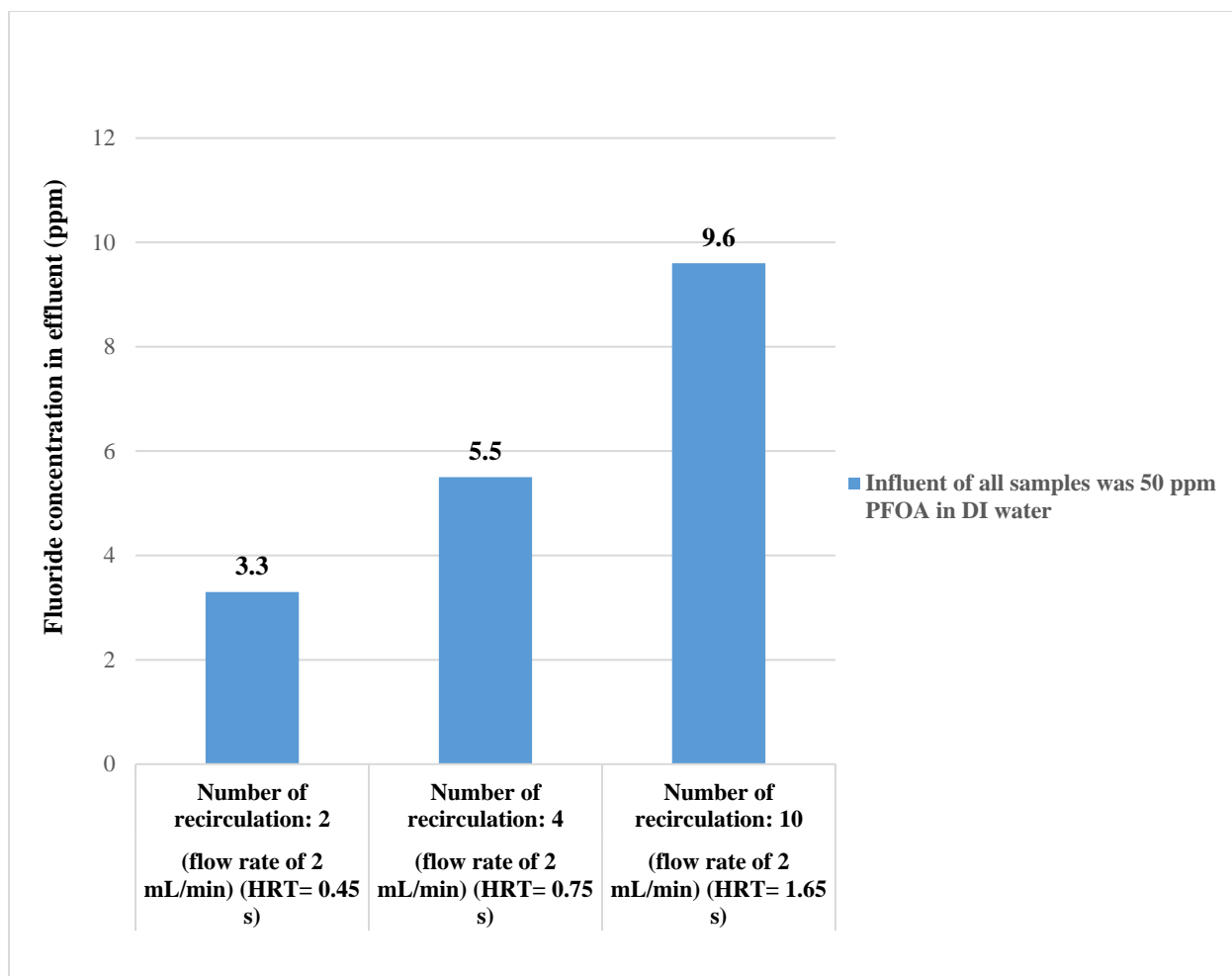


Figure 6. F<sup>-</sup> Concentrations in effluents with different flow rates (50 ppm of PFOA in DI water as influent of plasma reactor)

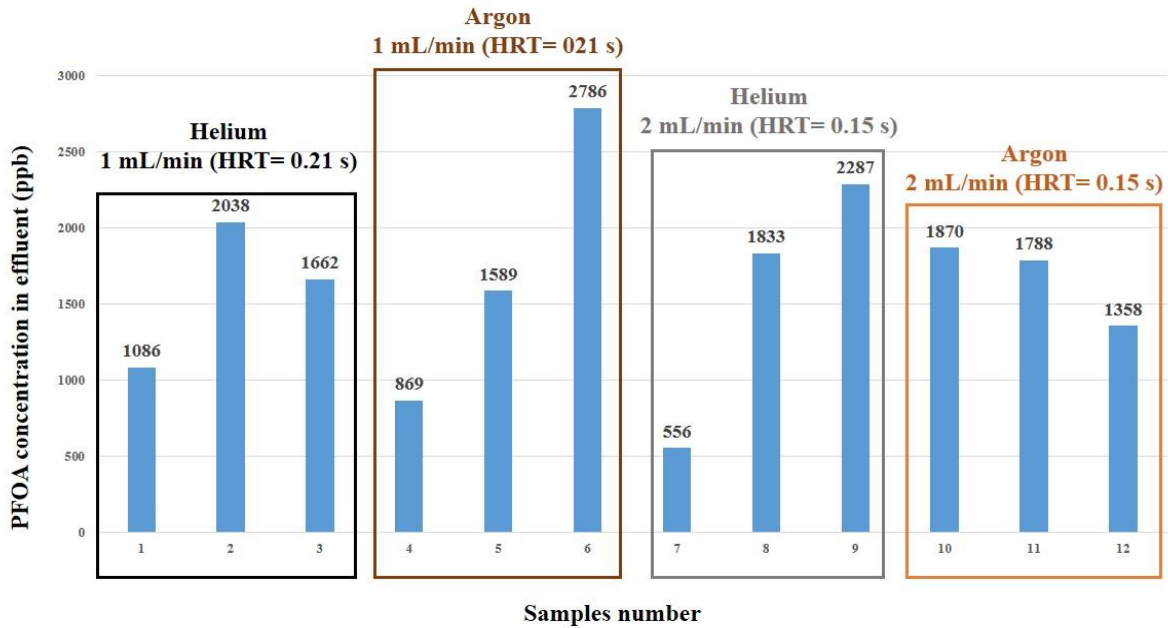


**Figure 7. Comparing F<sup>-</sup> concentration for effluent of 2, 4 and 10 times recirculation in plasma reactor (50 ppm of PFOA in DI water as influent)**

### **3.2 Effect of carrier gas (argon and helium) on PFOA degradation and F<sup>-</sup> and intermediates production in plasma reactor**

#### **3.2.1 PFOA measurements**

Figure 8 shows the results for the PFOA concentration measurements. Table 2 contains the average PFOA removal for two different carrier gasses (argon and helium) and two different flow rates (1 mL/min (HRT= 0.21 a) and 2 mL/min (HTR= 0.15 s)). Figures 9 and 10 show the MS-1 and MS-2 retention time peaks for PFOA from LC/MS/MS. Interestingly, the carrier gas and flow rate did not have a significant effect on the PFOA removal.



**Figure 8. PFOA concentrations in the plasma reactor effluents**

Note: The influent PFOA concentrations were 9325 and 8820 ppb (= ~6500 ppb as F<sup>-</sup>)

**Table 2. Average PFOA concentrations in the plasma reactor influent and effluents**

Samples	Average concentration (ppb)	Average concentration (μM)	Average defluorination (%)	Standard deviation (ppb)
Helium; 1 mL/min (HRT= 0.21 s)	1595	3.85	22	479
Argon; 1 mL/min (HRT= 0.21 s)	1748	4.22	11	968
Helium; 2 mL/min (HRT= 0.15 s)	1559	3.77	8.6	897
Argon; 2 mL/min (HRT= 0.15 s)	1672	4.04	6.5	275
Influent (HRT= 0 s) (8.28 ppm PFOA)	9073	21.9	0	357

20180423 p on 100dil is 50ppb 20 80b\_30mingrad\_1pt7kv\_4 #2489 RT: 31.69 AV: 1 NL: 4.01E4  
F: FTMS - p NSIFull ms [250.00-1500.00]

