Degradation of Perfluorooctanoic Acid in Water by A Continuous Flow Liquid-Phase Plasma Discharge Process

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Authorization to Submit Thesis

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ABSTRACT

Perfluorinated Alkyl Substances (PFAS), commonly known as the "forever chemicals." are comprised of a group of anthropogenic, fluorinated organic compounds that have been used for over 60 years in numerous products, including water-repellent clothing, stain-resistant fabrics, firefighting foams, cosmetics (lipstick and mascara), and other household items. They are highly hydrophobic due to strong carbon-fluorine bonds in their structure. Although no longer produced in the United States, these compounds are ubiquitous in the environment and have been detected in plants, animals, and humans. Source emissions include various manufacturing processes that once discharged their wastes into ground- and surface waters. Many studies have documented that PFAS are found in drinking water and bioaccumulate in the food chain. In the U.S., PFAS have been detected in more than 712 locations in 49 states and Puerto Rico. The same attributes that lead to their persistence in the environment makes their complete destruction difficult. The available remediation technologies used to remove or degrade PFAS in water have limitations, either due to cost or generation of PFAS solid wastes that require disposal. Research shows that plasma discharge processes can break the carbon-fluoride bonds of PFAS, but still do not achieve consistently high levels of removal. In this study, we developed a novel, continuous flow, liquid-phase plasma discharge (CFLPPD) process that shows promise for PFAS remediation. The reactor design generates a stable plasma discharge in a continuous/calculational operation to improve the treatment efficiency by producing reactive chemical species. This research included establishment of the CFLPPD treatment system; identification, screening, and evaluation of the significant operational parameters in order to determine the optimal treatment conditions; and exploration of the degradation pathway of an exemplar PFAS by this novel process.

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DEDICATION

I dedicate this thesis work to my family, especially my Mom Cecilia Aponte Ortiz and my Dad Ruben Ayala Morales (who passed away in early 2021), who gave me the courage to go for what I wanted in the future and believed in me when I decided to move from Puerto Rico for a brighter future. I want to thank my life partner Skye Swoboda-Colberg and his family (Patricia Colberg and Norbert Swoboda-Colberg) for helping me during the process and for supporting me in my career. Thank you for all your help, support, and learning experience. Thank you, Skye, for being an amazing partner in life and for all your love and caring. I want to thank Lubia Cajas and Karen Duran-Hansen for all their support during all these years. Thank you, Lubia, for encouraging me to pursue this master's degree program and for opening my eyes to a whole new area. Thank you, Karen, for been an amazing person and sister; thank you for being there for me.

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NOMENCLATURE

Advanced Oxidation Processes	AOP
Advanced Reduction Processes	ARP
Aqueous Film-Forming Foam	AFFF
Carbon	C
Centers for Disease Control and Prevention	CDC
Conductivity	µs/cm
Contaminant Candidate List	CCL
Continuous Flow Liquid-Phase Plasma Discharge	CFLPPD
Deionized Water	DIW
Environmental Working Group	EWG
Fluorine	F
Fluoride	F^-
Glow Discharge Electrolysis	GDE
Granular Activated Carbon	GAC
Hour(s)	Hr
Molecular Hydrogen	H_2
Hydrogen Peroxide	H_2O_2
Hydroxyl Radical	OH•
Ion Exchange	IX
Kilohertz	kHz
Liquid Chromatography/Mass Spectrometry	LC−MS
Liters per minute	L/min
Maximum Contaminant Level	MCL
Megahertz	MHz
Microfiltration	MF
Micrograms per liter	µg/L
Milligram	Mg
Milligrams per liter	mg/L
Milliliter per minute	mL
Milliliter per minute	mL/min
Minutes	Min
Nanofiltration	NF
Nanogram per liter	ng/L
Nitrate	NO_3^-
Molecular Oxygen	O_2
Particle-Induced γ-Ray Emission	PIGE
Parts per billion	ppb
Parts per million	ppm
Parts per trillion	ppt
Perfluorinated Alkyl Substances	PFAS

Perfluorocarboxylic Acids	PFCA
Perfluorooctanesulfonic Acid	PFOS
Perfluorooctanoic Acid	PFOA
Hydrogen ion concentration	pH
Public Waters Systems	PWS
Resource Conservation and Recovery Act	RCRA
Reverse Osmosis	RO
Safe Drinking Water Act	SDWA
Sodium Chloride	NaCl
Solid Phase Extraction	SPE
Third Unregulated Contaminant Monitoring Rule	UCMR 3
U.S. Environmental Protection Agency	EPA
Ultrafiltration	UF
Ultraviolet Light	UV
United States of America	U.S.A
Voltage	V
Watt	W

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INTRODUCTION

Clean water is one of the most critical of global concerns and is often related to treatment of the pollutants. Recently, there has been an increasing attention paid to Perfluorinated Alkyl Substances (PFAS), commonly known as the "forever chemicals." They are comprised of a group of anthropogenic, fluorinated organic compounds that have been used for over 60 years in numerous industrial products, including water-repellent clothing, stain-resistant fabrics, firefighting foams, and other household items. They possess unique properties of water resistance (1,2) due to very strong carbon-fluorine bonds (C-F) in their structure. Although no longer produced in the United States (U.S.), these compounds are ubiquitously distributed in the environment and have been detected in plants, animals, and humans (3). The source emissions include various manufacturing processes that once discharged their wastes into ground- and surface waters (4,5). Many studies have documented that PFAS are found in drinking water (3) and may bioaccumulate in the food chain (6). The same attributes that lead to their persistence in the environment makes their complete destruction extremely difficult. There is not much information about PFAS toxicology, making it challenging to develop risk assessments (1). Severe health issues, including increased cholesterol levels, diabetes, heart and kidney failure, liver disease, and different cancers, have been related to PFAS exposure [see, e.g., (7)]. Because of its potential for bioaccumulation (5), there is an urgent need to better understand PFAS distribution in the environment and develop efficient, cost-effective solutions to manage and/or destroy PFAS-contaminated water and wastes (5,8).

Although still evolving, there are currently only a limited number of effective treatment technologies for degrading or removing PFAS from water including filtration, adsorption, ion exchange (9); however, most of these processes do not result in complete removal or high treatment efficiency. One of the emerging technologies for PFAS remediation that has gained recent attention is the use of a plasma-based treatment process. By 2019, Singh et al. (2019) had published two papers showing significant removal of PFAS using a laboratory-scale, batch-operated plasma reactor to treat water samples obtained from monitoring wells located on 13 different U.S. Air

Force bases (10,11). They reported a 90% removal efficiency when using Argon as a gas alternative (10,12). The detection of short-chain perfluoroalkyl carboxylic acids (C_1-C_7) in the treated water suggested a stepwise reduction of the PFAS as the carbon-fluoride bonds were broken (10-13). Their work suggests that the plasma-based process appears to be a very promising technology for the complete destruction and removal of PFAS from water (10,11).

This study aims to develop a novel continuous flow liquid-phase plasma discharge (CFLPPD) process for destroying PFAS compounds from water and achieve a destruction and defluorination rate of greater than 90%. Perfluorooctanoic acid (PFOA), the most pervasive representative in the PFAS family, was used as a model chemical for establishing and evaluating the CFLPPD treatment process. Specific objectives for this project were to: [1] Set up the CFLPPD treatment system and investigate the feasibility and operation modes for PFOA removal; [2] Screen CFLPPD process parameters that significantly influence PFOA removal from water; [3] Explore the PFOA degradation and defluorination pathway by CFLPPD and the quality of treated water; and [4] Optimize the CFLPPD process for highest PFOA removal efficiency based on operating parameters identified in [2].

Chapter 1 focuses on the literature review; it introduces PFAS structure, sources, distribution, health and environmental impacts, and remediation technologies. Chapter 2 focuses on the experimental design and the materials and equipment used in the study. Chapter 3 presents a discussion and critical analysis of the results. Finally, Chapter 4 summarizes the conclusions with recommendations for future work.

Chapter 1:   LITERATURE REVIEW

1.1   Source and Use of Perfluoroalkyl and Polyfluoroalkyl Substances

Per- and polyfluoroalkyl substances (PFAS) are emerging contaminants consisting of a group of more than 3,000 synthetic organic chemicals composed of alkyl chains with multiple fluorine atoms (13). They were first discovered in the 1930s (14). In the 1960s, the development of these chemicals accelerated after a fire broke out on a U.S. Navy aircraft carrier and caused more than 130 deaths and resulted in development of a PFAS-containing, aqueous film-forming foam (AFFF) (14,15). The AFFF spreads rapidly, making it extremely effective against fuel fires and other flammable liquids (14,16). These products are still routinely stored and used on both military and civilian ships and aircraft and at airports (17). Other than in AFFF, PFAS have also been used for over 50 years in thousands of household products, including food packaging, various industrial materials including paints, waxes, polishes, cleaning products, and cookware coatings (e.g., Teflon™) (18).

PFAS have many unique properties such as thermal stability, high electronegativity, strong acidity, chemical stability, among others that make them resistant to biodegradation (19); in fact, they are commonly referred to as "forever chemicals." Some PFAS are no longer made because studies have suggested adverse effects on human health and the environment (20). Figure 1 illustrates the family hierarchy class and subclasses of PFAS.
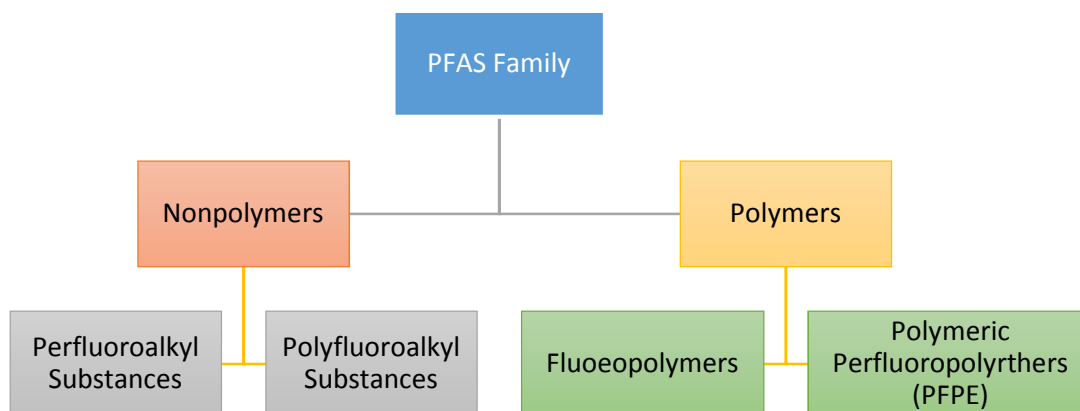
Figure 1. The PFAS Family of Chemicals

1.1.1 Perfluorooctanoic acid (PFOA)

Perfluorinated substances, such as Perfluorooctanoic Acid (PFOA), whose chemical formula is $C_8HF_{15}O_2$ (see Figure 2), is the PFAS that has been most widely manufactured and studied (21). The PFOA molecule is composed of eight carbon and 15 fluorine atoms with a carboxylic acid group on the end (20).

PFOA has been used in a variety of consumer products and in the manufacture of other fluoropolymers. For years, this chemical was used for waterproofing and stain resistance in carpets, leathers, textiles, upholstery, paper packaging, and coating additives. PFOA was also used in combination with other PFAS to make aviation fluid fire resistant (22). This compound is hydrophobic, so is frequently used as surface-active agent that modifies the surface tension of a liquid substance (22).

Like all PFAS, PFOA is a very stable compound and so accumulates in the environment and in human tissues. It is readily detectable in air, soil, food, and in both surface- and ground waters (19). For this reason, PFOA was selected for use as a model compound in this work for investigating PFAS degradation by the proposed treatment process.
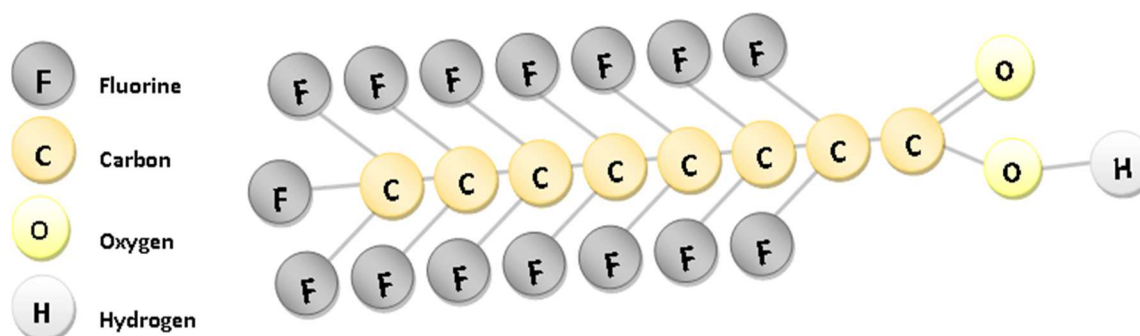
Figure 2. Structure of Perfluorooctanoic acid (PFOA) ($C_8HF_{15}O_2$)

1.1.2   Carbon–Fluorine Bond

PFAS are highly fluorinated, aliphatic chemicals that are distinguished by carbon atoms that are bound to fluorine atoms. Fluorine is the one of the strongest of electronegative elements, resulting in the development of strong polar C-F bonds with very high detachment energies (Figure 2) (14,19,23). In fact, the C-F bond is the one of the strongest polar covalent bonds known and is a feature of all organofluorine substances (18,23,24). Because of this bond, PFAS compounds are very difficult to degrade or/and remove with conventional water and wastewater treatment processes.

