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Removal of PFOA from Water Using UV Treatment, Chemical Oxidation, & Adsorption by Activated Carbon & Zeolites

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Removal of PFOA from Water Using UV Treatment, Chemical Oxidation, & Adsorption by Activated Carbon & Zeolites

Major Qualifying Project completed in partial fulfillment
Of the degree requirements at
Worcester Polytechnic Institute, Worcester, MA

Submitted by:

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Professors John Bergendahl , Nikolaos Kazantzis, and Robert Krueger, faculty advisors

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Abstract

The objective of this project was to evaluate the removal of perfluorooctanoic acid (PFOA) from water through various oxidation and adsorption treatment methods. PFOA is a fluorosurfactant and is found in many firefighting foams. Even though the manufacture of PFOA has declined over the past few years due to its persistence in water and toxicity, there are still traces of PFOA in numerous water bodies. Treatment by chemical oxidation was performed with dichromate, calcium hypochlorite, sodium persulfate, potassium permanganate, potassium ferrate, and UV light. Adsorption with granular activated carbon and zeolites was also attempted. None of the oxidation methods presented coherent results due to strong interference of the oxidant with the PFOA solution. Nonetheless, adsorption proved to be a successful and promising technique for removing PFOA from water as compared to oxidation techniques. All PFOA solutions were adjusted to pH of 7 through the dropwise addition of dilute base, NaOH. The most feasible solution for minimizing exposure of PFOA to humans is to implement an in-home activated carbon filter to remove PFOA in drinking water.

Acknowledgements

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Authorship

The research and writing presented in this paper was achieved through the collaboration of the authors in the manner outlined below. Each member of the team acknowledges responsibility for the entire report.

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Chapter 2 - Background: Introduction	Aakriti Bhakhri
Chapter 2 - Background: PFOA Chemistry	Thomas Finelli
Chapter 2 - Background: Environmental Impacts	Aakriti Bhakhri
Chapter 2 - Background: Chemical Oxidation	Thomas Finelli
Chapter 2 - Background: COD	Aakriti Bhakhri
Chapter 2 - Background: UV	Kashane Roberts
Chapter 2 - Background: Adsorption Methods	Zhixin Wang
Chapter 2 - Background: Adsorption Isotherms	Smita Kurrumchand
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Chapter 3 - Methodology: Standard Curve	Aakriti Bhakhri
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Chapter 3 - Methodology: Zeolites	Zhixin Wang
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Chapter 4 - Results & Discussion: Chemical Oxidation	Thomas Finelli
Chapter 4 - Results & Discussion: UV	Kashane Roberts
Chapter 4 - Results & Discussion: Activated Carbon	Zhixin Wang, Smita Kurrumchand
Chapter 4 - Results & Discussion: Zeolites	Smita Kurrumchand
Chapter 5 - Conclusions & Recommendations	Smita Kurrumchand
Chapter 6- Limiting Exposure of PFOA	Julie Bliss
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Chapter 1: Introduction

Technological advancement has enabled mankind to increasingly develop chemicals and other products while mostly keeping productivity, cost effectiveness and marketability in mind. However, environmental concern was more than often overlooked over the factors mentioned above. It was not until these chemicals started affecting the wellbeing of the human race as well as decreasing life expectancy that such trepidations were brought to attention. A common problem faced by human beings is the exposure to dissolved chemicals in their drinking water supply. Though many improvements have been achieved nowadays to ensure the distribution of clean and safe water to homes, much is left to be done to protect humans and the environment from harmful chemicals which are discharged into freshwater supplies.

Perfluorooctanoic acid (PFOA), created in 1947 by a chemical manufacturing company, 3M, is an example of such a detrimental chemical (3M Environmental Communications, 2012). "PFOA, also known as "C8", is a synthetic chemical and one of the perfluoroalkyl acids used to make fluoropolymers during the manufacture of a wide variety of products" (Encyclopedia of Earth, 2011). It is a surfactant and is chemically stable which renders it virtually indestructible when released in the environment. Surfactants or surface active agents are foaming agents that lessen the tension between two interacting surfaces, usually between a foreign medium and another in which they are dissolved (P&G, 2005). The properties mentioned above made PFOA an ideal and widely used chemical in the manufacture of fire resistant foam among other products which include Teflon and grease-resistant food wrapping.

"When PFOA was first used in manufacturing processes, in 1951, no statute required manufacturers of chemicals to submit information prior to marketing" (George Washington University School of Public Health and Heath Services, 2011). In 1961, after carrying out toxicity studies, DuPont scientists found potential health risks associated with exposure to PFOA. Further research revealed that PFOA remained persistent in the environment once it was released and that accumulation in human blood could cause serious health problems. Following this, workers directly exposed to the chemical at the industrial level were forced to wear protective clothing while female plant workers were forced to relocate from a facility in Washington after two children were born with birth defects in the early 1980's. The scientists additionally conducted experiments on drinking water supply in towns located close to a plant in West Virginia bordering the Ohio River. Even though traces of the compound were found in tap water in the tested locations, none of the data was reported to the Environmental Protection Agency, EPA. Animal testing conducted during

1980 to 1990 to test the adverse effects of PFOA on human beings showed that increased accumulation caused liver damage as well as tumors in pancreatic cells (George Washington University School of Public Health and Heath Services, 2011). Some researchers also directed their attention to the effects of PFOA in wildlife and surface water. Traces of the chemical were found in albatross birds' livers in the North Pacific as well as in water bodies such as the Mediterranean Sea, Pacific and Atlantic Ocean as shown in Table 1. The main source responsible for contaminating these aquatic bodies was associated with the discharge of municipal water in the ocean water (Encyclopedia of Earth, 2011).