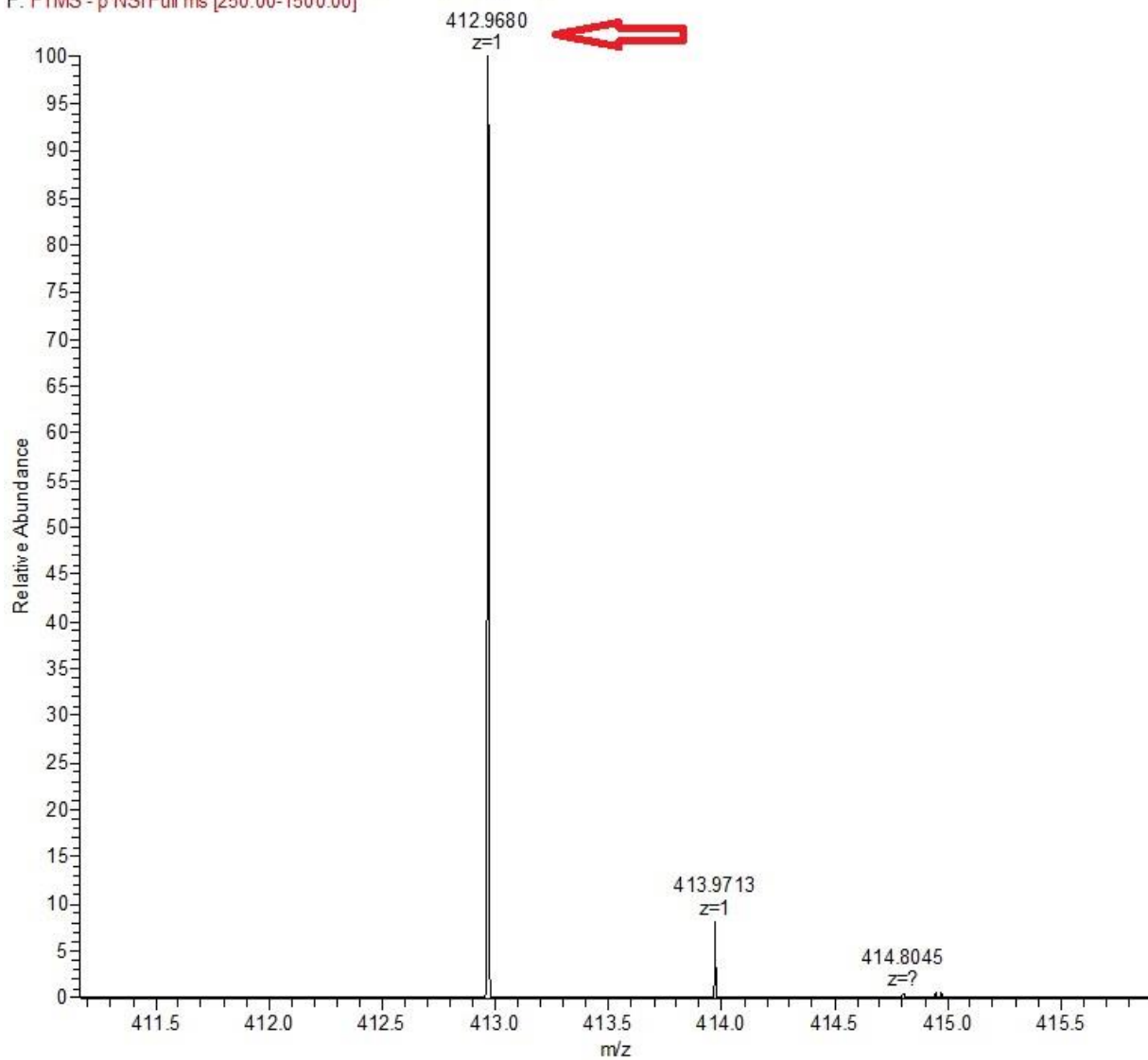


Figure 9. MS-1 peak for PFOA in plasma reactor influent

20180423 p on 100dil is 50ppb 20 80b 30minrad 1pt7kv\_4 #2434 RT: 31.41 AV: 1 NL: 3.39E3  
F: ITMS - c NSI d Full ms2 412.97@cid10.00 [100.00-425.00]

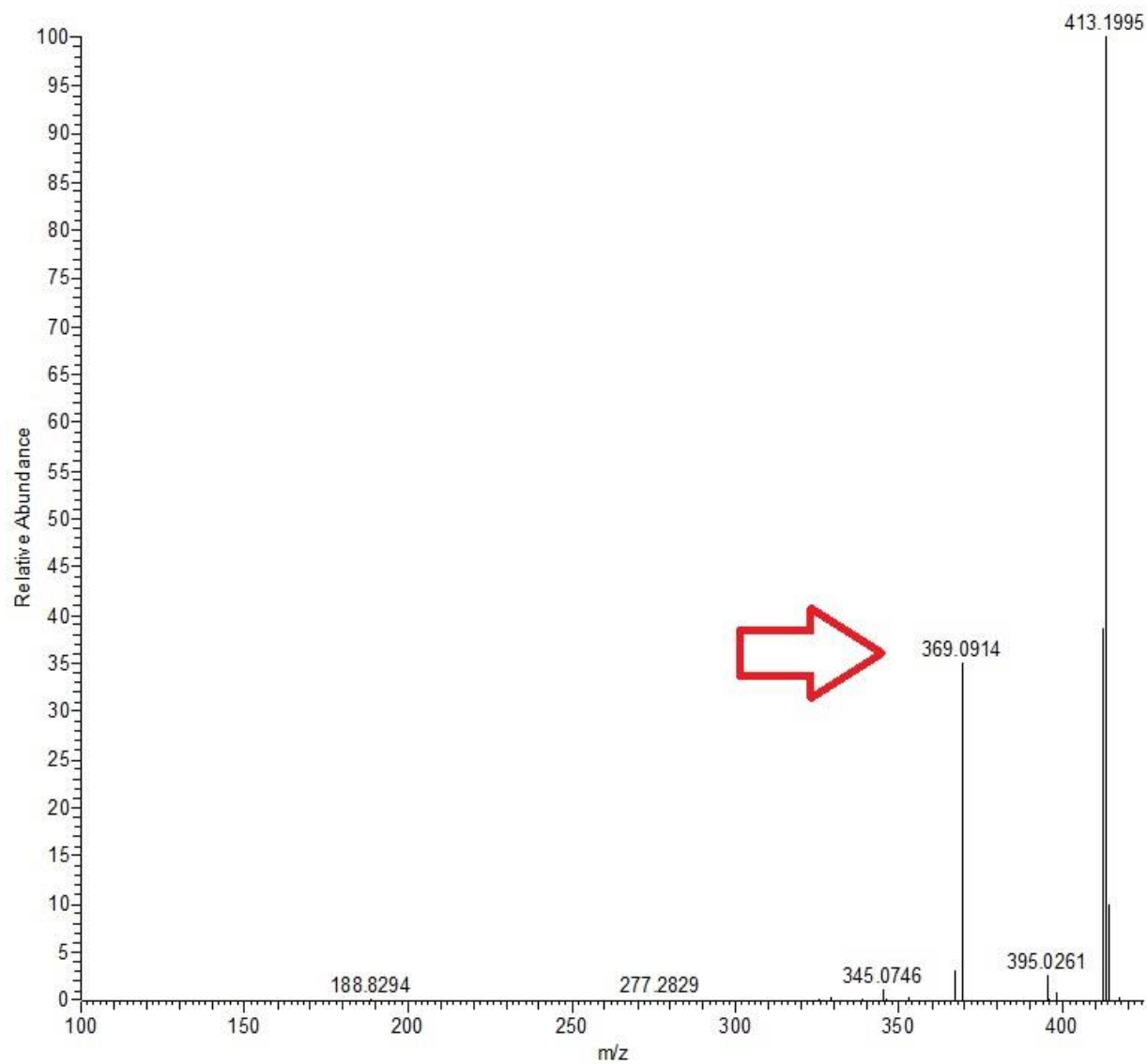


Figure 10. MS-2 peak for PFOA in plasma reactor influent

### 3.2.2 Fluoride measurements

Figure 11 shows the effect of hydraulic retention time (HRT) and carrier gas on  $F^-$  concentrations in the effluent of the plasma reactor (with 8.28 ppm (8280 ppb) of PFOA in DI water as the influent). Table 3 summarizes the results in average concentrations and standard deviations. As expected, the production of  $F^-$  in the non-thermal plasma reactor increased when the hydraulic retention time increased. Interestingly, helium gave higher defluorination than argon.

### 3.2.3 Intermediates measurements

In the plasma treated effluents, PFHpA and PFHxA were found to be intermediates since their MS-1 and MS-2 data matched well with those in the Metlin database. Figures 12 to 15 show the retention time peaks for the two intermediates. Concentrations of the intermediates were not determined due to the absence of standards. However, the intensity of the PFHpA peaks are compared among the influent, effluent at the HRT = 0.21 s, and effluent at the HRT = 0.15 s in Figure 12 for argon and Figure 13 for helium. Similarly, the intensities of the PFHxA peaks are compared among the influent, effluent at the HRT = 0.21 s, and effluent at the HRT = 0.15 s in Figure 14 for argon and Figure 15 for helium.

Figures 12 to 15 show that increasing hydraulic retention time (HRT) led to an increase in the concentrations of intermediates in all cases. This trend was the same as the fluoride production trend (Table 3).

Figures 12 to 15 also show that argon as the carrier gas produced much more PFHpA and PFHxA than helium. This trend was opposite to the fluoride production trend (Table 3), suggesting that the carrier gas affected the degradation of PFOA and its intermediates in different ways.

### 3.2.4 TFA measurements

No TFA was detected in any effluent samples.