1.2   Exposure to PFAS and Contaminated Sites

Drinking water is the most common pathway of exposure to PFAS. As shown in Figure 3, these chemicals have contaminated the drinking water sources of at least 16 million people in 33 states and Puerto Rico, as well as groundwater sources in at least 38 states (25). PFAS are being spread worldwide and can be found in every nonstick pan, in various waterproofed items, and in firefighting foam (AFFF) described previously. PFAS have been found in the drinking water supplies of major cities like New York, Washington, D.C., and Chicago, as well as cities throughout Florida and California (22,26).

PFAS-containing water sources are primarily contaminated by firefighting foam and industrial discharges. For years, U.S. military bases around the country used AFFF for training exercises. A report released in March 2020 by the Department of Defense reported that more than 600 military sites and their surrounding communities are exposed to PFAS in drinking water supplies (27).

The industrial disposal of PFAS is another pathway of exposure and water contamination. The disposal of waste liquids to the ground from manufacturing contaminates ground water and creates air pollution. For example, in 2016, investigators found high levels of new generation-PFAS in North Carolina's Cape Fear River, caused by a manufacturing plant owned by The Chemours Company, a company that holds DuPont's patent for Teflon^{TM} (26,28).

Humans may also be exposed to PFAS through food and food packaging. An article published in 2017 reported levels of PFAS in one-third of all fast food packaging and containers, where it can simply migrate into the foods (29). In the study, researchers collected some 400 samples of food contact papers, paperboard containers, and beverage containers from fast food restaurants around the country and measured total fluorine using particle-induced γ-ray emission spectroscopy (PIGE) (29). The study showed that 46% of the food contact papers and 20% of paperboard samples contained high levels of fluorine (see Table 1), a variety of PFAS (70%), and other unknown polyfluorinated compounds (29).

Table 1. PFAS Content in Food Items

Item	Percentage of Fluorine
Dessert & bread wrappers	56%
Sandwich & burger wrappers	38%
Paperboard	20%

The transportation and disposal of PFAS plays a key role in environmental contamination. The release processes of these chemicals can influence their biological, chemical, and physical distribution as well as the magnitude of migration within and between plume development, groundwater discharge to surface water, and other areas (25). Because of the wide variety of PFAS, their different physical and chemical characteristics (e.g., chain length, ionic state) can alter their behavior in the environment (17). Some of the waste disposal sources are industrial wastes, landfills, wastewater treatment plant effluent, land-applied biosolids, vapors, and particulates. In fact, the company 3M used PFAS as the major component for the AFFF that has been widely used since the 1960s on military bases, at airports, in fire training areas and at chemical refineries (14). Figure 4 shows a conceptual diagram of how PFAS may be transported to and distributed in soils, water, and food sources.

The long history of PFAS usage and its improper disposal have caused contamination in landfills as well; wastes containing PFAS release contaminants at slow but steady rates over decades and have a very high potential to contribute to the pollution of both ground and surface waters. More than 110 million people in the U.S. may be exposed to PFAS contamination in their raw water supplies.
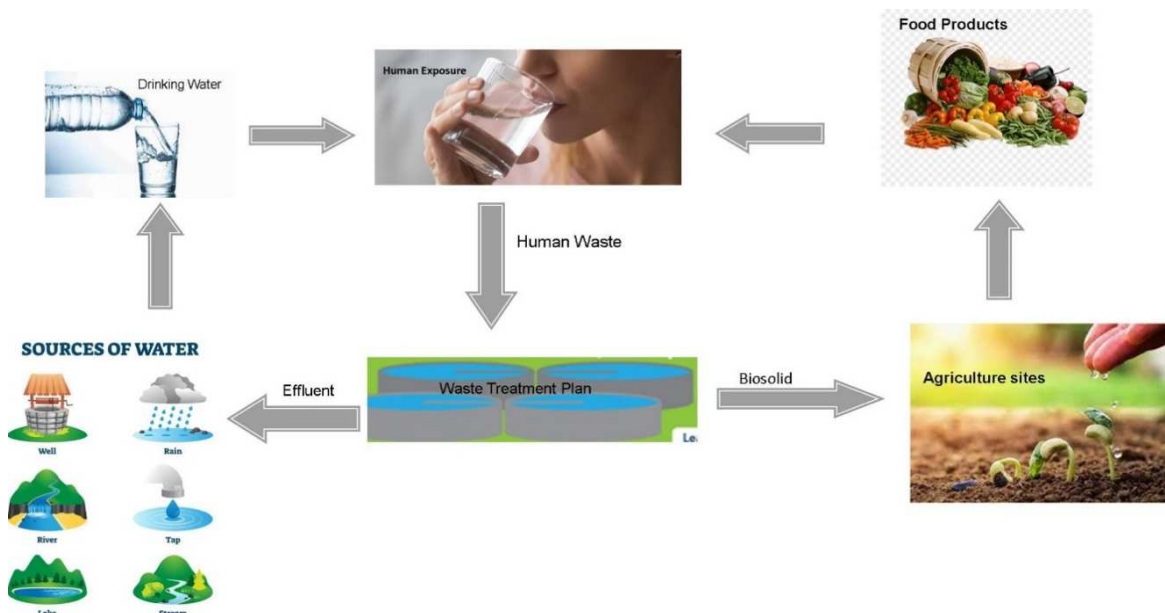
Figure 3. Transport Pathways of PFAS

1.3 Environmental and Human Health Effects of PFAS

Although production of most PFAS have been discontinued, the persistence of PFAS in the environment has been a cause for international concern, especially over the last decade (30). All PFAS are readily detectable in air, soil, food, and in both surface- and ground waters (19). A study by the Environmental Working Group (EWG) shows that 712 locations in 49 states have been discovered to be contaminated, including public water supplies, military bases, and airports (31). According to the National Center for Biotechnology Information, PFAS have been found in the blood of more than 98% of the population in the United States, especially near military bases and manufacturing facilities (17,32,33). Oral exposure occurs through contamination from paper packaging and food wrappers, absorption from food and water, inhalation of fabrics containing PFAS, and ingestion of PFAS-contaminated particles (19). There have been several recent studies clearly suggesting that the major human exposure pathway for PFAS is food and water (16,34,35).

The overall effect of PFAS on human health is not clear, so there is an urgent need to better understand PFAS toxicology in humans. A 2003 study found a positive correlation between the health effects of PFAS and elevated blood levels of uric acid

(hyperuricemia) (34,36). The study also reported increased blood pressure levels, various metabolic syndromes, and cardiovascular disease in both children and adults (34). Tempkin et al. (2020) reported that long-term exposure to these chemicals may cause prenatal problems and cancer development (20). The available literature also suggests that these chemicals are not metabolized by humans; in other words, they may accumulate in our tissues over many years since there is no specific metabolic function for these chemicals. (16,34,35). It can only be excreted in the urine in low quantities (19). PFAS are also suspected carcinogens and endocrine disruptors (15). Developing a better understanding of PFAS toxicology is critical to understanding the human health effects of PFAS contamination (18,35). Without it, it is very difficult to develop guidance on PFAS use and draft regulations for their proper treatment and disposal (19,37).

In the State of Idaho, there are currently three known PFAS-contaminated sites (Figure 4). In 2017, Elmore County was informed about a contaminated area due to the use of firefighting foam at Mountain Home Air Force Base. The primary raw water source for this area is groundwater and serves over 7,500 people (38). On the Idaho Department of Environmental Quality website, they report that the State of Idaho has adopted the EPA national primary drinking water standard for PFAS. Currently, however, PFAS are not regulated contaminants, which means that "public drinking water systems are not required to monitor for these contaminants" (38).
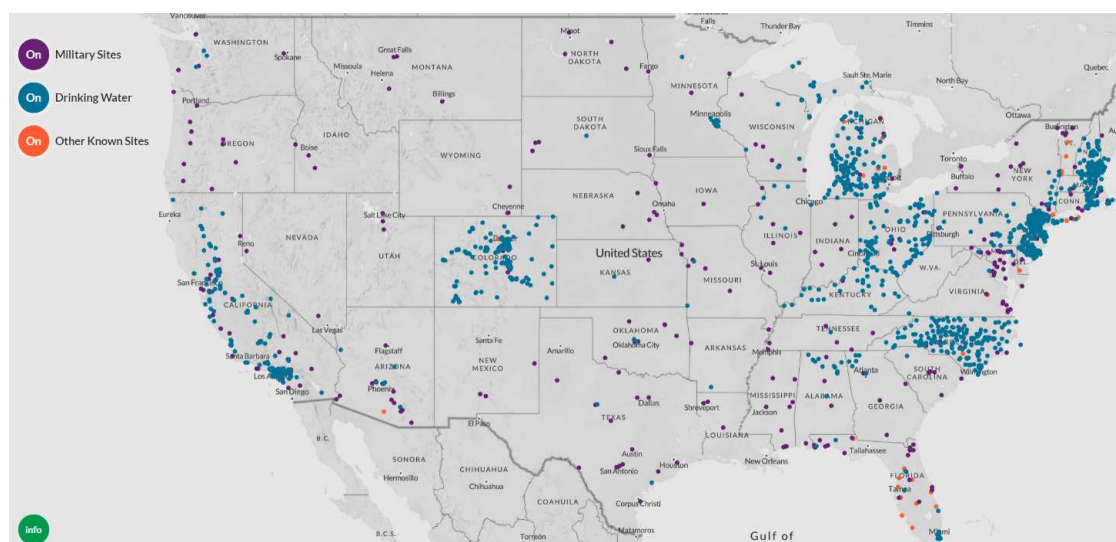
Figure 4. Map of PFAS Contamination in the United States as of January 6, 2021

1.3.1 Human and Environmental Impact

As already discussed, correlations between severe health issues and PFAS exposure have been reported. According to the Centers for Disease Control and Prevention (CDC), 95% of the U.S. population has been exposed to PFAS, and because of its pervasiveness, these substances can persist in the human body for decades and potentially cause severe health problems (39). In 2021, the EWG reported at least 610 locations in 43 states were identified as contaminated with PFAS (see Figure 4), as well as drinking water systems serving around 19 million people (28).

Studies have shown that the best known PFAS, called PFOA, is linked to kidney, liver, and other types of cancer, as well as endocrine disruption in humans and animals (26,39). Researchers and governmental agencies have also found uncommon clusters of severe medical illnesses in communities with widespread PFAS-contaminated water, many of which are near military bases (22,28,39). In addition, toxicological research in animals has shown that exposure to PFOA and other PFAS can interfere with mammary gland development, contribute to testicular cancer and obesity, and result in immune suppression (40,41). While health impact data are limited because of the lack of studies, results from preliminary work have shown that these compounds are a threat to both humans and to the environment. This information helps support the efforts to develop and use nonfluorinated replacements.

These compounds are insoluble in water and oil and are unaffected by high temperatures. Their use has increased since they were first synthesized by corporate chemists in the 1920s (42). Because of their unique bonding, PFAS are difficult to biodegrade and so accumulate over time. PFAS contamination can damage the environment and have a significant impact on the ecosystem (43). As in humans, some mammals exposed to high levels of PFAS variations in hormone levels and significant damage to vital organs (6,19) Table 2 shows the list of the known health effects linked to PFAS Exposure.