Table 1: PFOA Concentrations in Oceanic Water and Offshore Coastal Seawater (Encyclopedia of Earth, 2011)

Location	PFOA (pg/L)
Tokyo Bay	1,800 - 192,000
Offshore of Japan	137 - 1,060
Coastal area of China	243 - 15,300
Western Pacific Ocean	136 -142
Central to Eastern Pacific Ocean (Surface)	15 - 62
Central to Eastern Pacific Ocean (Deep water, 4,000-4,400 m)	45 - 56
North Atlantic Ocean	160 - 338
Mid-Atlantic Ocean	100 - 439

It was not until the late 1990's that the EPA started publicly raising awareness against the use of PFOA. Initially, the EPA started investigating perfluorooctyl sulfonate (PFOS) in 1999 to later expand to PFOA compounds in 2000. However, the specific origin of these chemicals or their presence in human blood at small concentrations could not be explained. It was believed that there had to be other sources other than industrial plants responsible for the release of PFOA in the environment since certain case studies have demonstrated the presence of the chemical in residential areas where there were no plants nearby. By May 2000, the increasing health risks associated with the chemical caused 3M to stop manufacturing PFOA. Following these studies, the EPA started taking legal actions against DuPont for continuing the manufacture of the C-8 compound despite being aware of its health and environmental issues (George Washington University School of Public Health and Heath Services, 2011). "In April 2003, the EPA completed preliminary risk assessments on PFOA, and later that year took the first steps towards developing an enforceable consent agreement for PFOA and related fluoropolymers" (Encyclopedia of Earth, 2011). In an effort to encourage the decrease in use of PFOA, the organization also developed a program which aimed at eliminating PFOA use by 2015. Meanwhile in July 2006, "The Bureau of

Safe Drinking Water (BSDW)" conducted a study to determine the presence of PFOA in the water supply of the city of New Jersey (New Jersey Department of Environmental Protection – Bureau of Safe Drinking Water, 2007). Several such studies are increasingly being encouraged to detect the presence of PFOA in water bodies. Currently the EPA is also trying to find alternatives to the use of the PFOA or any similar chemicals (Environmental Protection Agency, 2010).

As of now, little work has been accomplished regarding the removal of PFOA from water. The major long-term goal of this project is to investigate the possible treatment methods that would be effective in the elimination of PFOA from water. This project was initiated after it was hypothesized that firefighting foams, which contain PFOA surfactant, was contaminating underground water. To accomplish this, the group addressed the following objectives:

- Investigated the different types of foams currently in use as well as their impacts on the environment
- Identified that firefighting foams are major sources of PFOA release into the environment
- Evaluated the common treatment methods used for the removal of dissolved chemicals from water on PFOA: activated carbon adsorption, chemical oxidation, UV treatment, and treatment with zeolites

The objectives mentioned above were accomplished by researching major case studies which account for the presence of PFOA in the environment and lay the basis on how much work has been done to accurately detect the presence of PFOA in those surroundings. The team then proceeded with a series of experimental analyses to determine which treatment methods would be most effective to remove PFOA from contaminated water. The data collected helped establish a start-up point which could be useful in the future to eliminate the presence of PFOA in tap water in various environments worldwide.

Chapter 2: Background

This chapter provides an overview of PFOA as a surfactant and contaminant. The case studies presented in this section allowed the determination of the fact that the use of firefighting foams could be a possible pathway through which PFOA reaches the environment. A detailed description of these foams and their environmental impacts are outlined in this background chapter. In addition, common treatment methods used in the industry were reserved in order to find an effective method for the removal of PFOA in water.

2.1 Properties of PFOA

PFOA is one of many perfluorinated surfactants. To be more specific, PFOA is a perfluorocarboxylic acid since it has a carboxyl group on one end. The prefix perfluoro- means that the hydrogen has been replaced with fluorine, causing it to be very stable. Figure 1 shows PFOA's structure. PFOA has been reported to have a pKa value of approximately -0.1 (Vecitis et al., 2009). As a result, PFOA is almost always found in its deprotonated form. The critical micelle concentration (cmc) of PFOA has been found to be between 8.7-10.5 mmol/L (Kissa, 2001). This study neither approached nor exceeded the minimum value for the range of the cmc. Some physical properties of PFOA include: a melting point of approximately 55°C, boiling point of 189°C, and density of 0.900 g/cm^3 (Sigma-Aldrich, 2012).

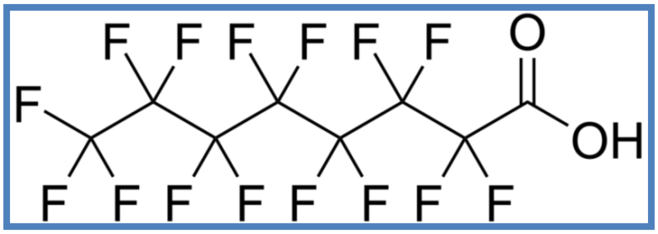


Figure 1: Structure of perfluorooctanoic acid (PFOA)

2.2 Case Studies

The following case studies testify for the presence of traces of perfluorinated surfactants which have been found in bodies of water and drinking water across the world. The studies helped to establish a possible explanation for the presence of PFOA in the environment.