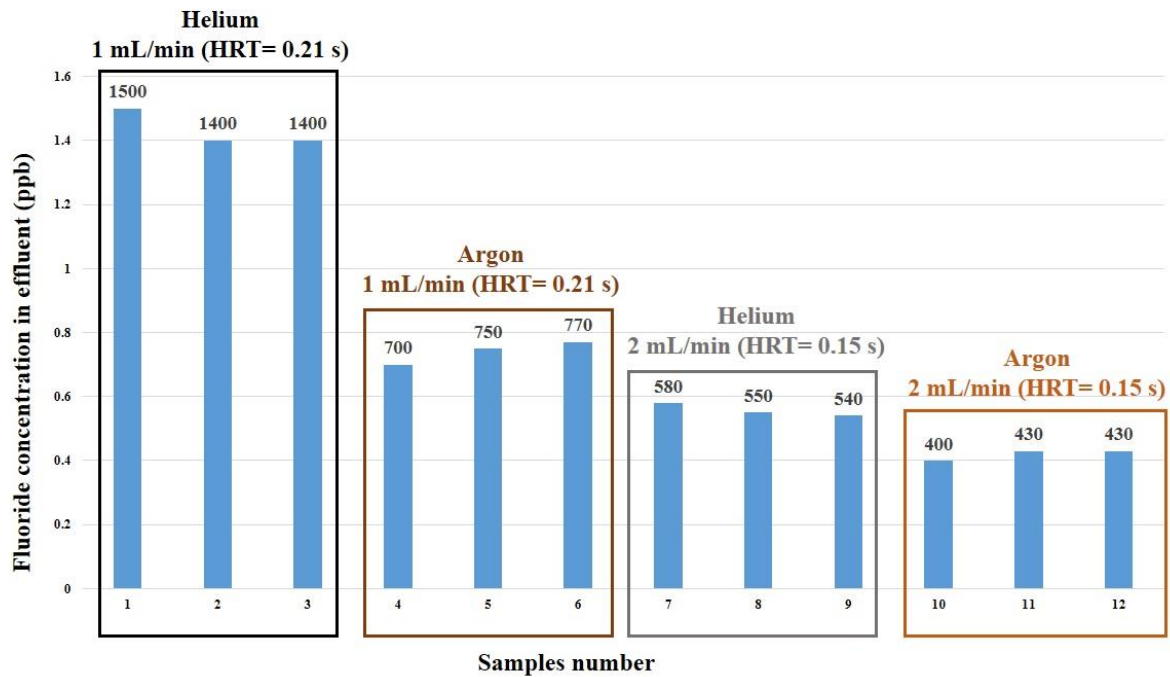
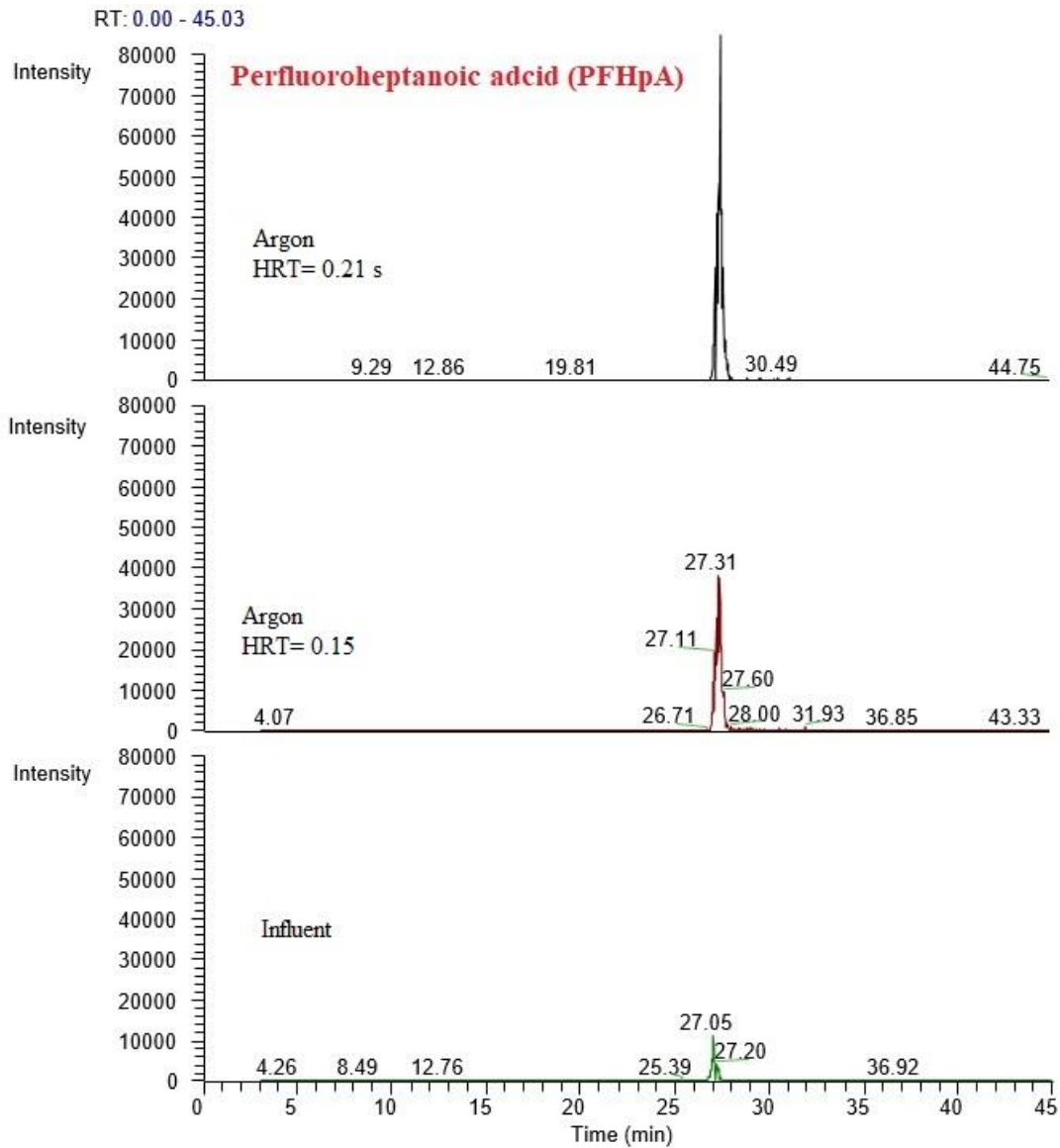


Figure 11. Fluoride concentrations in the plasma reactor effluents

Table 3. Average fluoride concentrations in the plasma reactor influent and effluents

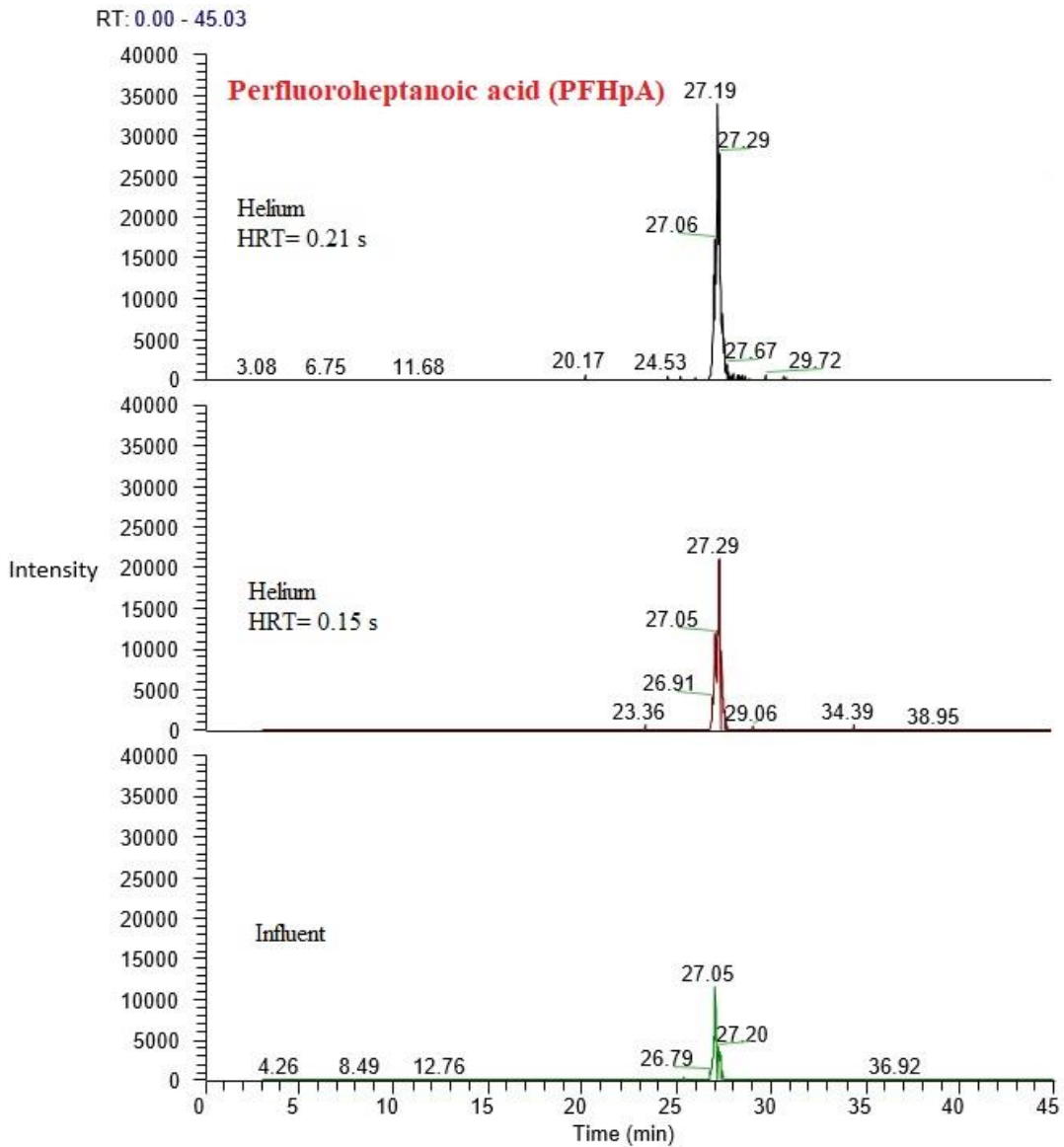
Samples	Average concentration (ppb)	Average concentration ( $\mu\text{M}$ )	Average defluorination (%)	Standard deviation (ppb)
Helium; 1 mL/min (HRT= 0.21 s)	1430	76	22	60
Argon- 1 mL/min (HRT= 0.21 s)	750	39	11	40
Helium- 2 mL/min (HRT= 0.15 s)	560	30	8.6	20
Argon- 2 mL/min (HRT= 0.15 s)	420	23	6.5	17
Influents (IC measurements)	~0	~0	0	0



**Figure 12. Comparing the intensity of the peaks for PFHpA in influent and effluents (HRT = 0.21 s and 0.15 s, respectively) when argon was the carrier gas**

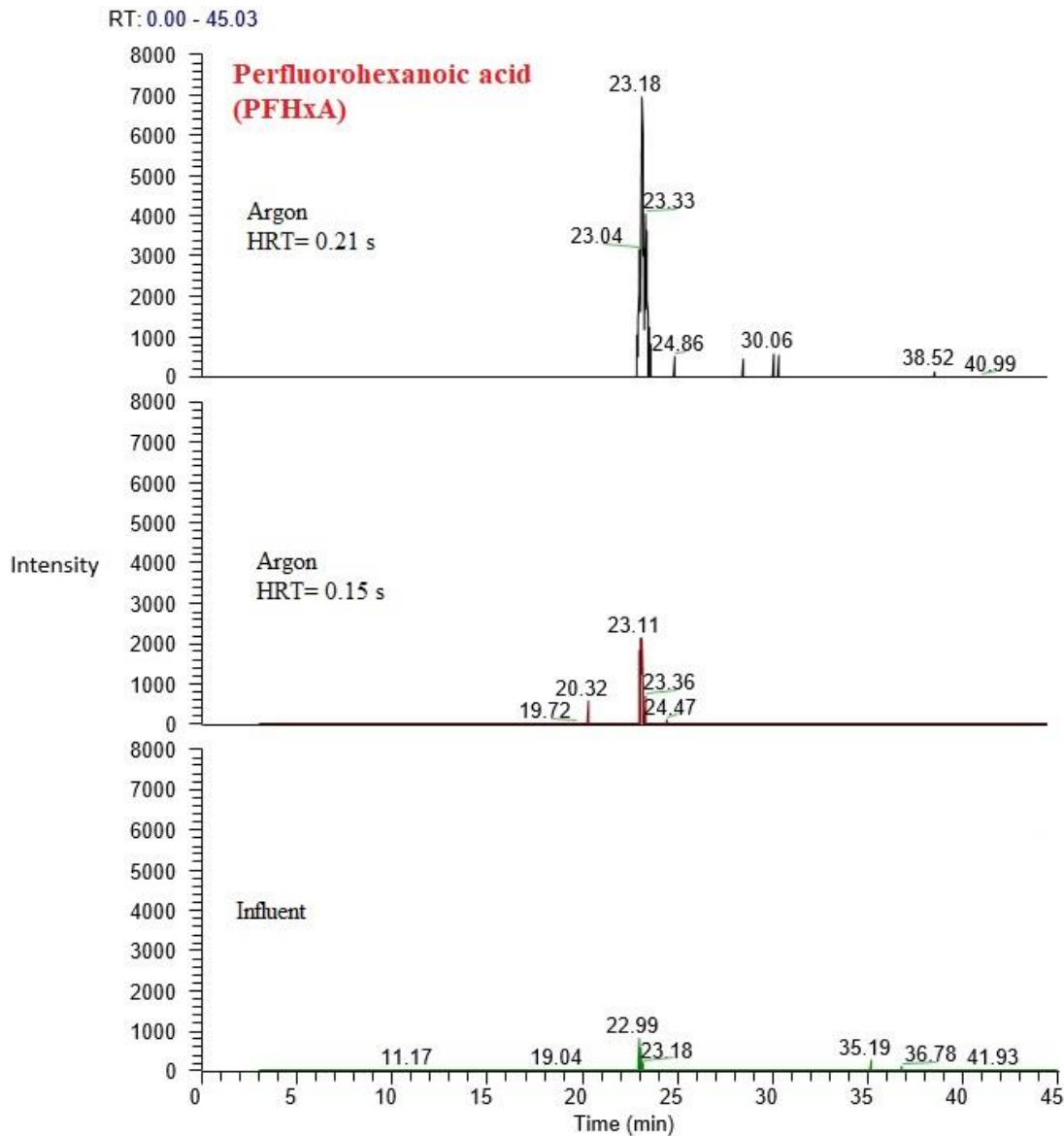
Note: The PFHpA retention time was ~27 min