Table 2. Known Health Effects Linked to PFAS Exposure

Category	Health Effects
Metabolic Disease	Liver damage
	Increase serum cholesterol levels
Immuno-toxicity	Decrease immune responses
	Increased risk of asthma
Developmental Outcomes	Lower birth weight
Carcinogenicity	Testicular liver and kidney cancer
	Increased risk of thyroid disease
Endocrine Disruption	Pregnancy-induce hypertension/pre-eclampsia
	Delayed menstruation and earlies menopause

1.3.2 Socioeconomic Impacts and Environmental Costs

In contrast to the industrial benefits of using PFAS, these chemicals have social and economic costs (43). Industry and regulatory scientists have studied the exposure and harmful impacts of PFAS chemicals for decades (44). Malits et al. (2017) conducted an assessment of direct costs (hospitalization for medical concerns), indirect costs (loss of IQ points) and other economic costs [e.g., out-of-pocket expenditures, parental lost workdays, low birth weight of children (45)]. Their study aimed to assess the ratio of PFAS exposure and its relation to low birth weight and costs in the US from 2003 to 2014. They found that the in-utero exposure to PFAS has been associated to decreased birth weights. A total of 12,764 serum PFAS levels among women aged 18 to 49 years were obtained. Their estimates attributable burden and economic costs from 2003 to 2014 in the U.S. was about $13.7 billion (45).

Gabbert et al. (2018) also published an economic assessment of the environmental and health impacts attributed to PFAS compounds and concluded that there are both direct and indirect health and environment costs (46). However, there is a lack of numerical assessments of external costs resulting from environmental and human exposure to PFAS. The long-term environmental and health impacts and damage cost measures are not available because of the lack of information on PFAS toxicology and risk assessments. There is an urgent need of information on risk management outcomes based on economic impact that reflect industrial, social, health and environmental costs in order to determine the real impact of PFAS usage.

1.4 Current Advisory and Guidelines for PFAS

Despite the health problems that such chemicals may cause, many PFAS are still used by industry because of their unique and valuable properties. To protect human health and the environment, the U.S. Environmental Protection Agency (EPA) administers and enforces federal laws enacted by Congress and have set a general health advisory level for PFAS of 70 parts per trillion (ppt) in drinking water (30). In February 2020, the EPA proposed an Action Plan under the auspices of the Clean Water Act for PFAS-contaminated water in an effort to assist states to monitor and protect the health of affected communities (19,47). Based on recent studies, EPA's recommended limit is considered by many to be too high due to the known or suspected health effects of PFAS and their bioaccumulation in the environment (48). For example, the Michigan Environmental Council recommends a cumulative standard, requires health reviews to ensure the well-being of its population, and conducts continuous water sampling of its military bases (19,49). In addition, some scientists have made recommendations to the EPA to lower the current health advisory level to 2 ppt (19,47,48).

Since there are no PFAS standards at the federal level, some state governors have decided to take action by mandating that manufacturers reduce their generation of PFAS waste (19,47). Some states have implemented their own Maximum Contaminant Levels (MCL) to further reduce PFAS disposal in liquid wastes. They have also recommended that PFAS-containing wastes be labeled as "hazardous materials" under the Resource Conservation and Recovery Act (RCRA). There have been some efforts by private and non-profit organizations to help with the standards process. Recently, the U.S. Congress began to address the matter and drafted the PFAS Action Act. It is still under consideration in the U.S. Senate, but if this plan is approved, it will help with the cleanup of PFAS, especially at sites with water contaminated with PFAS. Meanwhile, the implementation of stringent regulations will require well-developed and viable PFAS remediation technologies that can effectively and efficiently remove PFAS in drinking water and wastewater to meet the standards.

1.4.1 PFAS Safety Guidelines and Limits

There are a variety of policies and guidelines to protect the environment and human health. The Safe Drinking Water Act (SDWA) is the act that protects the public drinking water supplies across the nation. This act can only be applied to the public water systems (PWSs), but does not apply to domestic drinking wells in the United States (50). Under this act, the EPA regulates over 90 different contaminants in water. For the protection of consumers, the EPA sets enforceable Maximum Contaminant Levels (MCLs) for specific chemicals that can be released in water (35,50). In January 2009, EPA established a temporary health advisory for PFOA in drinking water of 0.4 micrograms per liter (µg/L) (22). To note, each state may develop their own guidelines values for PFAS and other contaminants that are not fully regulated by the EPA or other federal agencies. Table *3* shows the guideline values set by different states.

Table 3. State Guideline Values for PFOA

State Departments	Guideline Value (µg/L)
Delaware Department of Resources and Environmental Control	0.4
Maine Department of Health and Human Services	0.1
Michigan Department of Environmental Quality	0.42
Minnesota Department of Health	0.3
New Jersey Department of Environmental Protection	0.04
North Carolina Division of Water Quality	2
Vermont Agency of Natural Resources	0.02

In 2012, EPA added PFOA in its Third Unregulated Contaminant Monitoring Rule (UCMR 3), which mandated that all public water systems that serve more than 10,000 people to be monitored for a one-year period (22). The data collected between 2013 and 2015 from these PWSs reported levels of PFOA at or above the minimum levels (0.02 µg/L) by nearly 2% of PWSs nationwide (22). Until now, there has been no MCL established for PFAS released in water. EPA initiated the evaluation process for PFAS in November 2016 (50); however, several states have set parameters for these chemicals released in water. For example, in July 2018, the state of New Jersey adopted an MCL of 0.013 µg/L (43). Also, in 2017, the state of Minnesota decided to reevaluate its guidelines and lower its MCL based on the U.S. EPA health advisory.

The common chemicals found in water, like PFOA, are listed on the Contaminant Candidate List (CCL). The CCL is the list of contaminants that are currently not subject to any proposed regulations, but are known or anticipated to occur in public water systems (30,50,51). The agency issued the lifetime no regulatory Health Advisory for PFOA and PFOS in May 2016, based on their studies indicating that exposure to these chemicals over certain levels may result in health effects, including developmental impacts during pregnancy or to breastfed infants, immune effects, and cancer (21). The current EPA health advisory level for PFOA and PFOS are 70 parts per trillion (ppt) in drinking water (30). In 2016, PFOA has been monitored and found to be greater than the new health advisory level of 0.07 μg/L by nearly 0.3% of PWSs. In addition, 1% of the PWSs have reported levels above the health advisory recommendations (22). EPA's health advisories are non-enforceable and non-regulatory standards that provide technical information to states agencies and other public health organizations for the control of contaminants in water (50).

While the first-generation of PFAS are known to be toxic and were phased out of production in the U.S. in 2015, (28,52), there is no policy that prohibits companies from using them or from importing them into the country. Chemical companies have produced similar first-generation PFAS with other compounds in their family. These new PFAS versions are have been deemed as toxic as the first-generation of PFAS (17,38).

1.5 Treatment Technologies for the Removal or Degradation of PFAS in Water

As stated earlier, the strong C-F bonds in PFAS make them difficult to remove or degrade (53). Over the decades, there have been different water treatment technologies investigated to remove or degrade PFAS in water, but few results have demonstrated a high rate of removal (54). Adsorption, filtration, and electrochemical processes are the most common techniques employed (53,55,56). Figure 5 contains a list of the common processes used for PFAS treatment, which are classified into two major categories: degradation or removal. Detailed information about these available technologies and their treatment capacity and efficacy is described in the subsections of this chapter.
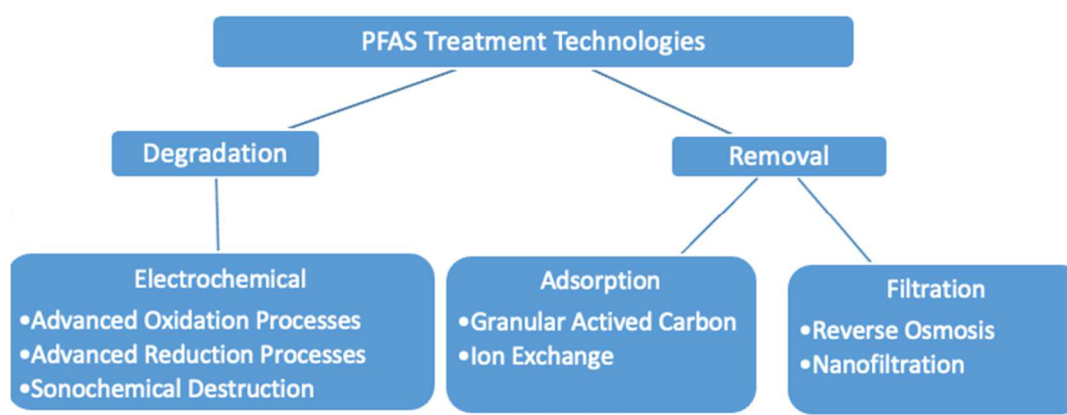
Figure 5. Different Treatment Technologies for PFAS Degradation or Removal

1.5.1 Adsorption Treatment Technologies

Adsorption techniques have been used for almost a century (57) and are widely used to remove organic contaminants from water (53). Adsorption employs highly porous surface structures that result in the deposition of compounds from the water at the surface layer of the adsorbent (58). The most frequently used adsorption materials for the removal of PFAS from water are Granular Activated Carbon (GAC) and Ion Exchange (IX) (10,58).

1.5.1.1 Granular Activated Carbon (GAC)

Granular activated carbon (GAC) is an effective adsorption medium for the removal of organic compounds and is recommended by the EPA because it can remove PFOA from water with 90% efficiency and is very cost-effective (55,59). The PFAS sorb to the small particles of carbon as the water passes through the filters (30). This process may result in no detectable PFOA levels in the treated water (59); however, GAC does not involve any transformation process or induce any form of degradation (60). It also requires frequent replacement due to the accumulation of PFOA on the GAC (61). Temperatures of 800°C or more are required for the destruction of the PFAS after removal from treated water. For most water treatment applications, GAC has low operational and treatment costs because of its widespread availability (62). GAC is a low cost and efficient alternative treatment but is not a degradation or destructive treatment technology. As such, PFAS still accumulates as waste and represents a continuing disposal challenge (55,61,63).

1.5.1.2 Ion Exchange (IX)

Ion exchange (IX) is another potentially efficient and cost-effective adsorption option for removing PFAS from water. This technology has been used since the 1930s, mainly to soften water (64). In most applications, sodium ions are exchanged for calcium and magnesium ions (64). Ion Exchange is particularly effective for the sorption of short-chain sulfonic PFAS using a single-use resin (65,66). But because PFOA has a long carbon chain (C8), IX is not effective for its removal (19). As with GAC, IX does not involve any transformation or degradation of the PFAS (54). Zaggia et al. (2016) also note that IX resins used for this purpose may not be regenerated, which makes this process expensive and unsuitable for large-scale treatment (67).

1.5.2 Filtration Treatment Technologies

Filtration is the process whereby molecules (or particles) of different sizes are retained as the fluid passes through a membrane (55,64). There are different types of membranes that may remove PFAS from water, including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and Reverse Osmosis (RO). Reverse osmosis and nanofiltration have been shown to have the highest PFAS removal efficiencies. The greatest concern about filtration technologies is the high cost of treatment and the wastes generated by the process. Since the PFAS remains on the membrane surface, disposal following EPA guidelines is required. In most cases, the membranes need to be incinerated, which leads to additional costs and environmental contamination (30,55,56).

1.5.2.1 Reverse Osmosis (RO)

Reverse Osmosis (RO) is a filtration process that removes the majority of contaminants in water by transferring the water under pressure through a semipermeable membrane. This technology is effective in eliminating the majority of mineral- and carbon-based compounds from water. Studies suggest that RO combined with nanofiltration has a removal efficiency of 90% for PFAS (53,60,66); however, it requires that the water be pretreated because the membranes are susceptible to fouling (60,62). The membranes accumulate materials that cannot be easily removed, which results in higher operating pressures and shortened membrane life (53).

Reverse osmosis is not a cost-effective technology for PFAS removal, with costs ranging from \$2.65 to \$3.80 per thousand gallons of treated water (68).

1.5.2.2 Nanofiltration (NF)

Nanofiltration (NF) is a membrane-based treatment process used for purifying water by removing most of the organic compounds, microorganisms, and other molecules. This process uses spiral wound membranes that operate at low pressures (55,69). In combination with RO, NF membranes can remove 85% to 90% of PFAS from water (70). In contrast to RO, nanofiltration removes more long-chain PFAS because of its slow pressure flow of molecules through the small pores on the surface of the membrane (55,62). As with the other membrane-based processes, NF has the problem of disposal and incineration of the membranes.

1.5.3 Electrochemical Processes

Electrochemical treatments induce degradation processes that result in both direct and indirect oxidation and reduction of organic and inorganic compounds in water by producing chemically reactive species. These types of technologies are known for degrading organic compounds that are resistant to other types of treatment, but have a high energy demand which makes them very costly (55,62,71).