2.2.1 Toronto Airport

On June 8, 2000, a fire alarm at L.B. Pearson International Airport in Toronto, Canada malfunctioned and accidentally released 22,000 L of firefighting foam and 450,000 L of water from the sprinkler system (Moody et al., 2001). The effluent containing perfluorinated surfactants discharged directly into nearby Moore's Creek and ultimately to Etobicoke and Spring Creeks which lead to Lake Ontario. 330-1650 kg of perfluorinated compounds were discharged and traveled about 15 km from the airport to Lake Ontario. In addition to rainwater, many storm water sewers in Mississauga, ON, empty into Etobicoke Creek, which increases the volume of water in Etobicoke Creek. Water levels and flow rates of Etobicoke Creek were monitored during the month of June to estimate the total volume of water in Etobicoke Creek. (Moody et al., 2001; Bhavsar, 2011)

Surface water samples were collected over a period of three weeks after the release. An additional round of samples was taken on November 8, 2000. Perfluoroalkanesulfonate (PFOS) and PFOA in surface water were analyzed by the LC/MS/MS and F NMR methods. Of the fifty-four surface water samples from Etobicoke Creek that were analyzed for PFOA by LC/MS/MS, concentrations ranged from non-detectable to 11.3 μg/L. Concentrations of PFOA were highest in surface water samples one day after the spill and decreased for the most part. After 20 days, there was a slight increase in concentration of PFOA. 153 days after the initial spill, concentrations of PFOA were still detectable up and down stream in Etobicoke Creek. Reasons for this detectability include possible releases of more firefighting chemicals, "sediment sorption/desorption, and/or hyporeic zone/bank storage and release" (Moody et al., 2001). PFOA concentrations in surface water by LC/MS/MS are displayed in Figure 2 below.

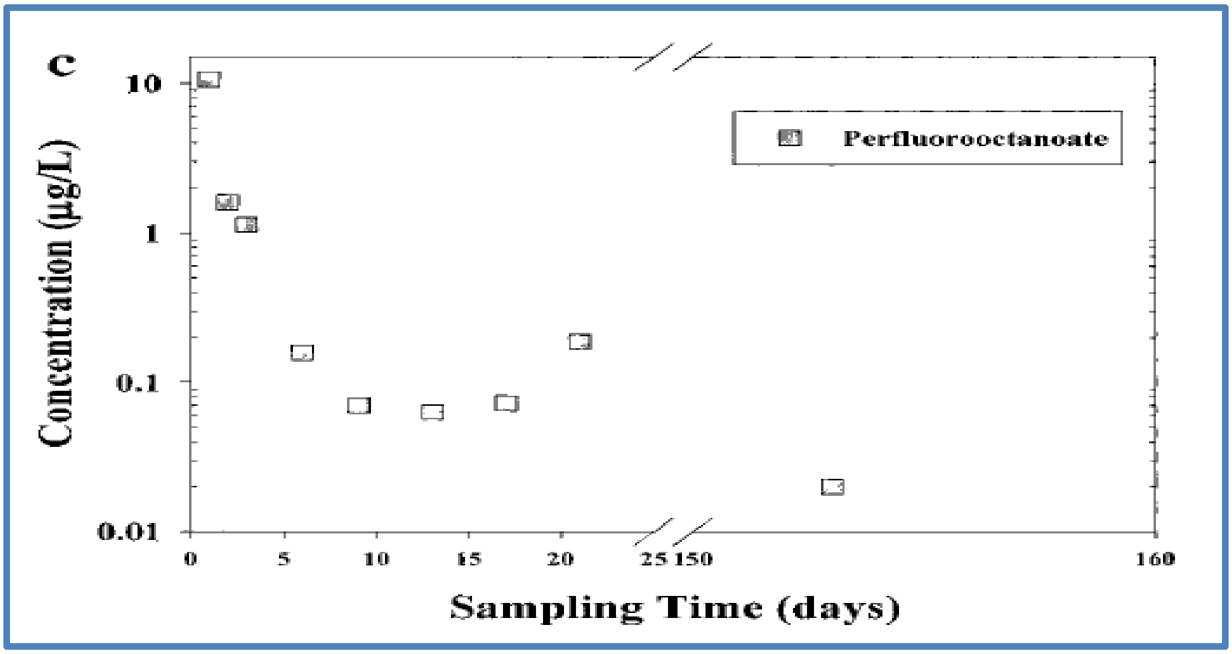
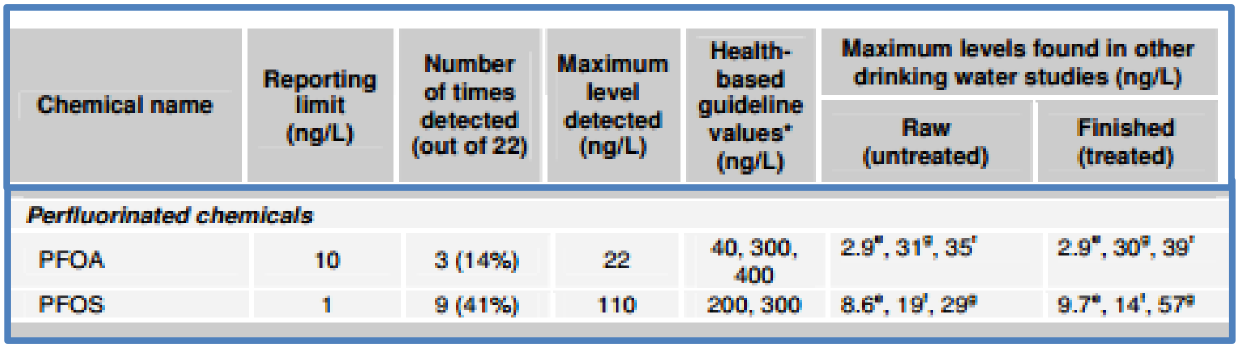