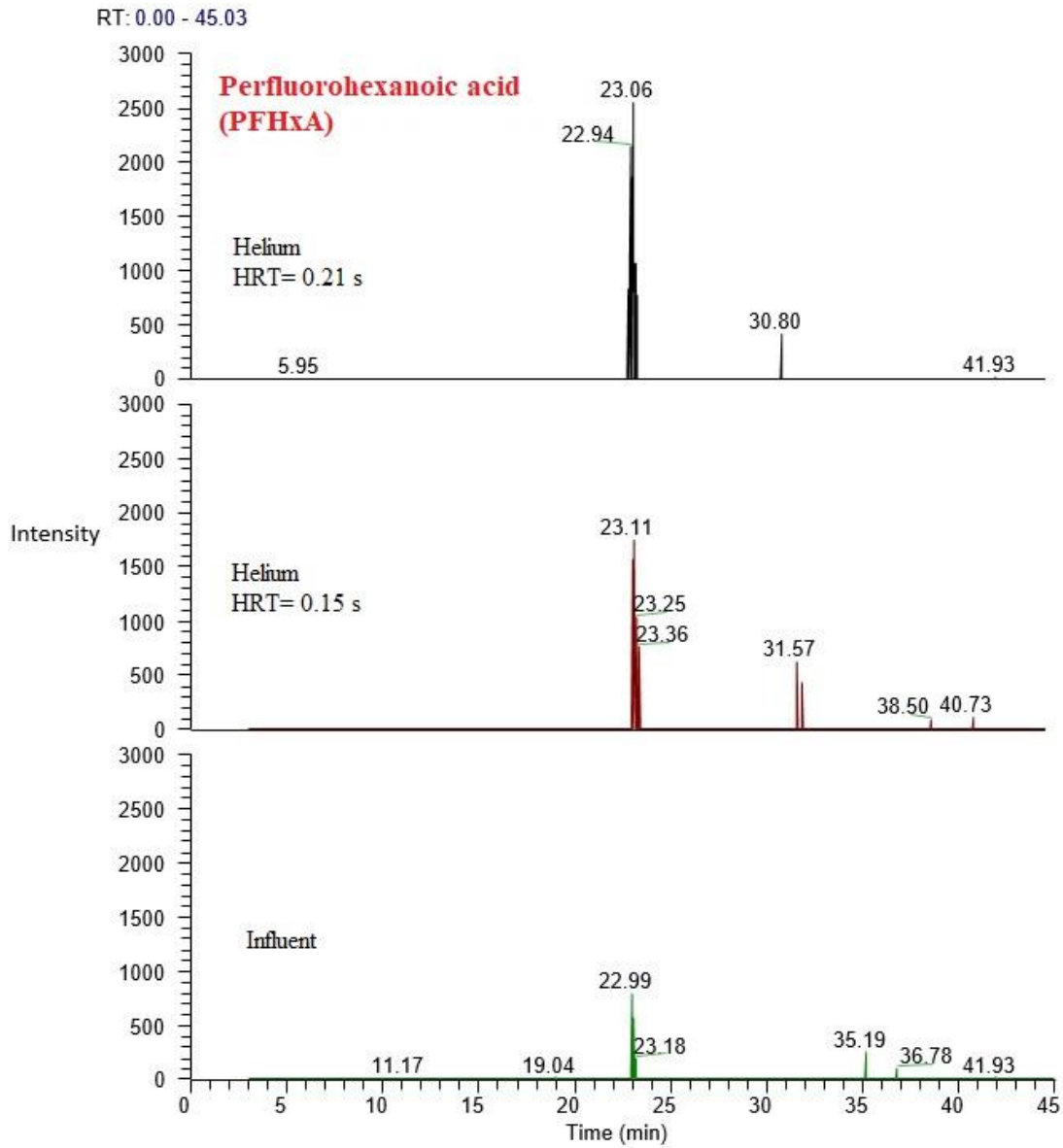
**Figure 13. Comparing the intensity of the peaks for PFHpA in influent and effluents (HRT = 0.21 s and 0.15 s, respectively) when helium was the carrier gas**

Note: PFHpA retention time was ~ 27 min



**Figure 14. Comparing the intensity of the peaks for PFHxA in influent and effluents (HRT = 0.21 s and 0.15 s, respectively) when argon was the carrier gas**

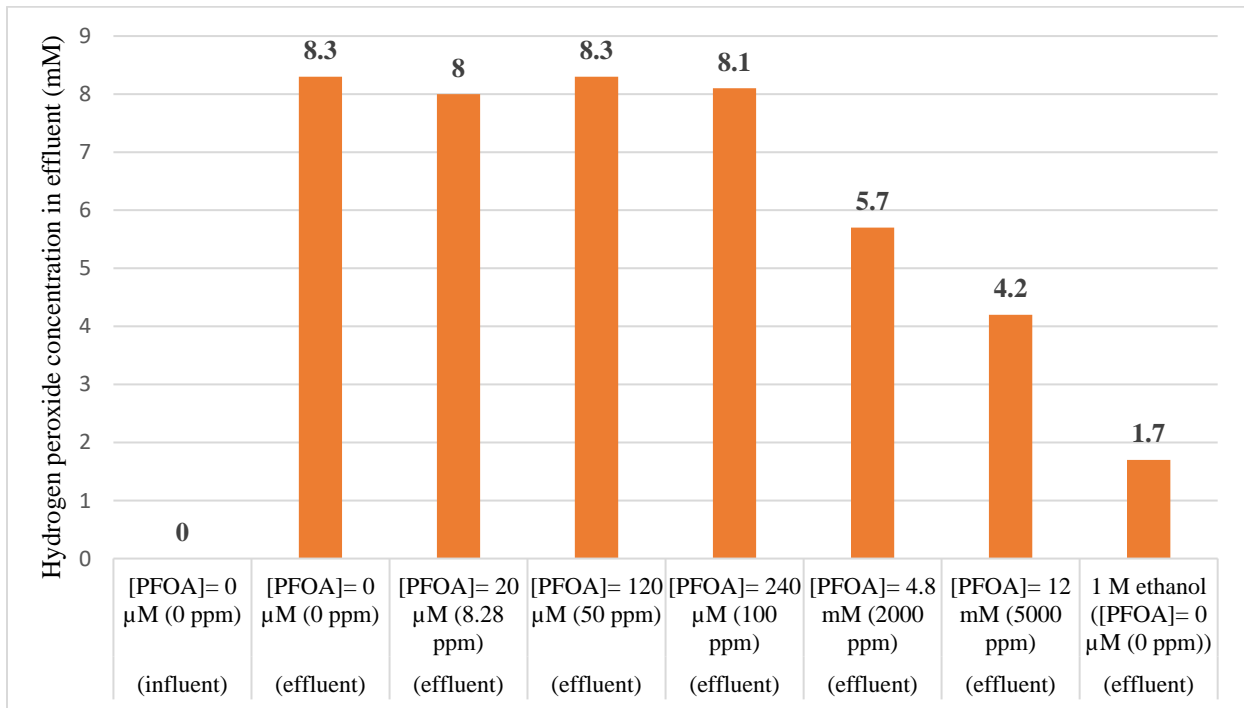
Note: PFHxA retention time was ~ 23 min



**Figure 15. Comparing the intensity of the peaks for PFHxA in influent and effluents (HRT = 0.21 s and 0.15 s, respectively) when helium was the carrier gas**  
 Note: PFHxA retention time was ~ 23 min

### 3.3 H<sub>2</sub>O<sub>2</sub> production in the plasma reactor

Figure 16 compares the concentrations of H<sub>2</sub>O<sub>2</sub> in the influents and effluents of the plasma reactor treating DI water containing various PFOA concentrations (0 – 5000 ppm) and a high concentration OH radical scavenger ([C<sub>2</sub>H<sub>5</sub>OH]= 1 M). Measurement of H<sub>2</sub>O<sub>2</sub> was performed to determine the effect of ·OH on the degradation of PFOA. Usually, the presence of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) reflects the formation of ·OH since it is more stable than ·OH and easier to measure (Wang et al., 2018; Locke and Shih, 2011). The PFOA concentration did not have an effect on the H<sub>2</sub>O<sub>2</sub> production with lower PFOA concentrations. However, there was significant decrease in H<sub>2</sub>O<sub>2</sub> concentration with higher PFOA concentrations, suggesting that PFOA did have a correlation with the ·OH in the reactor. Therefore, ·OH seemed to have an effect on PFOA degradation. Even very high concentration (1 M ethanol) of OH radical scavenger could not quench all OH radicals: There was 1.7 mM of H<sub>2</sub>O<sub>2</sub> in the effluent, which was much higher than the PFOA concentrations (0.02 mM and 0.12 mM) in the influent.