1.5.3.1 Advanced Oxidation Processes (AOP)

Advanced Oxidation Processes (AOP) comprise water treatment alternatives that use reactive species like hydroxyl radicals (OH•) for the oxidation of organic contaminants (72). These technologies are often combined with ozone and UV irradiation for higher treatment efficiency and are commonly used for the removal of organic contaminants in wastewater (55). Because of the high stability of the C-F bond of PFAS, AOP are not useful for the destruction of PFAS. Some studies report removal rates as low as 10%, while others achieved no more than 50% removal (2,60). In general, AOP are not considered cost-effective methods for removal of PFAS from water (60).

1.5.3.2 Advanced Reduction Processes (ARP)

Advanced Reduction Processes (ARP) oxidize pollutants by producing highly reductive but short-lived radicals -- so-called hydrated electrons (73,74). These processes are similar to AOP in that they both use UV light, but they differ in the radicals that are formed (75). Some ARP employ narrowband ultraviolet light, electron beams, ultrasound, or microwaves (74). ARP are effective in reducing organic compounds, but because of the structure of PFAS, they can only achieve up to 70% removal from water (73–75).

1.5.3.3 Sonochemical Destruction (SD)

Sonochemical Destruction is the application of ultrasound to produce chemical responses in a aqueous solution (55,76). The sound fields collapse the bubbles in the cavitation, resulting in a high gas temperature and breakdown of the PFAS compounds (55,77). Typically, the range for sonochemical treatment for PFAS are from 20 to 1000 kHz or megasonic (>0.5 MHz) (76). In 2009, Rayne et al. reported that at 43 minutes, half of the PFOA had been degraded using argon and in 102 minutes using air (57). Their study reported removal rates from 39% to 44%. Vecitis et al. (2010) demonstrated that sonochemical treatment can decrease PFAS concentrations by 73% in 120 minutes (78).

1.5.4 Summary of remediation rate and cost of the established treatments

In summary, adsorption and filtration technologies do not degrade PFAS; they remove them from water, but their residuals remain on the media or membranes, respectively (79). Electrochemical technologies can degrade PFAS, but because of the high stability of the C-F bonds, their removal efficiency is generally low. A comparison of the removal efficiencies and costs of currently available methods for PFAS treatment is summarized in Table 4. Because existing technologies have low efficiencies for the removal or degradation of PFAS from water and/or produce solid wastes that essentially concentrate the PFAS, there is a need for developing new technologies that are both effective and cost-efficient.

Table 4. Removal and Costs for Different PFAS Treatment Technologies

Treatment	% Removal	Average Cost / 1,000 gal
Granular Activated Carbon	Up to 90%	$0.10 - $1.00
Ion Exchange	57% - 70%	$0.30 - $0.80
Reverse Osmosis	84% - 90%	$2.65 - $3.80
Nanofiltration	84% - 90%	$2.65 - $3.80
Advanced Oxidation Processes	10% - 50%	$0.10 - $10.00
Advanced Reduction Processes	Up to 70%	N/A
Sonochemical Destruction	39% - 73%	~$0.74

1.5.5 Liquid Plasma-based Technologies

The interaction of plasma with liquids was first reported in 1789 by Troostwijk and Deinman when they wrote about the breakdown of water by an electric discharge (80–82). But it was not until 1887 that Gubkin was able to initiate reactions with liquid products using Glow Discharge Electrolysis (GDE) as an exclusive electrochemical practice. In Gubkin's plasma process, the discharge is produced between the metal contact and the fluid cathode by applying high voltages. He detected visible metal particles created by the interaction with the free electrons from the liquid plasma discharge. Gubkin's work initiated a new research area, which was later called plasma electrochemistry (80,81,83,84).

Over the last 15 years, the focus of research on the interactions of plasmas with liquids has broadened to address a variety of applications, including electrical switching (85), analytical chemistry (86), material synthesis (nanoparticles) (87), chemical synthesis (limited to H_2O_2, H_2) (88), degradation of organic compounds (89–91), destruction of bacteria and viruses (92,93), oxidation of inorganic ions (94,95), synthesis of polymers (96), and biomedical engineering (97).

1.5.5.1 Plasma-Based Technology for Water Treatment

Interest in liquid-phase plasma discharge has been growing in recent years as an alternative technology to treat polluted water. The process of plasma occurs when the electrical discharges diffuse in water to initiate different physical and chemical effects, such as high electric fields, powerful UV emission, oxidative and reductive reactive species (H•, O•, OH•, H_2O_2, H_2, O_2, O_3), and localized high pressure and acoustic waves, which are created independently or synergistically in a rapid and efficient way (98,99). Moreover, plasma-based technologies have been reported effective for the removal of both organic and inorganic compounds, including emerging contaminants such as cyanide and dye compounds wastewater (9,10,53,55,63). The advantages of plasma-based processes for water and wastewater treatment include no chemical additions, operating at ambient temperatures and pressures, and being insensitive to contaminants and environmental disturbances. All of these features greatly simplify the scale-up process for commercial applications without the need to invest in capital costs for equipment.

1.5.5.2 Plasma Discharge for PFAS Removal

Deemed as a combined physical/chemical process that produces a much stronger effect than the conventional chemical oxidation/reduction processes, plasma discharge is a promising remediation technology that can degrade PFOA by breaking the carbon-fluoride bonds and eliminating it from water (68). The plasma treatment operates with electricity and gas in a system that degrades PFOA in minutes (10,11,60). Recent studies have shown that the Plasma Discharge Process can degrade PFOA in water in very short periods of time (30 minutes) with 90% removal, while the presence of other contaminants does not appear to interfere with the process (10,62). Unlike other methods discussed previously, recent studies suggest that the process completely oxidizes the PFAS to its mineral constituents (7,53,55). Table 5 summarizes some of the operating conditions and PFOA removal results obtained from various plasma processes.

Table 5. Comparison of Various Plasma Processes for PFOA Removal

Reactor Type	Initial conc	Time (min)	Gas Type	Removal	Defluorination	Reference
Laminar jet w/ bubbling	20 µg/L	30	Argon	90%	N/A	Stratton et al. (100)
Batch w/ground electrons	8.3 mg/L	120	Argon	90%	77%	Singh et al. (10)
Nanosecond pulsed gas liquid flow	50 mg/L	120	Argon	90%	3.65%	Bulusu et al. (101)
Atmospheric plasma	0.58 µg/L	7	Oxygen	90%	5.50%	Jovicic et al. (102)
Gliding arc plasma	70 mg/L	60	Air	90%	98.2 %	Lewis et al. (103)

Thagard et al. (2016) maintain that it is currently impossible to measure the direct contribution at the interface process to the degradation of the PFAS compounds (104). This process consists of diffusion, evaporation, sputtering, electrolysis, and chemical reaction, and so on (104). They add that the current way to quantify PFAS removal rates is to monitor the intermediates resulting from the treatment process (12,104).

Singh et al. (2019) used a four-liter, semi-batch, pilot-scale plasma reactor to treat PFAS wastes at a U.S. Air Force base (11). Their objective was to reduce the PFAS concentrations below the EPA health advisory concentration level (70 ppt). There were a variety of PFAS concentrations measured in the 13 samples collected from raw water. In the experiment, the PFAS concentrations decreased rapidly (<10 min) and were lower than the EPA recommended health advisory level. There was no consequence of non-PFAS co-contaminants on the degradation process (11). The remediation process achieved more than 90% removal within 30 min of treatment. This was the first study to use a large volume plasma reactor for PFAS remediation. lists the various types of plasma reactors in existence today and the experimental parameters reported for each system. The table includes a comparison of reported defluorination rates and removal efficiencies. Understanding the interface process is essential to understanding how plasma mediates the degradation process of PFAS and how the radical species work. Also, it can help to increase the efficiency of plasma treatment in the future. The time of the solution circulating through the reactor and the

use of argon instead of air can have a significant impact on the degradation process for PFAS (105). It is notable that previous published studies used batch reactors; in this study, we used a recirculating batch reactor.

1.6 Summary

PFAS contamination of water is a global environmental issue. In the U.S., PFAS have been detected in more than 712 locations in 49 states. The available remediation technologies used to remove or degrade PFAS in water have limitations, either due to cost or generation of toxic solids wastes that require disposal. Research shows that plasma discharge processes can break the carbon-fluoride bonds of PFAS, but still do not achieve consistently high-levels of removal.

In this study, we developed a novel continuous flow liquid-phase plasma discharge (CFLPPD) process that shows promise for PFAS remediation. The reactor design generates a stable plasma discharge in a continuous/calculational operation to improve the treatment efficiency by producing concentrated reactive chemical species. This research included establishment of the CFLPPD treatment system; identification, screening, and evaluation of the significant operational parameters in order to determine the optimal treatment conditions; and exploration of the PFOA degradation pathway by this novel process. With the completion of this project, we have generated valuable new information and that hopefully contributes to advancing environmental science and engineering in remediating these emerging contaminants of global concern.

Chapter 2:   EXPERIMENTAL DESIGN

2.1   Research Objectives

Based largely on the literature review, the primary focus of this thesis research was to establish and evaluate the effectiveness of a continuous flow, liquid-phase plasma discharge reactor in degrading Perfluorooctanoic Acid (PFOA) in water. It is intended that the findings of this study will contribute to the development of new designs for plasma discharge systems that may be scaled up and used at an industrial level for remediating PFAS-contaminated water and wastewater. This project has three specific objectives:

1. Design and construct the CFLPPD treatment system and identify operational parameters that may affect PFOA removal.
2. Using a two level, partial factorial design, evaluate the CFLPPD operational parameters for their significance in affecting PFOA degradation in water and assess PFOA removal rates.
3. Identify the PFOA degradation pathway.

2.2   Materials & Chemicals

Since PFOA is so widely used and found as a contaminant in water, it was selected as the PFAS of interest in this study. The PFOA was purchased from Thermo Fisher Scientific (Waltham, MA). For our experiments, we prepared a stock solution of PFOA by dissolving 150 mg of 95% PFOA powder in 150 mL of DI water for a final concentration of 950 mg/L. For all experiments, 3 mL of the stock solution was added to 297 mL of tap water for a final concentration of PFOA in the reactor of 9.5 mg/L. Sodium Chloride (NaCl) was used to adjust the conductivity. The standards of linear perfluoroalkyl carboxylic acids, sulfonates, and labeled internal standards were purchased from Wellington Laboratories (Guelph, ON). Analytical grade PFOA, methanol, and acetonitrile (LC−MS grade) were purchased from Thermo Fisher Scientific (Waltham, MA). The 99.99% purity Argon gas was purchased from OXARC Inc. (Lewiston, ID).

2.3   Reactor Design and Operation

The basic components of a Liquid-Phase Plasma Discharge reactor is shown in Figure 6. A schematic diagram of the entire CFLPPD reactor system used in this study is shown in Figure 7. The reactor was constructed of polycarbonate materials, divided into three sections, and was separated by two dielectric plates. These dielectric plates have a 0.75 mm opening in the center to concentrate the electrons generated to be the electrical discharge at the reactor and facilitate electron movement, mass transfer, and the degradation process. A stainless-steel bar is connected to each section of the reactor, with the top and bottom sections functioning as ground voltage electrodes, while the middle section is the high voltage electrode.
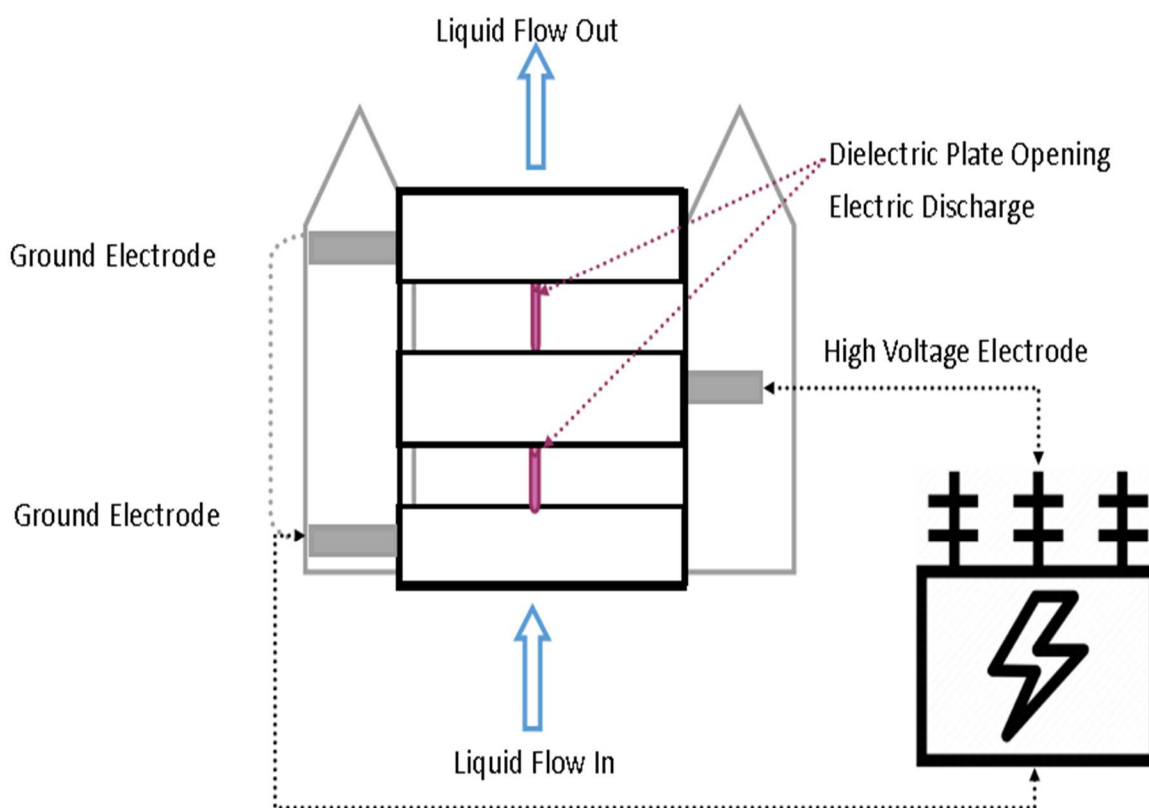
Figure 6. Configuration of the CFLPPD Reactor