Figure 2: Concentration of PFOS vs. Sampling Time in Surface Water Samples from Etobicoke Creek by LC/MS/MS (Moody et al., 2001)

Of the samples analyzed by the F NMR method, PFOA concentrations ranged from non-detectable to 17,000 µg/L. PFOA was not detected in samples analyzed six days after the spill. Because of the non-quantifiable perfluorinated surfactants using the F NMR method and obscurity in the data, analysis was discontinued for this method. The authors conclude that it is unlikely that PFOA biodegrades and this leads to the issues of bioaccumulation of PFOA in the environment (Moody et al., 2001). There have been no cleanup efforts published in literature to date to remove PFOA from the surface waters of Toronto.

2.2.2 Hyannis, MA

In October 2009, Silent Spring Institute along with nine public drinking water utilities sampled and tested untreated water from twenty wells and two distribution systems on Cape Cod for emerging contaminants including PFOA. "Chemical analyses were performed at two commercial laboratories that have the analytical capabilities to measure these types of chemicals at the parts per trillion levels typically found in drinking water" (Schaider et al., 2010).Three out of the twenty two sites tested contained PFOA. The highest concentration of PFOA detected was 22 ng/L, which does not exceed health-based guidelines from EPA and multiple state guidelines, and is shown in Table 2 below.



Chemical name	Reporting limit (ng/L)	Number of times detected (out of 22)	Maximum level detected (ng/L)	Health-based guideline values* (ng/L)	Maximum levels found in other drinking water studies (ng/L)	
					Raw (untreated)	Finished (treated)
Perfluorinated chemicals						
PFOA	10	3 (14%)	22	40, 300, 400	2.9^e, 31^g, 35^f	2.9^e, 30^g, 39^f
PFOS	1	9 (41%)	110	200, 300	8.6^e, 19^f, 29^g	9.7^e, 14^f, 57^g

Table 2: Summary of Perfluorinated Chemicals in 20 Cape Cod Public Supply Wells and Two Distribution Systems (Schaider et al., 2010)

The three sites where PFOA was detected were all located in the Hyannis Water System at two wells which are located down gradient of Barnstable Municipal Airport and the Hyannis distribution system. Possible sources of contamination include materials from septic systems and discharges from Barnstable Municipal Airport. The study concluded that there is a need for a comprehensive strategy to protect Cape Cod's drinking water. (Schaider et al., 2010)

In 2010, Barnstable Municipal Airport prepared a plan to expand the airport to include a new terminal and other infrastructure additions/improvements. Local residents were concerned about the additions to the airport because they were concerned about an increase of discharges to local lakes and eventually groundwater plumes. The airport sits on a Sole Source Aquifer which "provides at least 50% of the Cape's public drinking water" (Breault, 2012). Also, numerous public water supply wells are located near the airport which supplies millions of gallons of water per day. There are two ponds located on the airport's property, Upper Gate Pond and Lewis Pond, which have received untreated storm water runoff for decades. The runoff into these ponds is permitted through EPA although storm water, surface water, and sediment quality from the ponds are low (Breault, 2012).

In August of 2010, Barnstable Municipal Airport and Horsley Whitten Group, Inc. prepared a master plan which addressed environmental considerations. The plan outlines mitigation techniques to improve water quality of various water bodies. Such mitigation techniques include storm water management, wastewater management, and hazardous waste management. One standard is providing water quality testing and treatment on site to remove at least 80% of total suspended solids load. This will be accomplished by pretreatment including deep sump catch basins, oil/grit separator, proprietary separators, sediment fore bays, and vegetated filter strips. Treatment will be accomplished using methods such as filtering bio-retention areas, proprietary media filters, sand filters, and organic filters. Infiltration practices can include bio-retention, infiltration basins, infiltration trenches, and subsurface structures (Breault, 2012). The Silent Spring study states that "treatment of water from these two wells effectively reduces the levels of regulated contaminants, but it is not effective for chemicals with low volatility, such as PFOS and PFOA" (Schaider et al., 2010).

Since the implementation of this master plan, levels of PFOA have decreased the Barnstable Municipal Airport area. In a study conducted by Silent Spring in November of 2011, PFOA was tested in twenty wells and was found at very low levels in samples (3-7 ng/L). This is a significant decrease from the 2009 study. Silent Spring opted to not include PFOA as a detected chemical in the 2011 report (Schaider et al., 2011).

2.3 Firefighting foams

Firefighting foams are foams that are used to suppress fire by blocking air supply to the fire causing fuel. These foams are a stable mass of bubbles and have a density lower than that of water and of most flammable liquids (Kidde Fire, 2011). Firefighting foam was invented in 1902 by Russian scientist, Aleksander Loran, while trying to develop a method of combating wide scale fires caused by oil (Fowler, 2011). The foam Loran developed was chemical foam, consisting of a mixture of sodium bicarbonate and aluminum sulfate in addition to small amounts of stabilizing agents. Chemical foams are, however, considered obsolete today since a number of chemicals are required to produce the foam. The most commonly used foam nowadays is mechanical foam and it is produced through the agitation of a mixture of foam components. Firefighting foams consist of three main components: water, solvents, and surfactants. Additionally, corrosion inhibitors and preservative dyes are added to further enhance the fire retardant action of these foams. The make-up and some major constituents of foams are shown below (Ruppert et al., 2011).