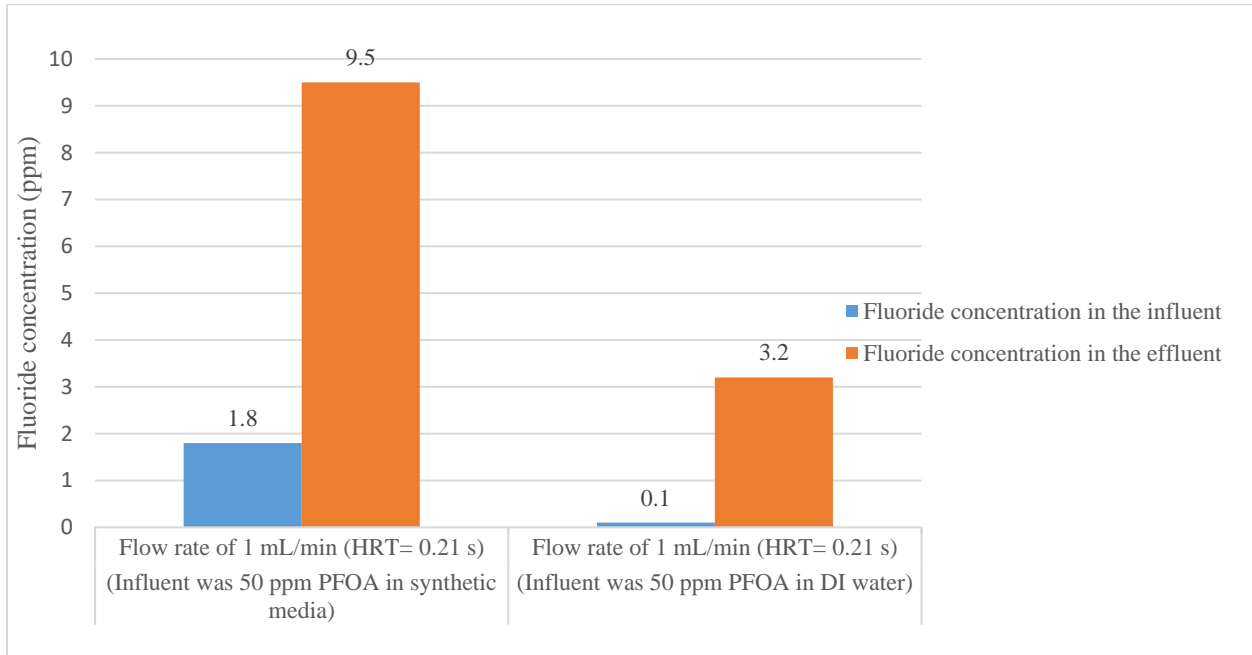


**Figure 16. H<sub>2</sub>O<sub>2</sub> concentration in the influent and effluent of the plasma reactor treating DI water containing various PFOA concentrations**

Note: Flow rate = 1 mL/min (HRT = 0.21 s)

### 3.4 Biodegradation of PFOA and its plasma degradation intermediates

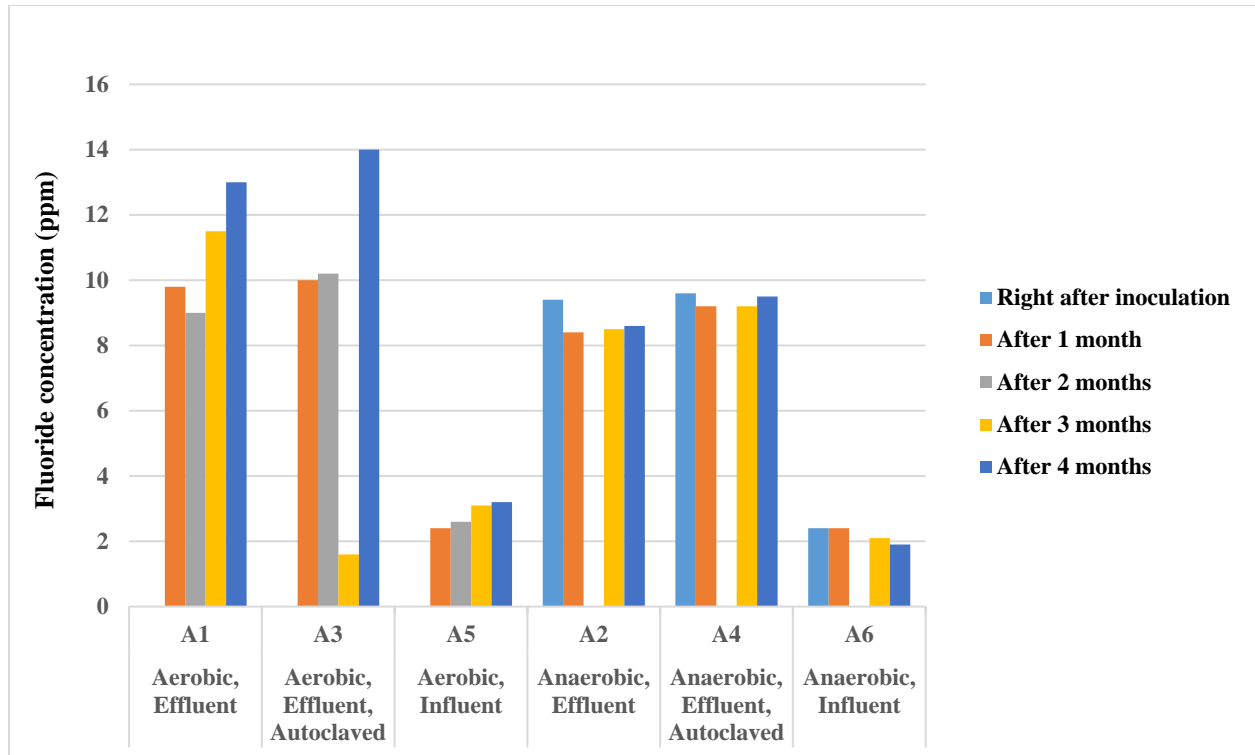
The biodegradation experiments were done with a modified nitrate mineral solution (NMS). To evaluate the effects of chemicals on plasma removal of PFOA, Figure 17 compares the concentration of fluoride production when NMS and DI water were used in the experiments. The NMS seemed to have a positive effect on fluoride production.



**Figure 17. Comparing  $F^-$  production in DI water and synthetic media (NMS) containing 50 ppm of PFOA at flow rate of 1 mL/min (HRT = 0.21s)**

#### 3.4.1 Fluoride ( $F^-$ ) production in the bioreactors

After four months of sampling and measurements, we found that there was no  $F^-$  production in the bioreactors (Figure 18). The slight increase in  $F^-$  concentration in the aerobic reactors was due to evaporation, based on the autoclaved control. This means that no mineralization happened in the bioreactors. This finding is similar to other studies (Vecitis et al., 2009; Sinclair and Kannan, 2006; Schultz et al., 2006; Hollingsworth et al., 2005; Key et al., 1998; Office of Pollution Prevention & Toxics, 1978; 1994).



**Figure 18. Fluoride concentration in bioreactors as a function of time**

### 3.4.2 PFOA degradation in the bioreactors

The PFOA concentrations in the anaerobic bioreactors (containing PFOA not treated by the plasma reactor) was 49,646 ppb after 12 months of biological treatment. There was no degradation of PFOA in the anaerobic bioreactor since the influent PFOA was 50,000 ppb.

## CHAPTER 4

### DISCUSSION

#### 4.1 Comparing this study with some other AOPs

There are two ways to measure the energy yield for this type of experiment. The first way is directly based on the degradation of the pollutant (PFOA) and the second way is based on the production of the product of the reaction ( $F^-$ ) (Stratton et al., 2017; Yasouka et al., 2011). We calculated the energy yield with the second method (based on  $F^-$  production). Helium as a carrier gas provides a higher rate of defluorination than argon (especially with flow rate of 1 mL/min). Consequently, there is higher energy yield with helium ( $11.3 \times 10^{-11}$  mole/J for the flow rate of 1 mL/min and  $8.4 \times 10^{-11}$  mole/J for the flow rate of 2 mL/min) than argon ( $5.8 \times 10^{-11}$  mole/J for flow rate of 1 mL/min and  $6.43 \times 10^{-11}$  mole/J for flow rate of 2 mL/min).