The reactor design allows both batch studies and batch studies with continuous recirculation. The reactor also allows the fluid to be exposed to the plasma discharge two times as it moves through the reactor, which should result in increased degradation efficiency. This design allows for continuous circulation with the liquid entering the reactor at the bottom and exiting from the top by a peristaltic pump. The reactor is controlled by a high-voltage Variac transformer regulator (ISE, Inc., Cleveland, OH), which is connected to the stainless-steel electrodes in the reactor. Voltage is measured using an oscilloscope (Tektronix) and a Watt meter (Poniie). The Masterflex peristaltic water pump with an Easy-Load II pump head (Cole-Parmer, Vernon Hills, IL) is used to pump the water through the reactor. The airflow rate was controlled using a Sierra Smart Trak Mass Flow Controller (Sierra Instruments, Monterey, CA). The CFLPPD process was operated at room temperature and pressure using an AC power supply.
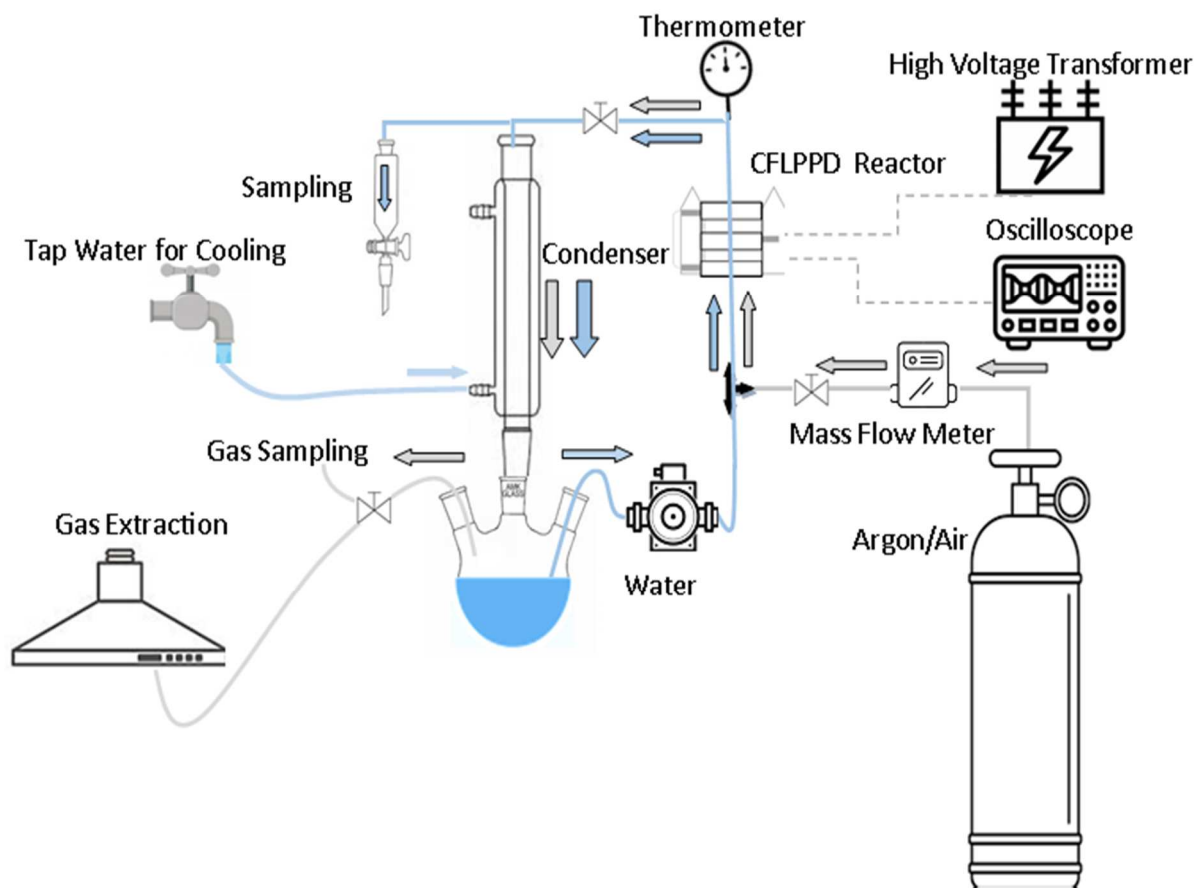
Figure 7. Schematic diagram of the CFLPPD Reactor System Used in this Study

2.4   Experimental Design

To identify the process parameters that affect PFOA degradation in water, a two-level partial factorial design was used. Table 6 lists the five process parameters that were chosen based on preliminary experiments: gas type (provided by a high-pressure gas cylinder); conductivity (adjusted by adding NaCl in the initial PFOA solution), power (determined by adjusting the Variac transformer), water flow rate (controlled by a peristaltic pump), and gas flow rate (standard liter per minute, L/min). A solution with a final concentration of 9.5 mg/L PFOA was prepared and used for each experimental run, and the total treatment time was 60 minutes with the PFOA solution pumped in a circulating mode through the reactor. A 20-ml sample was taken every 15 minutes, and the voltage, temperature, current, and power were each recorded. Conductivity, pH, as well as concentrations of nitrate ion (NO_3^-), fluoride ion (F^-), hydrogen peroxide (H_2O_2), PFOA and intermediate degradation products of each sample from each experiment run were measured.

Table 6. Experimental process parameters

Variable	Factors	Low	High	Unit
X1	Conductivity	300	900	μs/cm
X2	Water Flow Rate	70	150	mL/min
X3	Gas Flow Rate	0.5	1.5	sl/m
X4	Gas Type	Air	Argon	-
X5	Power	100	200	watt

PFOA removal rate and defluorination rate for each treatment condition were calculated by

Equation 1 *and*

Equation *2*, respectively, and used as the process responses analyzed in the Design Expert (Stat-Ease, Inc., 2021) software in order to determine the statistical significance of each process parameter. Process parameters with p values <0.05 were interpreted as significant. The significant factors for the PFOA removal rate and defluorination rate were evaluated in the next step by running five levels of those factors within the test. Conductivity, pH, NO_3^-, H_2O_2, F^- were also monitored. Potential

intermediates in the PFOA degradation pathways were analyzed using LC-MS. These results were compared with the degradation pathways reported by other investigators who have used plasma treatment techniques.

Equation 1. PFOA Removal

$$\textbf{PFOA Removal } \% = \frac{\textbf{C}_0 - \textbf{C}_f}{\textbf{C}_0} \times \textbf{100}\%$$

C_0 - initial PFOA concentration, in mg/L

C_f - final PFOA concentration, in mg/L

Equation 2. Defluorination Rate

$$\textbf{F}^- \% = \frac{\textbf{C}_{F-}}{\textbf{C}_0 \times \textbf{M}_F\%} \times \textbf{100}\%$$

C_{F-} - concentration of F- ion released in the solution, in mg/L

$M_F\%$ – mass percentage of the fluorine element in PFOA, 68.8%

2.5 Sample Analysis

Concentrations of PFOA and their derivative perfluorocarboxylic acids (PFCAs) were analyzed using Liquid Chromatographic–Mass Spectrometry (LC-MS/MS) (NanoAcquity UPLC/Xevo TQ MS) with a 2.1mm x 150mm C-18 HPLC column (University of Idaho MS Core Lab) following EPA Standard Methods 537 and 533. These methods use solid phase extraction (SPE) for sample enrichment and LC-MS/MS for analysis (EPA 2016). Fluoride ion (F-) and concentrations of residual nitrogen compounds commonly produced with air plasma discharge (e.g., NO_3^-) and other oxidative products were measured by Ion Chromatography (Dionex, Sunnyvale, CA) with an SI-90 4E column. Hydrogen peroxide (H_2O_2) concentrations were measured with the titanium sulfate colorimetric method using a UV/VIS spectrophotometer. Conductivity and pH were measured for each sample using a pH probe and conductivity meter.

For testing H_2O_2, a solution of titanium sulfate (TiSO4) colorimetric method using a UV/VIS spectrophotometer (Shimadzu 1201). The test was made right after the water sample saw collected. If the sample cooled down, the H_2O_2 results were lower and not readable. The concentrated yellow color is made when an acidic solution of titanium ions are mixed with the H_2O_2 (106). This test measures the oxidation of organic and inorganic compounds in the water samples. A H_2O_2 calibration curve was created for this study. The target for the calibration curve was from 0 to 300 mg/L. NO_3 concentrations were tested by using a Hach spectrophotometer (Model#: DR 3800, Hach Company, CO).

2.6 Experimental Procedure

A PFOA stock solution was made by using 150 mg PFOA (95% purity, Sigma-Aldrich, St. Louis, MO) plus 150 mL deionized water (DI) for a final concentration of 950 mg/L PFOA. The reactors were operated in semi-batch mode, with liquid circulating depending of the run values. For the experimental design, the runs were conducted for 60 minutes in a continuous pass, taking samples every 15 minutes plus the initial sample (control factor) for a total of five samples. Readings for the temperature (Celsius), power (watts), voltage (RMS and Peak – Peak), and the current (RMS and Peak – Peak) were taken every 5 minutes. For each run, the system was rinsed three times for control assurance and decontamination. For each reactor run, 3 mL of PFOA stock solution was added 300 mL of tap water for a starting concentration of 9.5 mg/L in the reactor. Tap water was used in the experiments was analyzed before use for the presence of other contaminants and particles.

Chapter 3:   RESULTS & DISCUSSION

3.1   Introduction

Five parameters were selected for their potential to impact PFOA degradation in the reactor: conductivity, water flow rate, gas flow rate, gas type, and power. Prior to the experimental process, the CFLPPD reactor was tested to determine the appropriate ranges for each of these parameters. As summarized in Table 7, the Design Expert software produced a list of 16 experiments with randomized parameter selection. For each experiment, the initial concentration of PFOA in the reactor was 9.5 mg/L, which is a higher concentration than used in most other published studies. The percentage removal of PFOA in each experiment is noted in the last column of Table 7.

Table 7. Two-level partial factorial experimental design (16 experimental runs)

Run #	Conductivity µs/cm	Water Flow Rate mL/min	Gas Flow Rate sl/m	Gas type	Power watt	PFOA Removal %
1	885	150	0.5	Air	200	77.6%
2	317	70	1.5	Air	100	80.2%
3	845	70	1.5	Air	200	70.0%
4	860	150	0.5	Argon	100	87.4%
5	303	150	1.5	Argon	100	93.4%
6	312	150	0.5	Air	100	80.1%
7	329	150	0.5	Argon	200	89.8%
8	294	70	0.5	Air	200	82.6%
9	886	150	1.5	Argon	200	93.4%
10	314	70	0.5	Argon	100	88.6%
11	877	70	0.5	Air	100	76.5%
12	882	70	0.5	Argon	200	87.4%
13	875	150	1.5	Air	100	78.1%
14	303	150	1.5	Air	200	81.5%
15	854	70	1.5	Argon	100	92.4%
16	332	70	1.5	Argon	200	92.6%

3.2 Effect of Operational Factors and on PFOA Removal

To identify those operational parameters that most impacted PFOA removal in the reactor, an ANOVA analysis was conducted. Table 8 shows the p-values of all parameters based on the PFOA removal results. p-values less ≤ 0.05 indicate the model terms are significant. Values greater than 0.05 indicate the model terms are not significant.