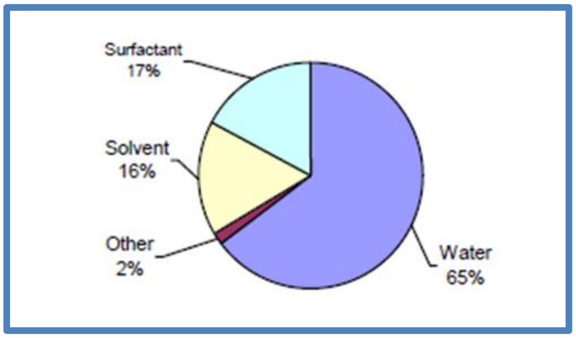


Figure 3: Average concentration of ingredients in firefighting foam concentrate (Ruppert et al., 2011)

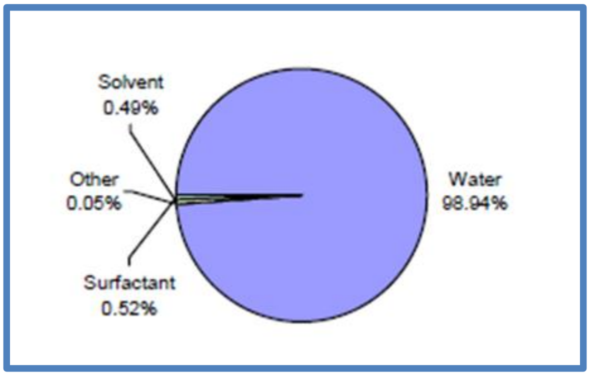
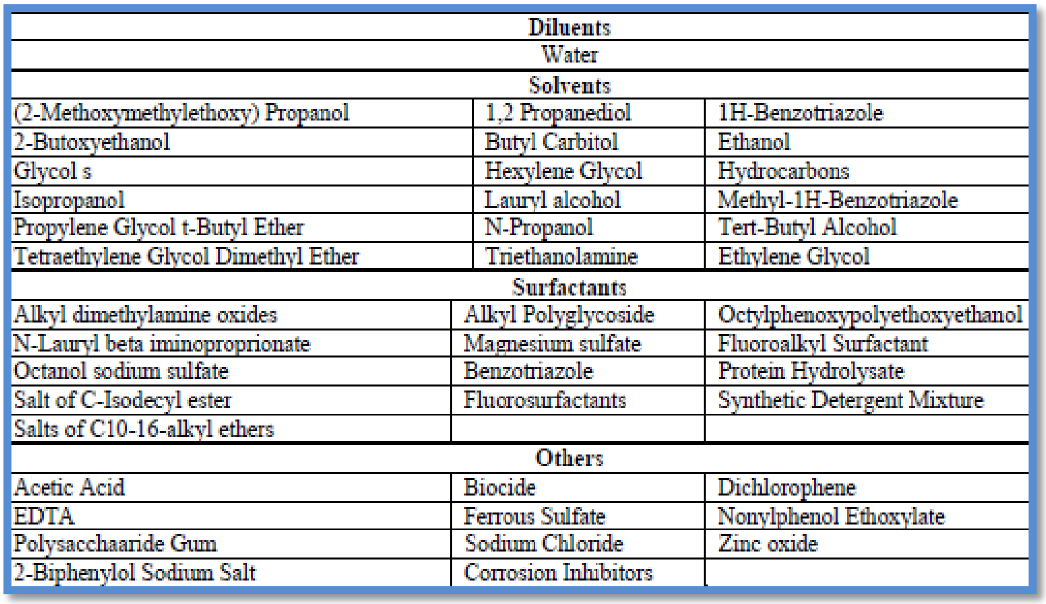


Figure 4: Average concentration of ingredients in firefighting foam solutions (Ruppert et al., 2011)

As can be seen from Figures 3 and 4, water comprises of 65% of the foam concentrate and 99.94% of the final foam solution (Ruppert et al., 2011). The surfactants constitute 17% of the concentrate and 0.52% of the foam solution. Solvents comprise 16% of the concentrate and 0.49% of the foam solution and the rest is comprised of corrosion inhibitors or chemicals like acetic acid, zinc oxide, EDTA, etc. which improve the overall performance of the foam. Some common ingredients of firefighting foam are listed below (Ruppert et al., 2011).

Table 3: Common ingredients of firefighting foam (Ruppert et al., 2011)



Diluents		
Water		
Solvents		
(2-Methoxymethylethoxy) Propanol	1,2 Propanediol	1H-Benzotriazole
2-Butoxyethanol	Butyl Carbitol	Ethanol
Glycol s	Hexylene Glycol	Hydrocarbons
Isopropanol	Lauryl alcohol	Methyl-1H-Benzotriazole
Propylene Glycol t-Butyl Ether	N-Propanol	Tert-Butyl Alcohol
Tetraethylene Glycol Dimethyl Ether	Triethanolamine	Ethylene Glycol
Surfactants		
Alkyl dimethylamine oxides	Alkyl Polyglycoside	Octylphenoxypolyethoxyethanol
N-Lauryl beta iminoproprionate	Magnesium sulfate	Fluoroalkyl Surfactant
Octanol sodium sulfate	Benzotriazole	Protein Hydrolysate
Salt of C-Isodecyl ester	Fluorosurfactants	Synthetic Detergent Mixture
Salts of C10-16-alkyl ethers		
Others		
Acetic Acid	Biocide	Dichlorophene
EDTA	Ferrous Sulfate	Nonylphenol Ethoxylate
Polysacchaaride Gum	Sodium Chloride	Zinc oxide
2-Biphenylol Sodium Salt	Corrosion Inhibitors	