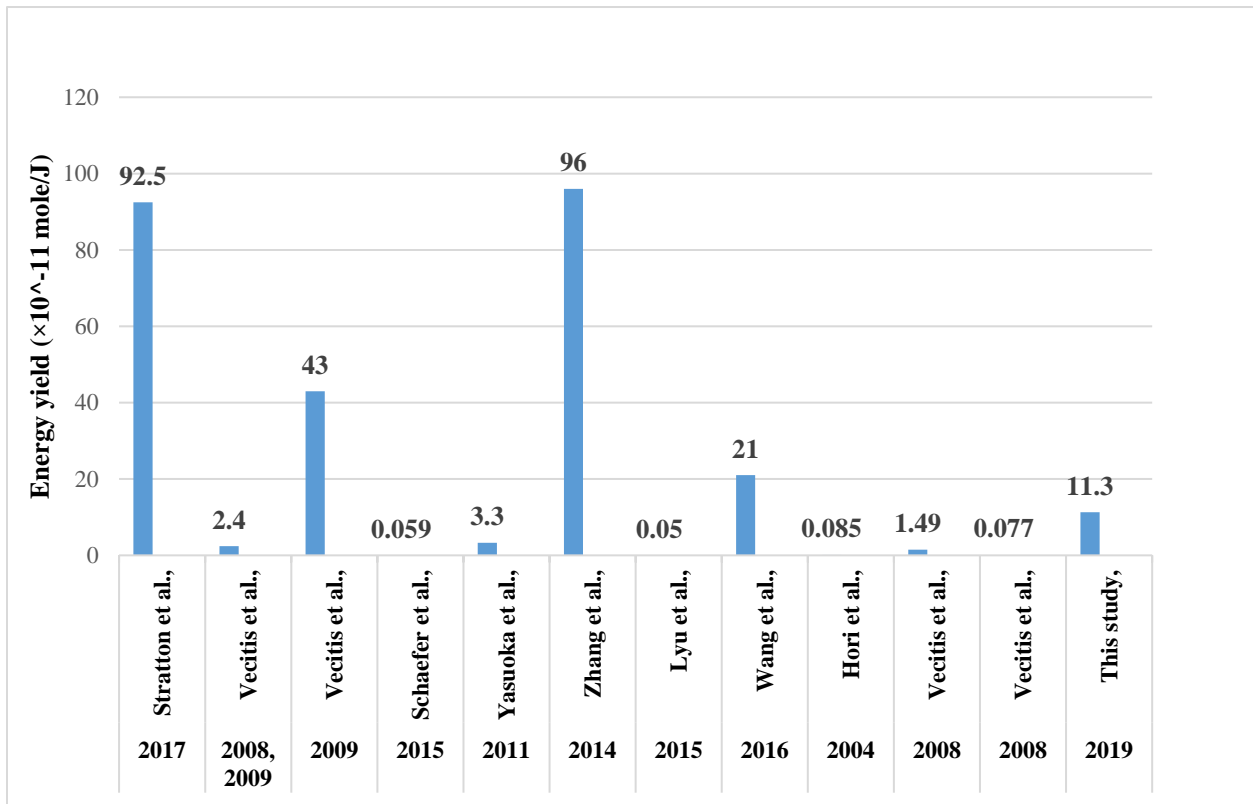


Figure 19. Comparing energy yield of this study with other AOPs

**Table 4. Comparing this study with other AOPs**

Treatment	[PFOA] ( $\mu\text{M}$ )	Energy yield ( $\times 10^{-11}$ mole/J)	Main reactants	Source
Non-thermal plasma, in and over water	20	45 to 140 (90.5 on average)	$e^-_{\text{aq}}$ , $\text{Ar}^+$	(Stratton et al., 2017)
Sonolysis	20	2.4	Pyrolysis, $\cdot\text{OH}$	(Vecitis et al., 2009; 2008)
UV-activated persulfate	50	43	UV, $\text{SO}_4^{\cdot-}$	(Vecitis et al., 2009)
Electrochemical treatment	0.031	0.059	Direct electron transfer at electrode	(Schaefer et al., 2015)
DC plasma in $\text{O}_2$ bubbles	100	3.3	+ oxygen ions	(Yasuoka et al., 2011)
Gamma radiation	50	96 (pH 13)	$\cdot\text{OH}$ , $e^-_{\text{aq}}$	(Zhang et al., 2014)
UV photo reactor	35	0.05	Photogenerated $e^-_{\text{aq}}$	(Lyu et al., 2015)
Electron beam	1.3	21	$e^-_{\text{aq}}$ , (possible role of nitrate radical ions)	(Wang et al., 2016)
UV direct Photolysis	1350	0.085	UV	(Hori et al., 2004)
Sonolysis	20	1.49	Pyrolysis	(Vecitis et al., 2008)
Sonolysis	0.2	0.077	Pyrolysis	(Vecitis et al., 2008)
Non-thermal plasma	20	11.3	$e^-_{\text{aq}}$ / $\text{M}^+$	This study

The energy yield of this study with helium as the carrier gas is compared with other advanced oxidation processes (AOPs) in Table 4. Figure 19 shows a schematic comparison between the energy yield achieved in this study with energy yield of other AOPs. The energy yield of our study is ranked fifth among the 12 studies. However, it should be noted that the comparison is based upon different reactor operating conditions (e.g., the influent PFOA) and is thereby not on the same basis.

Stratton et al. (2017) worked with a reactor very similar to ours but with a different kind of electrical discharge pulse power (see Table 5), but they got a higher energy yield in their reactor.

This could be explained by two factors: 1) a lower PFOA degradation and defluorination rate in



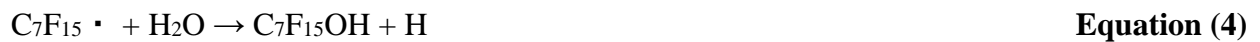
their reactor compared with our reactor, 2) a power supply with a polarity control in their reactor compared to no polarity control in our reactor.

## 4.2 Mechanism of PFOA degradation in the pulsed plasma reactor

### 4.2.1 Degradation pathway

The research most similar to this study is that of Stratton et al. (2017) and Yasouka et al., (2011). They are compared with our study in Table 5. Stratton et al. (2017) did not describe a complete pathway for the degradation of PFOA in their pulsed plasma reactor, but they mentioned that free electrons ( $e^-_{aq}$ ) were responsible for 90% of their PFOA degradation, and they suggested that free electrons initiated the degradation of PFOA. They examined their hypothesis by changing the electrode polarity from negative to positive and found that the degradation stopped in liquids with a positive electrode polarity and that, in gas, only 10% of the degradation happened while the equipment was working in the positive polarity mode. They suggested that  $Ar^+$  ions were responsible for that 10% degradation. Their research group reported PFHpA, PFHxA, and PFPeA as intermediates from the plasma degradation of PFOA. Statton et al. (2017) did not do OH radical scavenger experiments. Yasouka et al. (2011) suggested a pathway for the degradation of PFOA in their DC plasma reactor and proposed that some positive ions ( $M^+$ ) were initiating the degradation of PFOA, completely in contrast to the findings of Stratton et al. (2017). Yasouka et al. (2011) examined their hypothesis (that  $M^+$  was the primary responsible agent in the degradation of PFOA) by changing the polarity from positive to negative, and they reported that the degradation of PFOA stopped with a negative polarity. They did a scavenger experiment with 0.11 mM of scavenger, which might not be sufficient to quench all OH radicals.

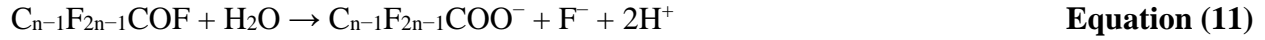
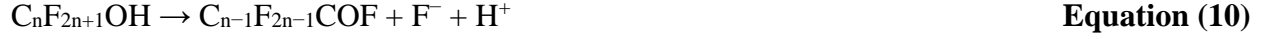
The PFOA degradation pathway proposed by Yasouka et al. (2011) is:



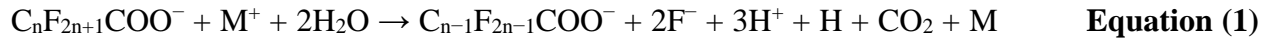
**Table 5. Comparing this study with Stratton et al. (2017) and Yasouka et al. (2011)**

	Stratton et al., (2017)	Stratton et al., (2017)	Yasouka et al., (2011)	This study
	High Rate	Removal	High Removal Efficiency	
Type of plasma	Pulsed Plasma	Pulsed Plasma	DC Plasma	Pulsed Plasma
PFOA Concentration in influent $\mu\text{M}$ , ppm	20, 8.28	20, 8.28	100, 41.4	20, 8.28
Carrier Gas	Argon	Argon	Argon > Helium > O <sub>2</sub>	Argon, Helium
Energy Yield ( $\times 10^{-11}$ mole/J)	40	140	3.3	11.3 (Helium; HRT= 015 s) 5.8 (Argon; HRT= 0.15 s)
Defluorination %	27	5	25	22 (Helium; HRT= 0.15 s) 11 (Argon; HRT= 0.15 s)
Power supply	With control	Polarity	With Polarity control	Without control
Effect of e <sup>-</sup> on degradation of PFOA, %	90-100		90-100	10
Effect of $\cdot\text{OH}$ on degradation of PFOA, %	~0		~0	~0
Effect of M <sup>+</sup> on degradation of PFOA, %	10		10	90
Effective Polarity	Negative		Negative	Positive
Free electron scavenger (& concentration of that)	NaNO <sub>3</sub> (10,000 $\mu\text{M}$ )		NaNO <sub>3</sub> (10,000 $\mu\text{M}$ )	Phosphoric acid (H <sub>3</sub> PO <sub>4</sub> ), 10 mg/l, 110 $\mu\text{M}$
$\cdot\text{OH}$ Scavenger (& concentration of that)	NA		NA	Formic acid (HCOOH), 5mg/l, 110 $\mu\text{M}$
Degradation initiator	Free electrons		Free Electrons	M <sup>+</sup> e <sup>-</sup> <sub>aq</sub> or M <sup>+</sup> or both

The overall PFOAs degradation pathway proposed by Yasouka et al. (2011) is:



The above equations can be summarized as follows:



(Yasouka et al., 2011)

Yasouka et al. (2011) found that PFHpA, PFHxA, and PFPeA were intermediates in the effluent (as did Stratton et al., 2017). In this study, we reported PFHpA and PFHxA as intermediates. However, we got different results with OH radical scavenger experiments. Therefore, we suggest that the degradation pathway of this study was close but not similar to that in Yasouka et al.'s (2011) and Stratton et al.'s (2017) research.

#### 4.2.2 The role of highly reactive species

The results of this study showed that the removal of PFOA in our plasma reactor was the same with argon and helium, but argon produced more intermediates and less final product ( $\text{F}^-$ ) compared with helium. Also, the experiments with different PFOA concentrations and high dose of OH radical scavenger shows that OH radicals might be partially responsible for the degradation of PFOA. These results could be explained by the hypothesis that aqueous electrons are mainly responsible for PFOA degradation into daughter products such as PFHpA and PFHxA while  $\cdot\text{OH}$  are mainly responsible for the degradation of the intermediates into fluoride.

Wang et al. (2018), working with the same reactor as in this study, found that the total electrons produced by argon and helium were almost the same. If the electrons in the liquid (aqueous electrons) are correlated with the plasma electrons, this might explain the similar PFOA

degradation rate for argon and helium. They reported that the electron density in the plasma with helium as the carrier gas ( $2E+15 \text{ cm}^{-3}$  when the discharge power was almost 1 Watt) was much less than the electron density of the plasma reactor with argon as the carrier gas ( $2E+16 \text{ cm}^{-3}$  when the discharge power was almost 1 Watt). For other discharge powers, the 1 to 10 ratio worked as well, but the plasma volume for helium was 10 times bigger than the plasma volume for argon. Therefore, the total amount of electrons are similar.

On the other hand, Wang et al. (2018) reported that the  $\text{H}_2\text{O}_2$  concentration, an indicator of  $\cdot\text{OH}$  concentration, was almost 2 times higher in the effluent when helium was the carrier gas; this explains why the reactor with helium had more conversion of PFHpA and PFHxA to fluoride (i.e., less PFHpA and PFHxA and more fluoride) than the reactor with argon.

Our hypothesis is consistent with the study in Zhang et al. (2014). Using  $\cdot\text{OH}$  scavenger, Zhang et al. (2014) found that the PFOA degradation remained constant, but the  $\text{F}^-$  production decreased when the OH radicals were scavenged.

To further test our hypothesis regarding the mechanism for the degradation of PFOA and its daughter products, we will need to have a power supply with polarity control. To measure the total intermediates, we will need a TOC-L (Laboratory total organic carbon analyzer that works based on 680 degree Celsius combustion catalytic oxidation). For more precise PFOA measurements, we will need a liquid chromatography-triple quadrupole mass spectrometry (Bentel et al., 2019).