Based on the ANOVA results shown in Table 8, the Gas Type (D) with a p-value less than 0.0001 is the most significant model parameter. The model suggested that if there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model. The model shows that conductivity and power also do not affect the PFOA removal rate. Detailed information about these factors are described in the subsections of this chapter.

Table 8. ANOVA for PFOA Removal Responses

Source	Sum of Squares	df	Mean Square	F-value	P-Value	
Model	0.0663	5	0.0133	13.50	0.0004	
A-Conductivity	0.0042	1	0.0042	4.26	0.0660	
B-Water Flow Rate	0.0008	1	0.0008	0.7859	0.3962	
C-Gas Flow Rate	0.0008	1	0.0008	0.8381	0.3815	
D-Gas Type	0.0605	1	0.0605	61.60	< 0.0001	Significant factor
E-Power	0.0000	1	0.0000	0.0185	0.8944	
Residual	0.0098	10	0.0010			
Cor Total	0.0761	15				

3.2.1 Gas type

Based on the experiment results, the p-values indicate that gas type plays a key role in the degradation process. For this study, either argon or air were used for the plasma discharge as provided by a high-pressure gas cylinder. The best PFOA removal within 30 min was achieved with argon. As shown in Figure 8, the initial rates of PFOA removal were similar for both argon and air. But after 15 min, the rate of PFOA removal with air slowed. After 60 min, the mean percentage of PFOA removal achieve in all experimental runs was 90% for argon and 78% for air.

The proposed pathway for PFOA transformation (10) starts with the formation of chemical radicals (e.g., hydrated electrons) that can break of the C-F bond; the release of fluoride ions increases as a result. As already discussed, the rate of PFOA removal was faster with argon than with air (Figure 8). This observation is consistent with other studies in which different gas types were compared. Plasma reactive species can lead to different chemical reactions that result in a large number of unstable intermediate compounds (101). The greatest amount of PFOA removal achieved in our experiments with argon was 93.4%; with air, it was 82.6%. Even the lowest amount of PFOA removal with argon was still higher than air at 87.4%. The experimental run using high parameters (Run #9 on Table 7) reached PFOA removal and defluorination rates compared to other leading technologies.

Gas type is a key factor since the experiments showed that there is a significant difference in PFOA degradation when using argon gas. Argon is a neutral, unscented, non-reactive gas that is inert. Argon as a noble gas, has good thermal conductivity, and a slight electron attraction that aids the plasma discharge process; however, argon has little or no known impact on hydroxyl radical production in contrast with air at the same flow rate (107). And even though argon has about the same solubility in water as oxygen, it is 2.5 times more soluble in water than nitrogen gas, which is the main constituent in air. So overall, argon is more soluble in water than air. As mentioned in previous studies, the plasma electrons, aqueous electrons, and argon are the main mediators responsible for PFOA degradation (10).
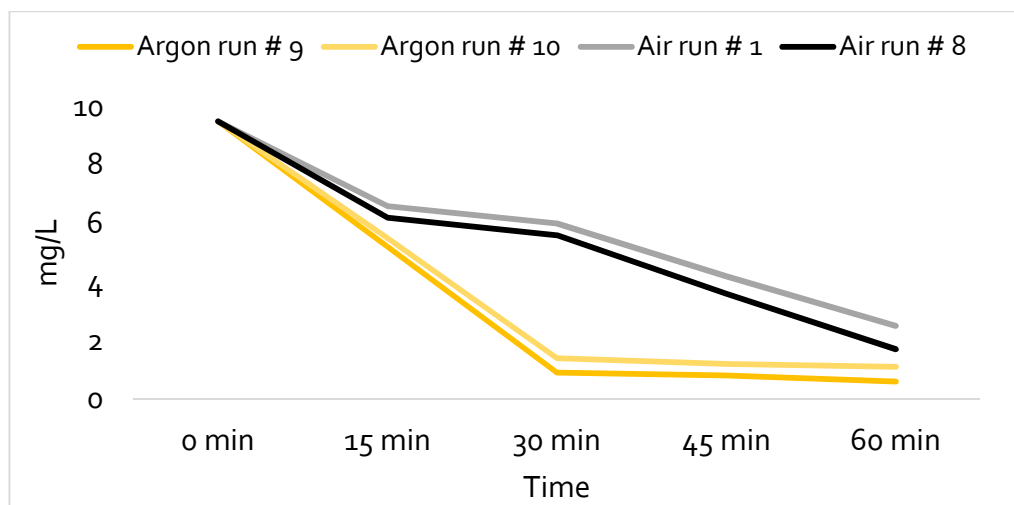
Figure 8. PFOA Degradation Rate: Air vs. Argon

3.2.2 Conductivity

Conductivity is useful in assessing general water quality and is a measure of the ability of water to pass an electrical current (108). Conductivity is an important factor in understanding the interaction by which power is combined to a radio-frequency ejection, as well for defining the external electrical features of the plasma discharge. The higher the conductivity, the higher the capacity to conduct a large amount of electrical current. Significant changes in the conductivity of water may indicate the presence of electrolytes or pollutants in the water. In the ANOVA analysis, conductivity was not determined to be a significant factor, meaning that an increase (or decrease) in conductivity did not affect the PFOA degradation process. Table 9 shows that Run #15 with high conductivity had about the same amount of PFOA removal as Run #16 with low conductivity.

For some experimental runs, the conductivity was adjusted to approximately 850 µS/cm by adding sodium chloride (NaCl) to the initial PFOA solution; in Table 9, these runs are labeled as conductivity = 1000. For experiments with no added NaCl, which are designated in Table 9 as 300 conductivity, conductivity was measured after adding the PFOA solution to the water, but before starting the treatment process. The conductivity of the tap water was approximately 300 µS/cm. Conductivity is affected by

temperature; higher temperatures result in higher conductivity measurements (Table 9).

In the experiments with high conductivity (labeled as initial conc of 900 μS/cm), it was noted that the water color changed over time possibly due to NaNO$_3$ produced with Na in the NaCl and NO$_3$- fixed from N$_2$ gas in the air. As soon as the PFOA was added to the reactor, the water formed a layer of foam and appeared pale yellow in color (see Figure 9). The temperature increased faster in the experiments that had added NaCl. In one of the runs, we noticed after 23 min that the temperature was rising fast, but there was no foaming; after 35 min, the water turned almost brown in color, and the temperature increased to 95°C, making some of the reactor parts fail. Some of these same observations about NaCl addition have been observed in other studies as well (102). In summary, conductivity did not affect the removal rate of PFOA.

Table 9. Conductivity Readings

Run	Initial Cond. μs/cm	Final Temp °C	Power watt	PFOA Removal %	Time / Conductivity Reading μs/cm				
					0	15	30	45	60
1	1000	95	200	77.6	885	865	854	873	885
2	0	71	100	80.2	317	335	341	4.11	370
3	1000	90	200	70.0	845	866	893	911	1005
4	1000	69	100	87.4	860	862	842	878	789
5	0	63	100	93.4	303	283	289	263	255
6	0	79	100	80.1	312	318	1978	316	315
7	0	95	200	89.8	329	317	218	189.1	189.6
8	0	93	200	82.6	294	310	156.2	302	314
9	1000	87	200	93.4	886	869	830	852	897
10	0	71	100	88.6	314	304	286	269	257
11	1000	69	100	76.5	877	851	862	858	833
12	1000	95	200	87.4	882	839	789	763	823
13	1000	70	100	78.1	875	850	836	840	819
14	0	88	200	81.6	303	334	402	399	422
15	1000	65	100	92.4	854	850	826	820	817
16	0	91	200	92.6	332	287	221	194.4	653
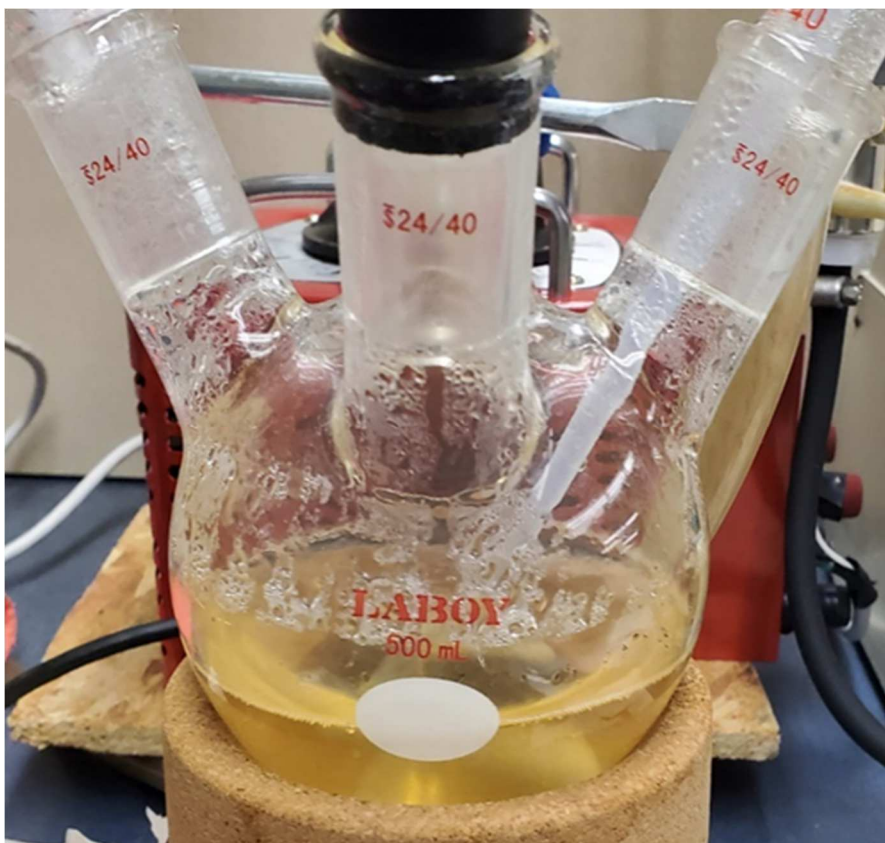
Figure 9. Color Changes in PFOA Solution upon Addition of NaCl

3.2.3 Power

Power was set by adjusting the Variac transformer. The voltage and current in the plasma reactor were measured using an oscilloscope with readings taken every 15 min. Also, the transformer position was recorded as an indicator for the factor setting in Volts (V). Voltage and current waveforms are provided in Table 10. In our experiments, power was adjusted to reach 100 watts as the lowest setting and 200 watts as the highest.

Based on the ANOVA analysis, power was not significant in determining PFOA removal. It is worth noting that the power readings during the experimental runs were consistent and stable. Also, the use of argon for the plasma discharge required less energy than using air. These data points can be useful for conducting an Energy Efficiency analysis for the CFLPPD in the future.

Table 10. Effect of Voltage and Current on PFOA Removal

Run	Initial Power (watt)	PFOA Removal %	Final Power (watt)	Voltage (kV)	Current (mA)
1	200	77.6	220	2.45	15.2
2	100	80.2	110	3.37	8.93
3	200	70.0	207	2.32	14.9
4	100	87.4	118	1.8	10.6
5	100	93.4	98.9	2.28	8.45
6	100	80.1	130	3.5	7.44
7	200	89.8	230	3.91	14.3
8	200	82.6	211	3.16	13.1
9	200	93.4	233	2.4	18.4
10	100	88.6	105	2.19	8.99
11	100	76.5	101	1.9	8.6
12	200	87.4	243	2.12	18.7
13	100	78.1	110	3.1	6.8
14	200	81.6	196	3.12	13.7
15	100	92.4	110	1.73	11.1
16	200	92.6	249	2.83	15.2

3.2.4 Significance of Water and Gas Flow Rate on PFOA Removal

In the first ANOVA analysis (see Table 8), neither the water flow rates (70-150 mL/min) nor the gas flow rates (0.5-1.5 sl/m) were significant factors in PFOA removal. That said, water and gas flow rates needed to be in balance for the experiments to succeed. If, for example, the water flow rate was too high (>150 mL/min) and the gas flow rate was too low (<0.5 sl/m), then the plasma discharge would be unstable. In preliminary experiments, water flow rates were set from between 50 mL/min to 200 mL/min and gas flow rates were set from 0 sl/m to 5 sl/m. These exploratory experiments helped clarify the balance of both flow rate parameters for optimal plasma discharge.