There are various different kinds of firefighting foams that are used in the industry today. The most common ones include protein foams, fluoroprotein foams, film forming fluoroprotein foams, aqueous film forming foams, alcohol resistant foams, and synthetic detergent foams (Kidde Fire, 2011). Protein foams have been extensively used in the market and were the first mechanical foams to be marketed. They are meant to be used on fires caused by hydrocarbon based fuels and are produced by the hydrolysis of granulated keratin protein. Fluorochemical protein foam is manufactured through the addition of fluorochemical surfactants to the regular protein foams. The addition of fluorochemical surfactants makes these surfactants stronger, more efficient, and capable of being used on hydrocarbons based fuels as well as certain oxygenated fuel additives. Film forming fluoroprotein foams are those fluoroprotein foams that are designed to form a film on the surface of the hydrocarbon once released onto the fire. Aqueous film forming foams (AFFFs) consist of synthetic foaming agents in addition to fluorochemical surfactants. Alcohol resistant –AFFF foams are produced by combining polysaccharide polymer with the fluorochemicals and synthetic detergents used in regular AFFFs. The polysaccharide polymer forms a tough membrane which helps in the separation of the foam from the fuel and thus prevents the destruction of the foam blanket.

Attention has been given to the environmental impact of surfactants used in the foams. While most foam manufactured today are claimed to be nontoxic and biodegradable, they may actually take a long time to biodegrade if at all and thus, pose toxicity threats to the aquatic life and human health for the duration that they are present in water non-degraded.

2.4 Environmental Impacts

"Foam is a dispersion of a gas in a liquid or solid separated by thin liquid films or lamellae. A pure liquid cannot foam unless a surface-active material is present. A gas bubble introduced below the surface of a pure liquid will burst immediately as soon as the liquid drains away" (Schilling & Zessner, 2011). In general, foam is made to be diluted with large quantities of water prior to its use as a firefighting agent. For this reason, it is easily washed away and ends up most frequently into water bodies such as aquifers, lakes or rivers or any other type of aquatic environment (Kidde Fire, 2011).

Firefighting foams in essence, combat fire by the use of chemical retardants. There are two types of retardants: short term retardants and long term retardants. By definition, short term retardants are those that do not have long lasting effectiveness when used to extinguish fires. They do not reduce the combustion once the diluent, which is water, has evaporated. Long term retardants are more effective since they have the ability to form a barrier after evaporation of water (Barreiro, 2010). These long term retardants usually consist of a mixture of surfactants, foam stabilizers, wetting agents and solvents. When these foams are used in natural areas, the retardants or fluorinated surfactants seep into the ground, making the water toxic and eventually harm the aquatic ecosystem as well as terrestrial vegetation.

Microorganisms present in soil are responsible for controlling the sustainability of soil ecosystems through the decomposition of organic matter present in the soil (Barreiro, 2010). Due to the increasing use of firefighting foam, there is a rising concern on the effect of the chemicals on the microorganisms present in soil. Microbial community-based measurements can be potentially useful for detecting changes in soil quality due to the application of firefighting chemicals and therefore to evaluate the environmental compatibility of these compounds (Barreiro, 2010). However, not much research that has been conducted to determine the short and long term effects of fire retardants on the soil ecosystem.

A study published in August 2010 investigated the effects of firefighting chemicals on forest ecosystems (Barreiro, 2010). The experimental analysis involved taking soil samples from a certain forested area in Spain and conducting varied tests pertaining to microbial activity. The results of the study were largely inconclusive about the effect of firefighting chemicals on soil degradation. As far as short term consequences are concerned, there were almost no negative impacts recorded on microbial activity. But, the long term exposure of the chemicals to soil did affect the microbial population and precautionary use of such firefighting chemicals in the soil was recommended.

Foam is mostly diluted with large amounts of water before being used. For this particular reason, most of the foam gets washed away in water bodies and is most likely to end up in rivers and lakes and other types of fresh water bodies (Schilling & Zessner, 2011). "The formation of stable foam which reduces oxygen transfer, decreases the quality of the effluent and therefore increases maintenance costs, is a widely observed phenomenon in wastewater treatment plants and was first noted in 1969" (Schilling & Zessner, 2011). A study conducted by J. Heard in 2008 showed that bacteria present in wastewater in waste water treatment plants presents a direct cause to the foaming in wastewater systems. However, they also found that foaming does not physically occur if there are no surfactants in the water (Heard, 2008).

Surfactants are known to have caused considerable damage to waste water treatment plants. "In April 1991, fire water run-off containing AR-AFFF from an internal floating roof tank fire in the USA disrupted a refinery's waste water treatment plant" (Kidde Fire, 2011). The main cause of this was due to the fact that certain commonly used surfactants such as the AFFF and alcohol resistant-AFFF have been hypothesized as toxic hydrocarbon carriers. The use of oil separators is growing greatly in wastewater treatment facilities to decrease the hydrocarbon content of fire water that has been exposed to oil and other hydrocarbons. The presence of the detergents and surfactants that come from firefighting foam acts as an emulsifying agent between oil droplets and the water being treated at the plant. The oils are transformed to small droplets and do not get sieved out of the water and eventually they find their way in freshwater bodies. Thus, these treatment plants also act as a pathway to transfer surfactants to freshwater bodies.