To know more about the PFOA degradation pathway, future researchers will need to do experiments using different concentrations of scavengers for OH radicals and  $e^-_{\text{aq}}$ . Also, there is need of doing experiments and measurements to find the relation between the free electrons and  $e^-_{\text{aq}}$ . Finally, there will be need of doing experiments with different carrier gasses that potentially can produce different amount of free electrons to consider the role of free electrons on the degradation of PFOA.

## CHAPTER 5

### CONCLUSIONS

In this study, we tested a plasma reactor for PFOA degradation. First, we evaluated the effects of the hydraulic retention time (HRT) on the fluoride production due to PFOA degradation and found that the fluoride production increased with the HRT. At the highest HRT tested in this study (i.e., 1.65 seconds), the defluorination rate of PFOA reached 25% for a DI water containing PFOA at 50 ppm.

Second, we evaluated the effect of the carrier gas (argon and helium) on the removal of PFOA and the production of daughter products and final product (fluoride). We found that the carrier gas had no effect on the PFOA removal, but the reactor with helium produced more fluoride and less daughter products (i.e., PFHpA and PFHxA) compared to the reactor with argon. This could be explained by the hypothesis that aqueous electrons are mainly responsible for PFOA conversion to daughter production while  $\bullet\text{OH}$  are mainly responsible for the conversion of the daughter products to fluoride. The hypothesis is based on the assumption that the electrons in the liquid (aqueous electrons) are correlated with the plasma electrons, which are the same for helium and argon. The hypothesis is also based on the fact that the helium reactor produces two times more  $\bullet\text{OH}$  than the argon reactor. Since we detected similar daughter products as in Stratton et al. (2017), who used a pulsed plasma reactor and Yasouka et al., (2011), who used a DC plasma reactor, the degradation pathway in our study might be similar to that in their studies.

Third, the energy yield in our study is  $11.3 \times 10^{-11}$  mole/J, which is ranked five out of 12 studies with advanced oxidation/reduction processes for PFOA degradation. It should be noted that the comparison is not on the same basis since the reactor conditions such as the influent PFOA concentration, the removal rate and the power supply are very different.

Finally, we also tested the biodegradation of PFOA and its plasma degradation daughter products and found no degradation of PFOA or defluorination within one year. Biodegradation of the contaminants is one of the cheapest methods for water and wastewater treatment. Therefore, for future works, a lot more experiments need to be done to measure the biodegradability of PFOA.

## REFERENCES

- Alexandrino, D. A. M.; Ribeiro, I.; Pinto, L. M.; Cambra, R.; Oliveira, R. S.; Pereira, F. & Carvalho, M. F. (2018) Biodegradation of mono-, di- and Trifluoroacetate by microbial cultures with different origins; *New Biotechnology*, 43, 23-19.
- Appleman, T. D.; Dickenson, E. R. V.; Bellona, C. & Higgins, C. P. (2013) Nanofiltration and granular activated carbon treatment of perfluoroalkyl acids. *Journal of Hazardous Materials*, 260, 740–746.
- Appleman, T. D.; Higgins, C. P.; Quiñones, O.; Vanderford, B. J.; Kolstad, C.; Zeigler-Holady, J. C. & Dickenson, E. R. V. (2014) Treatment of poly- and perfluoroalkyl substances in U.S. full-scale water treatment systems. *Water Research*, 51, 246–255.
- Bartlet, J. C. & Smith D. M. (1960) The determination of the areas of resolved and partially resolved chromatography peaks. *Canadian Journal of Chemistry*, 38(11): 2057-2065.
- Bentel, M. J.; Yu, Y.; Xu, L.; Li, Z.; Wong, B. M.; Men, Y. & Liu, J. (2019) Defluorination of Per- and Polyfluoroalkyl Substances (PFASs) with Hydrated Electrons: Structural Dependence and Implications to PFAS Remediation and Management. *Environmental Science and Technology*, DOI: 10.1021/acs.est.8b06648.
- Bruggeman, P. & Leys, C. (2009) Non-thermal plasmas in and in contact with liquids. *Journal of Physics D: Applied Physics*, 42, 053001.
- Bruggeman, P. J. et al. (2016) Plasma–liquid interactions: a review and roadmap. *Plasma Sources Science and Technology*, 25, 053002.
- Campbell, T. Y.; Vecitis, C. D.; Mader, B. T. & Hoffmann, M. R. (2009) Perfluorinated surfactant chain-length effects on Sonochemical kinetics. *Journal of Physical Chemistry A*, 113 (36), 9834–9842.
- Davies, R. A. & Hickling, A. (1952) 686. Glow-discharge Electrolysis. Part I. The Anodic Formation of Hydrogen Peroxide in Inert Electrolytes. *Journal of the Chemical Society*, 0, 3595-3602.
- Drinking Water Health Advisories for PFOA and PFOS. (2016) *U.S. Environmental Protection Agency (EPA)*.
- Hazen, T. C. (2010) Cometabolic Bioremediation. Chapter. In book: *Handbook of Hydrocarbon and Lipid Microbiology*, 10.1007/978-3-540-77587-4\_185.
- Hickling, A. (1971) Electrochemical Processes in Glow Discharge at the Gas-Solution Interface. In: Bockris J.O., Conway B.E. (eds) *Modern Aspects of Electrochemistry* No. 6. Springer, Boston, MA, 6, 329-373.

Hollingsworth, J.; Sierra-Alvarez, R.; Zhou, M.; Ogden, K. L. & Field, J. A. (2005) Anaerobic biodegradability and methanogenic toxicity of key constituents in copper chemical mechanical planarization effluents of the semiconductor industry. *Chemosphere*, 59(9): 1219– 1228.

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

Horneman, A.; Burnell, S.; Burdick, J.; Houtz, E.; Ahmad, M. & Ross, I. (2017) Advances in poly- and perfluoroalkyl substances (PFAs) analytical techniques; Implications for Conceptual Site Models. *Design & Consultancy for natural and built assets*.

Houtz, E. F.; Higgins, C. P.; Field, J. A. & Sedlak, D. L. (2013) Persistence of perfluoroalkyl Acid precursors in AFFF-Impacted Groundwater and Soil. *Environmental Science & Technology*, 47 (15), 8187–8195.

Hsieh, K. C.; Wandell, R. J.; Bresch, S. & Locke, B. R. (2017) Analysis of Hydroxyl radical formation in a gas–liquid electrical discharge plasma reactor utilizing liquid and gaseous radical scavengers Plasma Process. *Plasma Processes and Polymers*, 14:e1600171.

Joshi, A. A.; Locke, B. R.; Arce, P. & Finney, W. C. (1995) Formation of Hydroxyl Radicals, Hydrogen Peroxide and Aqueous Electrons by Pulsed Streamer Corona Discharge in Aqueous Solution. *Journal of Hazardous Materials*, 41, 3-30.

Kadjo, A. F.; Dasgupta, P.K.; Su, J.; Liu, S. Y. & Kraiczek, K. G. (2017) Width Based Quantitation of Chromatographic Peaks: Principles and Principal Characteristics. *Analytical Chemistry*, 89, 3884–3892.

Key, B. D.; Howell, R. D. & Criddle, C. S. (1998) Defluorination of Organofluorine sulfur compounds by Pseudomonas sp. strain D2. *Environmental Science & Technology*, 32(15): 2283–2287.

Kim, B. R.; Suidan, M. T.; Wallington, T. J. & Du, X. (2000) Biodegradability of Trifluoroacetic Acid; *Environmental engineering science*, 17(6):337-342.

Kwon, B. G.; Lim H. J.; Na, S. H.; Choi, B. I.; Shin, D. S. & Chung S. Y. (2014) Biodegradation of perfluorooctanesulfonate (PFOS) as an emerging contaminant; *Chemosphere* 109, 221–225.

Liou, J.S-C; Szostek, B.; DeRito, C.M. & Madsen, E.L. (2010) Investigating the biodegradability of perfluorooctanoic acid. *Chemosphere*, 80, 176–183.

Liu, C. S.; Higgins, C. P.; Wang, F. & Shih, K. (2012) Effect of temperature on oxidative transformation of perfluorooctanoic acid (PFOA) by Persulfate activation in water. *Separation and Purification Technology*, 91, 46–51.



Locke, B.R.; Sato, M.; Sunka, P.; Hoffmann, M.R. & Chang, J.S. (2006) Electrohydraulic Discharge and Nonthermal Plasma for Water Treatment; *Industrial & Engineering Chemistry Research*, 45, 882-905.

Locke, B. R. & Shih, K. Y. (2011) Review of the methods to form Hydrogen Peroxide in electrical discharge plasma with liquid water. *Plasma Sources Science and Technology*. 20, 034006.

Lyu, X. J.; Li, W. W.; Lam, P. K. S. & Yu, H. Q. (2015) Insights into perfluorooctane Sulfonate photodegradation in a catalyst-free aqueous solution. *Scientific Reports*, 5, 9353.

Mahendra, S. & Alvarez-Cohen, L. (2006) Kinetics of 1,4-Dioxane Biodegradation by Monooxygenase-Expressing Bacteria. *Environmental Science and Technology*, 40, 5435-5442.

Meesters, R. J. W. & Schröder, H. F. (2004) Perfluorooctane Sulfonate\_ a quite mobile anionic anthropogenic surfactant, ubiquitously found in the environment. *Water Science and Technology*, 50:235–242.

Office of Pollution Prevention & Toxics, Docket AR226-0489, ed. Biodegradation studies of fluorocarbons—III. Washington DC: *US Environmental Protection Agency* (1978) 19.

Office of Pollution Prevention & Toxics, Docket AR226-0058, ed. Biodegradation studies of Fluorocarbons. Washington DC: *US Environmental Protection Agency* (1994) 4.

Parsons, J. R.; Saez, M.; Dolfing, J. & Voogt P. (2008) Biodegradation of perfluorinated compounds. *Reviews of Environmental Contamination and Toxicology*, 196, 53, 10.1007/978-0-387-78444-1\_2.

Post, G. B.; Cohn, P. D. & Cooper, K. R. (2012) Perfluorooctanoic acid (PFOA), an emerging drinking water contaminant: A critical review of recent literature. *Environmental Research*, 116, 93–117.

Quiñones, O. & Snyder, S. A. (2009) Occurrence of perfluoroalkyl Carboxylates and Sulfonates in Drinking Water Utilities and Related Waters from the United States. *Environmental Science & Technology*, 43 (24), 9089–9095.