Base on the ANOVA analysis conducted for argon, it was concluded that the gas flow rate (C) with a p-value of 0.0029 is a significant model term (Table 11). In contrast, the ANOVA analysis suggests that water flow rate is not a significant factor in the PFOA degradation process. This difference in the impact of the gas type may be due to properties of the argon in the plasma discharge. Argon is a noble gas and so is inert.

Air is reactive and may oxidize the radical chemical species believed to be responsible for PFOA degradation.

Table 11. ANOVA Analysis for Impact of Gas Flow Rate of Argon

Source	Sum of Squares	df	Mean Square	F-value	P-Value	
Model	0.0046	4	0.0011	21.61	0.015	
A-Conductivity	0.0002	1	0.0002	3.06	0.1784	
B-Water Flow Rate	0.0001	1	0.0001	2.16	0.238	
C-Gas Flow Rate	0.0043	1	0.0043	80.73	0.0029	Significant factor
D- Power	0	1	0	0.4863	0.5358	
Residual	0.0002	3	0.0001			
Cor Total	0.0047	7				

3.3 PFOA Degradation and Defluorination

In this study, 90% of the PFOA was removed in 30 minutes reaching 93% removal in 60 minutes in the best case; the experimental apparatus was efficient in breaking the C-F bonds of PFOA as suggested by the release of F^-. These findings are consistent with the published literature; that is, plasma can degrade PFOA in 30 minutes. This study showed that the process implemented resulted in the same percentage PFOA removal as in other recent studies (see Table 12), but the extent of defluorination was significantly greater.

Most of the PFOA was removed within 30 min of treatment, with only 3% removal occurring between 30 and 60 min. Comparing the CFLPPD reactor with other plasma treatment technologies, the CFLPPD removes only slightly more PFOA from water. The highest level of PFOA removal observed was 93.43% with argon and 82.63% with air. Argon gas in combination with the configuration of our plasma reactor was clearly more effective in breaking the C-F bonds of PFOA.

Table 12. Comparison of PFOA Removal in the CFLPPD Compared to Other Plasma Treatment Systems

Reactor Type	Initial [PFOA] (mg/L)	Time (min)	Gas Type	Removal	Defluorination	Reference
CFLPPD	9.5	60	Argon	93%	63.7%	This study
Laminar jet with bubbling	0.02	30	Argon	90%	27%	Stratton et al. (100)
Batch with ground electrons	8.3	120	Argon	90%	58%	Singh et al. (10)
Nanosecond pulsed gas liquid flow	50	120	Argon	90%	3.6%	Bulusu et al. (101)
CFLPPD	9.5	60	Air	82%	49.1%	This study
Atmospheric plasma	0.00058	7	Oxygen	90%	5.5%	Jovicic et al. (102)
Gliding arc plasma	70	60	Air	90%	25%	Lewis et al. (103)

The release of fluoride (F^-) and other fluorine-containing intermediates, (as discussed in detail in section 3.3.1) suggests that the C-F bonds of PFOA are being broken during the treatment process. The main end products of PFOA degradation are F^- ions, which formed after one minute of treatment and continued to increase in concentration over 60 min. The fluoride data in Table 13 shows that the greatest amount of defluorination of PFOA was 63.7% with argon, but only 49% with air. It is noteworthy that the extent of defluorination was greater in this study than others cited in Table 12.

Table 13. Defluorination with Argon
(All units in mg/L)

min	F in PFOA	F^-	F^- in degraded PFCAs	F^- in other products	% Defluorination
0	6.539	0	0.000	0.000	0.0%
15	3.593	2.547	0.125	0.274	38.9%
30	0.647	3.9	0.251	1.742	59.6%
45	0.538	4.055	0.291	1.655	62.0%
60	0.430	4.167	0.331	1.611	63.7%

Figure 10 shows the mass balance of fluorine in the plasma reactor. The total mass of fluorine was determined by calculating the amount of organically-bound fluorine (F) in PFOA and free fluoride ions (F⁻) in solution. The mass of organically-bound fluorine was calculated based on the concentration of PFOA added to the reactor and an estimation of the F in the identified and anticipated intermediate byproducts. The results showed that the fluorine concentration in PFOA decreased as fluoride ion release increased with treatment time. Figure 11 plots data from Run # 9 which showed the highest rate of PFOA removal. Of the PFOA that was added to the reactor (total F = 6.54 mg/L), the four intermediate byproducts identified by LC-MS analysis accounted for only 5% of the original fluorine. Free fluorine measured by ion chromatography accounted for about 70% of the balance. These data indicate that there is another 25% of F that is not accounted for as either F⁻ or in PFOA intermediates.

The missing F⁻ in the mass balance may be due to the gas-phase conversion. For, these experiments, gas samples were not analyzed. There is limited information on how to test gas-samples after the treatment, but there is an expectation that some of the PFOA may be released as fluorine gas.
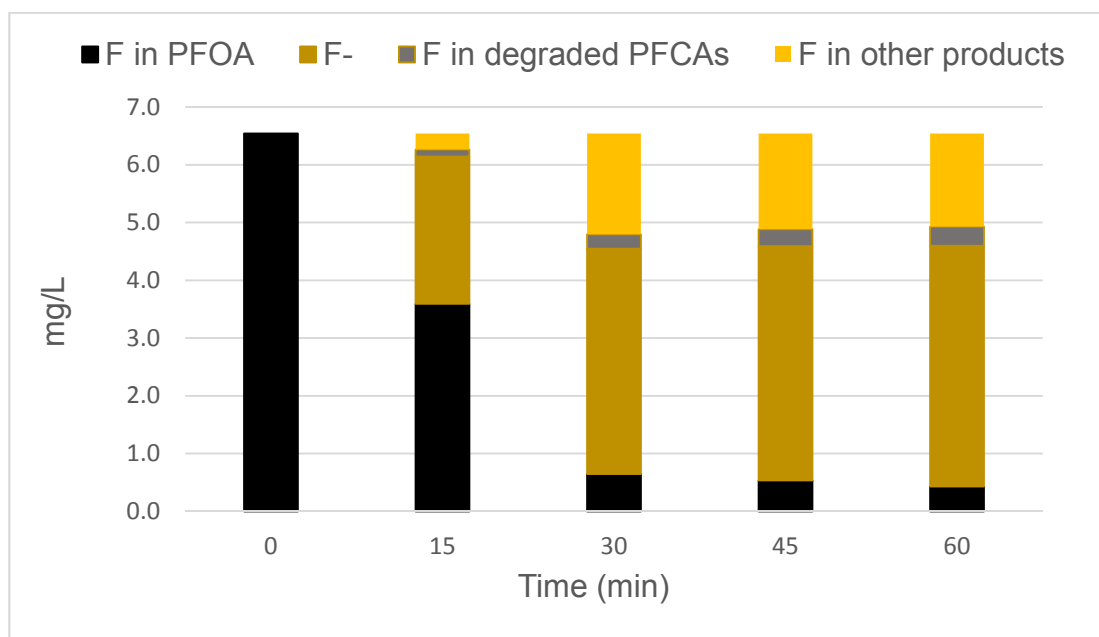

Figure 10. Fluorine Mass Balance
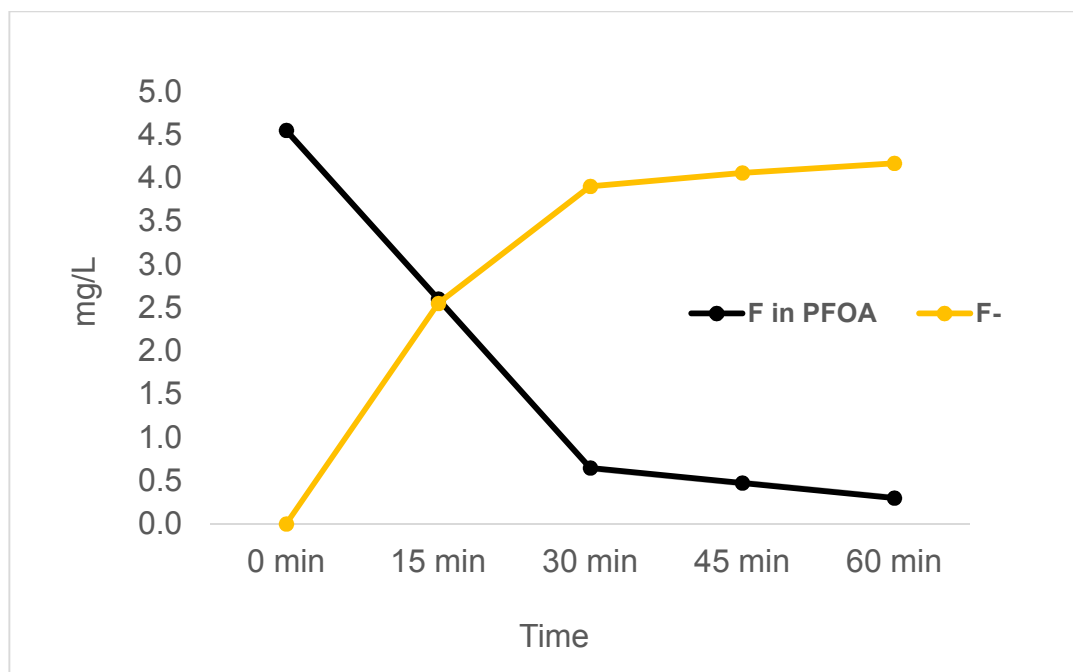
Figure 11. PFOA Degradation and F^- Formation (data from run # 9)

3.3.1 Byproducts of PFOA Degradation

In previous studies, researchers have reported the presence of shorter-chain PFAS during the plasma treatment process. Perfluoroheptanoic acid (PFHpA), perfluorohexanoic acid (PFHxA), perfluoropentanoic acid (PFPeA), and perfluorobutanoic acid (PFBA) are common intermediates of PFOA degradation (10,16,103). The presence of these compounds is an indicator of the breakage of the C-F bond (98). Figure 11.shows that PFOA decreases as CF_2-forming short-chain PFAS are released. The concentrations of these short-chain intermediates increased with increasing reaction time (Figure 12).

Figure 13 shows the expected order of the byproducts formed during treatment; they are as follows: PFHpA ($C_7HF_{13}O_2$) > PFHxA ($C_6HF_{11}O_2$) > PFPeA ($C_5HF_9O_2$) > PFBA ($C_4HF_7O_2$). Other byproducts were not quantified, but there is a possibility of the formation of even shorter-chain PFAS.