2.5 Perfluorinated Surfactants

Information on the treatment of perfluorinated surfactants is limited. However, past research efforts have shown some successes in terms of removal of perfluorinated surfactants from aqueous streams. A large extent of these efforts were focused on the more sophisticated and costly treatment methods, including reverse osmosis membrane separation (Tang, Fu et al. 2006), sonochemical decomposition (Moriwaki et al., 2005), and reduction with zero-valent iron in subcritical water (Hori et al., 2006). However, there are substantial technical and economic barriers for implementation in real life scenarios. In this section, attention will be focused on the investigations of the less sophisticated and costly treatment technologies, namely, adsorption and advanced oxidation.

2.5.1 Chemical Stability

Fluorinated surfactants in general are very chemical resistant, and PFOA is not an exception. The chemical resistance of PFOA is primarily due to the presence of fluorine. The following factors have been attributed to fluorine's chemical properties in organics: it is highly electronegative, it has three nonbinding electron pairs, and its 2s and 3p orbitals are complementary to elements of the second period, which includes carbon. Additionally, elemental fluorine has high ionization energy (Equation 1) and a high electron affinity (Equation 2), both of which are thought to contribute to the stability of perfluorinated surfactants. PFOA contains numerous covalent C-F bonds, which is one of the strongest covalent bonds. In contrast, C-H bonds are weaker than C-F bonds which are illustrated by the comparison of bond dissociation energies: C_2H_5–H of 101 kcal/mol vs. C_2F_5–F of 127 kcal/mol, and CH_3–CH_3 of 89 kcal/mol vs. CF_3–CF_3 of 99 kcal/mol (Vecitis et al., 2009). Additionally, as the degree of substitution of hydrogen atoms for fluorine atoms increases, the bond strength increases. This can be illustrated by the heats of formation: CH_3F 449 kJ/mol., CH_2F_2, 459 kJ/mol, CHF_3 480 kJ/mol, and CF_4 486 kJ/mol. Another factor that affects PFOA's stability is the absence of steric hindrance from the fluorine, which causes a shielding effect. The lack of hindrance is due to fluorine's small covalent atomic radius of 0.72 Å. The reduction potential of fluorine (Equation 3) is quite high, which is similar to many oxidizing agents. A small difference in the reduction potential between two species indicates low chances of redox reactions occurring. The sum of all these effects explains PFOA's exceptional chemical stability. (Kissa, 2001)

Ionization Energy	$F \rightarrow F^+ + e^-$	401.5 kcal/mol	(Equation 1)
Electron Affinity	$F + e^- \rightarrow F^-$	83.5 kcal	(Equation 2)
Reduction Potential	$F_2 + 2e^- \rightarrow 2F^-$	$E^0 = 2.87\ V$	(Equation 3)

2.5.2 Treatment of Perfluorinated Surfactants

In more recent years, research efforts were shown on using activated carbon and zeolites for the removal of perfluorinated surfactants. The earliest of such efforts were published in 2002 where the adsorption of perfluoroalkyl carboxybetain onto powdered activated carbon was conducted (Pabon & Corpart, 2002). Acticarbon® ENO, with a medium pore size ranging from 30 to 100 Å, was used to adsorb perfluoroalkyl carboxybetain, whose molecular length of 18 Å. Results showed that, with 250 ppm of activated carbon, more than 98% of the perfluoroalkyl carboxybetain was adsorbed. With 1000 ppm of activated carbon, almost 100% of perfluoroalkyl carboxybetain was adsorbed. The concentration of fluorinated surfactants in water after activated carbon treatment was below 1.5 ppm.

A surge of interest in the adsorption treatment of perfluorinated surfactants occurred beginning in 2008, when a series of papers were published detailing the isotherm studies of the adsorption of perfluorinated surfactants onto powdered activated carbon, granular activated carbon and zeolites, notably Ochoa-Herrera et al in 2008, Yu et al in 2008, and Yu et al in 2011.

In the 2008 Yu et al study, commercial granular and powdered activated carbon, with micro pore areas of 313 m^2 g^{-1} and 466 m^2 g^{-1} respectively and effective sizes of 0.9-1.0 mm and <0.1 mm respectively, were used as adsorbents for PFOA. Sorption capacities of 0.37 mmol g^{-1} and 0.67 mmol g^{-1} were observed using granular activated carbon and powdered activated carbon, respectively. Such difference in sorption capacities was attributed to the differences in surface areas available for adsorptive uptake between granular and powdered activated carbon. In the 2008 Ochoa-Herrera et al study, comparable results were obtained using Calgon F400 granular activated carbon, which exhibits an effective size of 0.55-0.75 mm, to adsorb PFOA. Adsorption capacity of 0.27 mmol g^{-1} was observed.

Ochoa-Herrera et al. (2008) also investigated the ability of zeolites to adsorb a perfluorinated surfactant similar to PFOA, perfluorooctanesulfonic acid (PFOS). Zeolites 13X, NaY, and NaY80 were used. NaY and NaY80 have surface areas of 700 m^2 g^{-1} and 800 m^2 g^{-1}. NaY80 adsorbed PFOS strongly, with an adsorption capacity of 0.28 mmol g^{-1}. However, 13X and NaY showed weak adsorption capacity for PFOS; 13X showed a small adsorption capacity of 0.03 mmol g^{-1}, and adsorption effect was almost insignificant using NaY.