Remde, A. & Debus, R. (1996) Biodegradability of fluorinated surfactants under aerobic and anaerobic conditions; *Chemosphere*, 32 (8): 1563-1574.

Sato, M.; Ohgiyama, T. & Clements, J. S. (1996) Formation of Chemical Species and Their Effects on Microorganisms Using a Pulsed High-Voltage Discharge in Water. *IEEE Transactions on Industry Application*, 32, 106.

Schaefer, C. E.; Andaya, C.; Urtiaga, A.; McKenzie, E. R. & Higgins, C. P. (2015) Electrochemical treatment of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) in groundwater impacted by aqueous film forming foams (AFFFs). *Journal of Hazardous Materials*, 295, 170–175.



Schäfer, H.; Läubli, M. & Dörig, R. (2003) Ion Chromatography Theory, Columns and Eluents. *Metrohm Monograph*; 8.014.5003.

Schröder, H. F. (2003) Determination of Fluorinated surfactants and their metabolites in sewage sludge samples by liquid chromatography with mass spectrometry and tandem mass spectrometry after pressurized liquid extraction and separation on Fluorine-modified reversed-phase sorbents. *Journal of Chromatography A*, 1020: 131–151.

Schultz M. M.; Higgins, C. P.; Huset, C. A.; Luthy, R. G.; Barofsky, D. F. & Field, J. A. (2006) Fluorochemical mass flows in a municipal wastewater treatment facility. *Environmental Science & Technology*, 40: 7350–7357.

Sei, K.; Miyagaki, K.; Kakinoki, T.; Fukugasako, k.; Inoue, D. & Ike, M. (2013) Isolation and characterization of bacterial strains that have high ability to degrade 1,4-dioxane as a sole carbon and energy source. *Biodegradation*, 24:665–674.

Sinclair, E. & Kannan, K. (2006) Mass loading and fate of perfluoroalkyl surfactants in wastewater treatment plants. *Environmental Science & Technology*, 40(5): 1408–1414.

Stahl, T.; Mattern, D. & Brunn, H. (2011) Toxicology of perfluorinated compounds. *Environmental Sciences Europe*, 23 (1), 1–52.

Stara, Z. & Krcma, F. (2004) The Study of H<sub>2</sub>O<sub>2</sub> Generation by DC Diaphragm Discharge in Liquids. *Czechoslovak Journal of Physics*, 54, C1050.

Stratton, G. R.; Dai, F.; Bellona, C. L.; Holsen, T. M.; Dickenson, E. R. V. & Mededovic Thagard, S. (2017) Plasma-Based Water Treatment: Efficient Transformation of perfluoroalkyl Substances in Prepared Solutions and Contaminated Groundwater. *Environmental Science & Technology*, 51, 1643–1648.

Sunka, P.; Babicky, V.; Clupek, M.; Lukes, P.; Simek, M.; Schmidt, J. & Cernak, M. (1999) Generation of Chemically Active Species by Electrical Discharges in Water. *Plasma Sources Science and Technology*, 8, 258-265.

Vecitis, C. D.; Park, H.; Cheng, J.; Mader, B. T. & Hoffmann, M. R. (2008) Enhancement of perfluorooctanoate and perfluorooctanesulfonate activity at acoustic cavitation bubble interfaces. *Journal of Physical Chemistry C*, 112(43): 16850–16857.

Vecitis, C. D.; Park, H.; Cheng, J.; Mader, B. T. & Hoffmann, M. R. (2009) Treatment technologies for aqueous perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA). *Frontiers of Environmental Science & Engineering in China*, 3(2): 129–151.

Visscher, P.T., Culbertson, C.W. & Oremland, R.S. (1994) Degradation of Trifluoroacetate in Oxic and Anoxic sediments. *Nature*, 369, 729–731.

Wandell, R. J.; Wang, H.; Tachibana, K.; Makled, B. & Locke B. R. (2018) Nanosecond pulsed plasma discharge over a flowing water film: characterization of electrical and plasma properties and their effect on Hydrogen Peroxide generation. *Plasma Processes and Polymers*, 15: e1800008.

Wang, L.; Batchelor, B.; Pillai, S. D. & Botlaguduru, V. S. V. (2016) Electron beam treatment for potable water reuse: Removal of Bromate and perfluorooctanoic acid. *Chemical Engineering Journal*, 302, 58–68.

Wang, H.; Wandell, R. J. & Locke, B. R. (2018) The influence of carrier gas on plasma properties and Hydrogen Peroxide production in a nanosecond pulsed plasma discharge generated in a water-film plasma reactor; *Journal of Physics D: Applied Physics*; 51; 094002 (13pp).

Watanabe, N.; Takata, M.; Takemine, S. & Yamamoto, K. (2015) Thermal mineralization behavior of PFOA, PFHxA, and PFOS during reactivation of granular activated Carbon (GAC) in Nitrogen atmosphere. *Environmental Science and Pollution Research*, 25:7200–7205.

Williams, R. J. (1983) Determination of Inorganic Anions by Ion Chromatography with Ultraviolet Absorbance Detection. *Analytical Chemistry*, 55 (6), 851-854.

Xiao, F.; Simcik, M. F. & Gulliver, J. S. (2013) Mechanisms for removal of perfluorooctane Sulfonate (PFOS) and perfluorooctanoate (PFOA) from drinking water by conventional and enhanced coagulation. *Water Research*, 47 (1), 49–56.

Xiao, J. F.; Zhou, B. & Resson H. W. (2012) Metabolite identification and quantitation in LC-MS/MS-based metabolomics. *TrAC Trends in Analytical Chemistry*, 32, 1-14.

Yan, H.; Cousins, I. T.; Zhang, C. & Zhou, Q. (2015) Perfluoroalkyl acids in municipal landfill leachates from China: Occurrence, fate during leachate treatment and potential impact on groundwater. *Science of the Total Environment*, 524–525, 23–31.

Yasuoka, K.; Sasaki, K. & Hayashi, R. (2011) An energy-efficient process for decomposing perfluorooctanoic and perfluorooctane sulfonic acids using dc plasmas generated within gas bubbles. *Plasma Sources Science and Technology*, 20; 034009 (7pp).

Zhang, Z.; Chen, J. J.; Lyu, X. J.; Yin, H. & Sheng, G. P. (2014) Complete mineralization of perfluorooctanoic acid (PFOA) by  $\gamma$ -irradiation in aqueous solution; *Scientific Reports*; 4; 7418.

## BIOGRAPHICAL SKETCH

### MEYSAM FARAHANI

#### Education

- **Master of Science**, Environmental Engineering (GPA 3.83/4.00), January 2017 – May 2019 (expected).

Department of Civil and Environmental Engineering. Florida State University, Tallahassee, FL.

Advisor: Dr. Youneng Tang, Florida State University.

- **Master of Science**, Chemical Engineering (Designing Chemical Processes) (GPA 3.44/4.00), January 2009- July 2011.

Department of chemical engineering, National University of Malaysia (UKM), Bangi, Malaysia

Advisor: Dr. Siti Rozaimah binti Abdullah, UKM.

- **Bachelor of Science**, Chemical Engineering (Petrochemical Industries) (GPA 14.15/20) September 2000- December 2005.

Department of chemical engineering, Islamic Azad University of Arak, Arak, Iran.

Advosor: Dr. Hassani.

#### Publications

**Farahani, M.;** Kashisaz, M. & S. R. S. Abdullah. (2015) Adsorption of Safranin O from aqueous phase using sugarcane bagasse. *International Journal of Ecological Science and Environmental Engineering*, Vol. 2, No. 3, 17-29.

#### Conference Presentations

**Farahani, M.;** Abdullah, S. R. S.; Hosseini, S.; Shojaeipour, S. & Kashisaz, M. (2011) Adsorption-based cationic dyes using the carbon active sugarcane bagasse, *Procedia environmental science*, Vol. 10, Part A, 203-208.

## Honors & Awards

- PIE Teaching Training Recognition, Florida State University, 2017.

## Research Experience

- **Master's Thesis topic:** Degradation of perfluorooctanoic acid by a non-thermal plasma reactor and bio-reactors.
- **Master's Final project topic:** Studied the kinetic and isotherm adsorption of Safranin O (Basic Red 2) on sugarcane bagasse and treated bagasse using NaOH and H<sub>2</sub>SO<sub>4</sub>.
- **Project:** Designed a water treatment plant (WTP) to remove perfluorooctanoic acid (PFOA) from water by a Pulsed Plasma reactor.
- **Project:** Designed aerobic and anaerobic bio-reactors to remove perfluorooctanoic acid (PFOA) from water.
- **Project:** Designed adsorption based reactor to remove Safranin O (Basic Red 2) from water using sugarcane bagasse (Raw and treated).

## Teaching Experience

- **Teaching Assistant:** Engineering Mechanics, 2017-2018. FSU (department of Civil and Environmental Engineering).

Duties:

- Taught on weekly recitation classes to review lectures and homework.
- Tutored students on one-on-one basis during office hours twice a week.
- **Graduate Assistant:** Engineering Mechanics, 2017, FSU (Department of civil and Environmental Engineering).

Duties:

- Graded student's homework assignments, quizzes and exams.

## Skills

- **Environmental Technology:** Bioreactor design and experiment, adsorption reactor design and experiments, non-thermal plasma reactor design and experiments for water and wastewater treatment, microbial culturing, chemical species analysis, bioremediation technology.
- **Analytical Instruments:** Ionic Chromatography (IC), UV-Visible Spectrophotometer, Total Organic Carbon (TOC-v), LC/MS/MS, Gas Chromatography-Mass Spectrometer (GC-MS) etc.
- **Software:** HYSYS, MATLAB. ICON (Petronas Malaysia), Microsoft office, Origin, Berkley-Madonna, Adobe Photoshop etc.
- **Others:** Soil/Air/Water Sampling, data analysis, Environmental Impact Assessment (EIA), Environmental Regulations/Policy.
- **Languages:** Persian (first language), English (fluent).

## Professional Experiences

- **Research Assistant:** 2013-2014. INC (Institute fur Nicht Klasseiche Chemie) Leipzig University, Leipzig, Germany. Research on: Advanced oxidation processes (AOPs) especially application of photo-catalysts in wastewater treatment under supervision of Dr. Roger Glaser.
- **Trainee:** 2006. Arak Petrochemical Factory in low density and linear Polyethylene unit. Arak, Iran.