Figure 12. Release of Fluoride (F-) and Formation of Byproducts during Treatment.
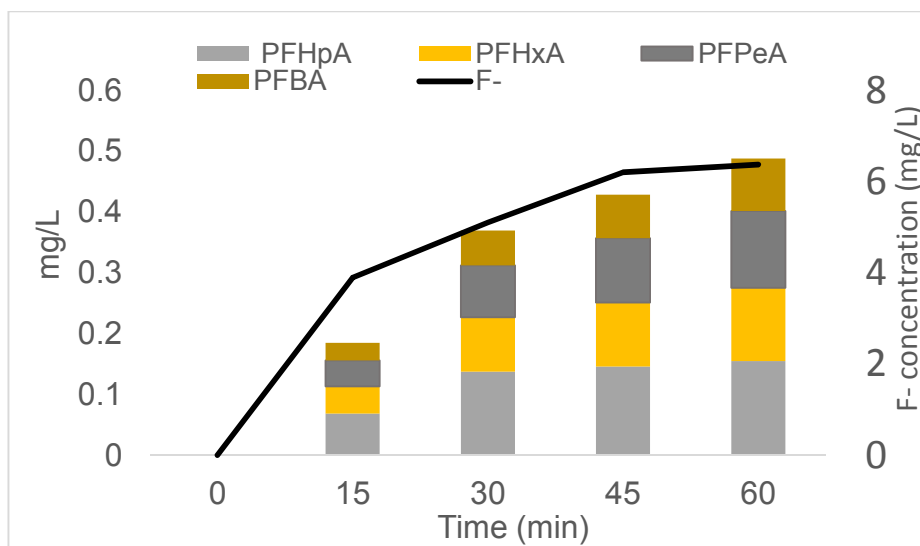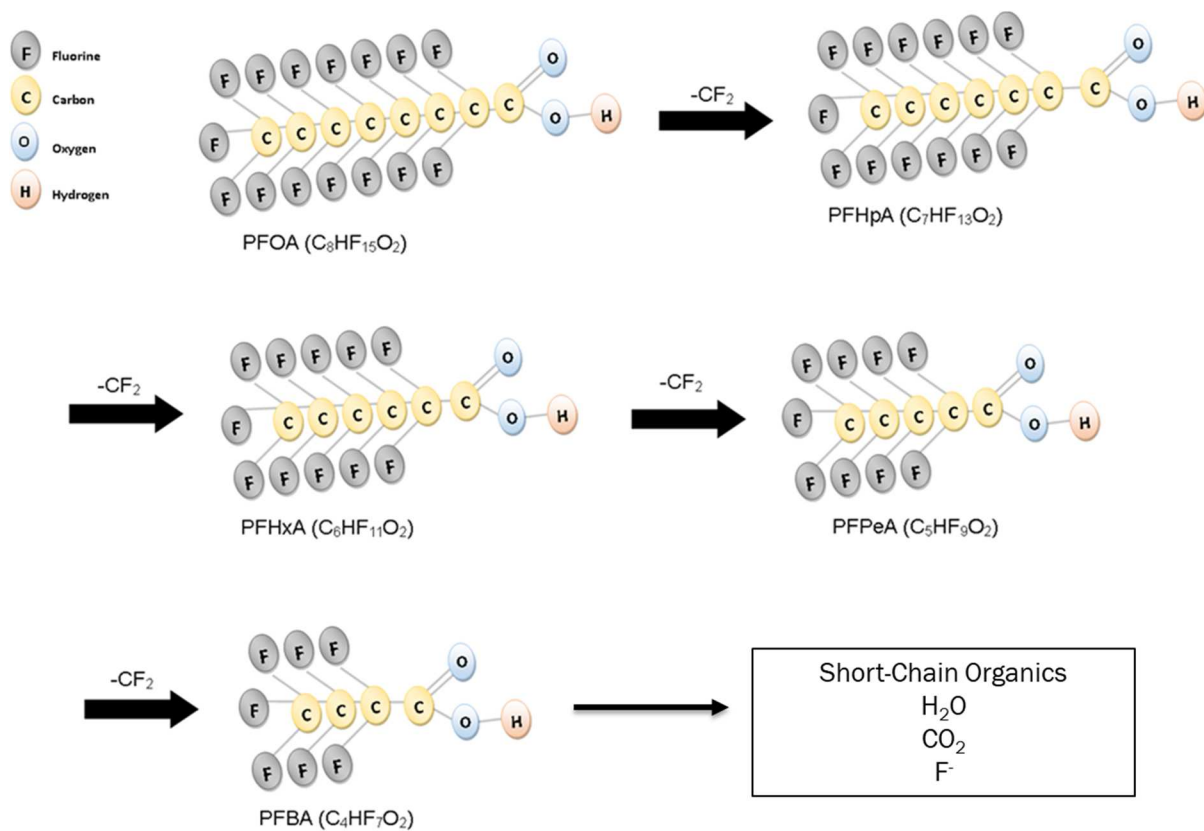

Figure 13. Possible PFOA degradation pathways

Table 14 shows the information utilized for the byproducts calculation using the initial concentration of PFOA (9.5 mg/L) and the molecular weight of fluorine (19 g/mol). The C-F bond of PFOA would break first and form C_7F_{15} and COO^-. Then the C_7F_{15} would be immediately hydrolyzed and converted into C_6F_{13} and F^- ion. The intermediate C_6F_{13} would degrade into a variety of perfluorinated carboxylic acids as shown in Figure 13.

PFOA shows a rapid release of F^- ions during the first 15 minutes of plasma treatment in our reactor. These results indicate substantial mineralization of the PFOA and its byproducts. By comparing the released amount of these identified byproducts, their total concentration ranged from 0.369 mg/L (at 30 min) to 0.488 mg/L (at 60 min), accounting for 25% of the total F (0.331 mg/L) present at the end of the experiment. Additional study is required to understand the complete array of byproducts generated, especially those in the gas phase.

Table 14. Concentration of Intermediate Byproducts Formed (mg/L)

TIme (min)	PFOA	F^-	PFHpA	PFHxA	PFPeA	PFBA	OTHER
0	9.5	0	0	0	0	0	0
15	5.220	3.895	0.069	0.045	0.043	0.029	0.200
30	0.940	5.100	0.137	0.089	0.085	0.057	3.091
45	0.782	6.201	0.146	0.105	0.106	0.072	2.088
60	0.624	6.372	0.155	0.120	0.126	0.086	2.016

3.4 Miscellaneous Experimental Observations

In this study, tap water was used instead of DI water was because it is a poor conductor of electricity. When DI water was used the plasma discharge was low and unstable. In every experimental run, it was observed that the water in the reaction vessel evaporated due to high temperatures and when air was the carrier gas, it produced detectable levels of ozone. During the experiment process, the production of reactive species in the liquid phase -- like hydrogen peroxide (H_2O_2), nitrate (NO_3^-), and chloride (Cl^-) -- were analyzed because they may be responsible for the oxidation

of PFOA (Table 15). Also, pH was measured for assure water quality and to understand the PFOA solubility in water. The pH did not affect the PFOA removal results, however, it does affect PFOA solubility in water The solubility of PFOA in water is higher at pH values greater than 7.5. The pH value of the PFOA solution with argon and air as carrier gases, increases during the plasma treatment process. The initial pH value with argon was 6.22; the end value was pH 9.58. The initial pH value with air was 6.84, the end value was pH 9.37. The pH results are summarized in Table 16.

Table 15. Cl^-, H_2O_2 and NO_3^- Formation after 60 min

Run	Cl^-	NO_3^-	H_2O_2
1	616.6	43.4	0.06
2	15.2	185.4	1.32
3	669.4	144.4	0.46
4	595.1	2.0	1.56
5	16.3	2.3	3.0
6	15.0	95.3	0.25
7	16.3	2.4	1.65
8	15.3	195.3	1.94
9	760.6	2.0	1.15
10	15.9	2.2	1.78
11	615.5	7.6	0
12	679.1	2.3	0.27
13	640.3	5.3	0.06
14	18.2	298.5	1.2
15	630.4	1.9	2.0
16	22.5	2.3	1.92

Table 16. pH Readings

Run #	Gas type	PFOA Removal %	Time / Reading (min)				
			0	15	30	45	60
1	Air	77.6%	7.46	8.64	8.75	9.5	9.13
2	Air	80.2%	6.97	7.04	7.94	2.11	6.66
3	Air	70.0%	7.77	8.28	8.67	8.94	8.4
4	Argon	87.4%	7.95	7.69	8.47	6.53	8.58
5	Argon	93.4%	7.06	8.6	8.93	9.25	9.19
6	Air	80.2%	7.49	7.88	2.53	8.63	9.28
7	Argon	89.9%	6.93	6.57	8.83	9.19	9.4
8	Air	82.6%	6.84	7.97	7.84	9.02	8.85
9	Argon	93.4%	7.32	8.08	9.16	9.17	9.43
10	Argon	88.6%	7.39	7.5	8.55	8.95	9.58
11	Air	76.5%	7.93	8.7	8.74	8.96	9.27
12	Argon	87.4%	7.38	8.48	9.1	9.14	9.46
13	Air	78.1%	7.87	8.54	8.84	9.14	9.37
14	Air	81.5%	7.27	7.6	6.53	5.81	8.7
15	Argon	92.4%	7.19	8.62	9.03	9.12	9.43
16	Argon	92.6%	6.22	5.69	8.55	8.78	3.14

Chapter 4:   CONCLUSIONS & FUTURE RESEARCH

4.1   Conclusion

Given the long history of their development and widespread use, it is often assumed that chemicals like PFAS are well standardized and their usage in consumer products is safe for both the environment and human health. In spite of recent initiatives and health advisories that has been set to reduce their omnipresence, the current processes for removing PFAS from water are either inefficient or prohibitively expensive. There is good data about the bioaccumulation of these substances and information about sites that are contaminated worldwide, which has caused awareness and concerns on how to reduce exposure. Currently, PFAS can be found in food, household products, raw water sources, soils, and other areas. Researchers at the University of Notre Dame have just published the results of a study in *Environmental Science and Technology* in which they report that half of the 230 cosmetics they analyzed contain fluorine, an indicator of the presence PFAS. Notably, some of the highest levels of PFAS were found in waterproof mascaras and long-lasting lipsticks (111).

PFAS enter the environment mainly by disposal of wastes in landfills that are contaminated with these chemicals; this is the pathway whereby they enter raw water sources. PFAS contamination of agricultural soils is also common, exposing humans, animals, and other organisms. Continued research is needed on the toxicology of these chemicals. Conventional technologies are not sufficient for the remediation of PFAS. Even adsorption and filtration technologies do not degrade PFAS. But the chemicals are still remaining on the membranes, and the disposal process is expensive and unsustainable. Various electrochemical technologies can help to degrade PFAS, but because of their innate stability, removal efficiency is low. Recent research has suggested that plasma discharge technologies may be more effective than other available treatment technologies in removing PFOA from water.

This thesis research had three specific objectives:

1. **Design and construct the CFLPPD treatment system and identify operational parameters that may affect PFOA removal.**

   - This objective was met.

   - The CFLPPD was configured and successfully operated in a series of 16 subsequent experiments designed to evaluate the removal of PFOA from water.

   - Five operational parameters were identified as potentially influencing PFOA degradation in water: conductivity, water flow rate, gas type, gas flow rate, and power.

   - The CFLPPD reactor was tested to determine the appropriate ranges for each of the five operating parameters.

2. **Using a two level, partial factorial design, evaluate the CFLPPD operational parameters for their significance in affecting PFOA degradation in water and assess PFOA removal rates.**

   - This objective was met.

   - The software produced a series of 16 experiments with randomized parameter combinations.

   - ANOVA analysis indicated that only gas type (argon or air) was significant in affecting the extent of PFOA degradation in water. The removal of PFOA was greater when argon was the carrier gas (up to 93% in 60 min for argon and up to 82% for air in 60 min). The overall amount of PFOA removal was also greater with argon.

   - While the PFOA removal results are consistent with other studies, the amount of defluorination measured in the experiments was significantly greater.

3. **Identify the PFOA degradation pathway.**

   - This objective was met.

   - The mass balance calculations suggest that PFOA undergoes initial C-F bond breakage. Once the C-F bonds are broken, fluoride (F^-) is released and PFOA is transformed into shorter-chain PFAS, some of which were identified.

   - About 25% of the F^- was not accounted for in the fluorine mass balance. But based on the literature, it may be present as fluorine gas (and so cannot be easily quantified) or in various of PFAS intermediates that we were not able to detect/identify. Some PFAS may have also absorbed to tubing or other reactor parts.

The main question in this study was whether or not and to what extent the CFLPPD reactor can break the C-F bond and remove high concentrations of PFOA from water. The study using argon gas and all five high parameters suggest that this process can remediate PFOA and other PFAS compounds in water. As mentioned in other studies, oxidative chemical species account for PFAS degradation and were detected in our reactor (e.g., H_2O_2, Cl^-, NO_3^-). In summary, the results from this study are generally consistent with previous studies of PFOA removal from water. The CFLPPD reactor is a flexible and distinctive design that can be run in both batch and continuous operation modes.

4.2   Future Research

There is a great deal of work that needs to be done to optimize operation of the plasma process and to better understand the PFOA degradation pathway. For example, gas-phase testing would greatly improve our understanding of mechanisms involved in PFOA degradation since PFOA is volatile and fluorine gas may be released during degradation. There is good reason to hypothesize that some of the 'missing' F in the mass calculations is due to the formation of fluorine gas. Likewise, the production of ozone and other oxidizing molecules (e.g., Cl^- H_2O_2, NO_3^-) also requires attention and may be critical to a more detailed understanding of how PFAS is removed from water during plasma treatment.

There is a lack of data on the toxicology of PFAS, which will be needed in order to better understand the risks of PFAS exposure, both to humans and other organisms. The U.S. and other nations also need to develop regulations to monitor PFAS in the environment, enact laws to restrict their manufacture and use, and develop protocols for their safe disposal.

As part of the conclusion, suture work recommendation was made:

- To better elucidate the PFOA pathway, experiments need to collect samples on a finer time scale to analyze for the short-chain PFAS

- More analysis on the formation and role of radical species (e.g., ozone and hydrogen peroxide) that are formed during the plasma reaction needs to be done.

- Analysis of the gas phase of the reactor needs to be conducted in order to achieve a better Flourine mass balance.

- The U.S. and other countries need to develop regulations to monitor PFAS in the environment, possibly enact laws to restrict their manufacture and use, and develop protocols for their safe disposal

- More research must be done on the toxicology of PFAS exposure in order to better understand risks to humans and other organisms; only this information can establish safe limits of exposure.

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