The 2011 Yu et al. study demonstrated a more sophisticated investigation of the adsorption of perfluorinated surfactants onto powdered activated carbon with the presence of effluent organic matter at an environmentally relevant concentration range. The powdered activated carbon used has a surface area of 764 m^2 g^{-1} and a pore diameter of 12.7 Å. The effluent organic matter was collected from the mixed liquor of a laboratory-scale membrane bioreactor. Sorption capacity of 0.2042 (μg/mg)(L/μg)1/n was observed when effluent organic matter was present, compared to sorption capacity of 10.03 (μg/mg)(L/μg)1/n without the presence of the effluent organic matter. The study confirms an earlier concern by Baudequin et al 2011 that, since the highly porous activated carbon exhibits high sensitivity to other types of polymers and proteins present in firefighting water, the treatment efficiency could be a lot lower in real-life scenario when compared to in laboratory scale where only fluorinated surfactants are present in the tested firefighting water.

2.6 Common Treatment Techniques

2.6.1 Ultraviolet Photodegradation

Ultraviolet (UV) light is described as electromagnetic radiation between x-ray and visible light, with wavelengths ranging from about 100 nm to 400 nm. UV radiation is separated into four groups based on its wavelength range; this is summarized in the figure below. Radiation with wavelengths below 320 nm are said to be actinic, because of their ability to induce photoreactions. Wavelengths ranging from 200 to 320 nm are termed as germicidal (Baruth, 2005; Kowalski, 2009; Vecitis et al., 2009).

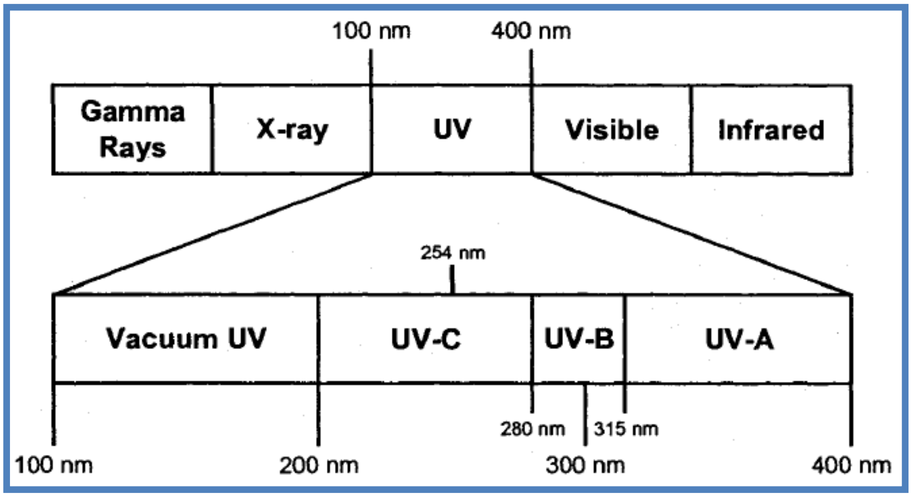


Figure 5: UV light in the electromagnetic spectrum (Baruth, 2005)

Prolonged exposure to these actinic wavelengths can lead to photo degradation of substances by photolysis, photo oxidation and other similar processes. UV has been shown to be effective for photolysis for several existing chemical compounds. This characteristic of UV, coupled with its ability to successfully inactivate the resistive pathogens, Cryptosporidium and Giardia, have led to its increase popularity in recent years for use in drinking water treatment, as an alternative to chlorine. (Baruth, 2005; Vecitis et al. 2009)

Photolysis is the decomposition of chemical compounds driven by the absorption of light energy or photons. When a molecule absorbs light it becomes electronically excited – having a bonding or non-bonding electron promoted to an antibonding orbital – leaving the molecule more reactive, and open to new reaction pathways (Li & Blatchley, 2008). As it pertains to treatment of the particular target molecule, there are two types of chemical photoreactions: direct and indirect. In direct reactions, the target molecule itself absorbs the radiation and then undergoes photolysis. In indirect reactions, the radiation is absorbed by a separate compound, which then acts as a mediate to react with the target compound (Vaalgamaa et al., 2011).

UV Photolysis of PFOA

In attempt to suppress the relatively recent issue of PFOA accumulation, research has been done to test the viability of UV degradation as a possible treatment method. Theoretically, UV should cleave the C-F bonds in the compound to form F- ions, which would bond with Ca^{2+} to form the more environmentally friendly CaF_2 (Hori et al., 2004). Experiments have been done with both direct and indirect photolysis with good overall results. For direct photolysis, it was shown that PFOA was effectively decomposed by irradiation under VUV light, but decomposed slowly under UV-C to form carbon dioxide, fluoride ions, and short-chained perflourocarboxylic acids (Cao et al., 2010; Hori et al., 2004).

The rate of decomposition was reduced when PFOA was treated with VUV radiation in aqueous periodate. Irradiating PFOA with UV-C in the presence of a mediator chemical, such as a photo catalyst or photochemical oxidant, had mixed results. Through experiments, it was shown that the decomposition rate of PFOA significantly increased when treated with UV-C radiation in the presence of ferric ions, phosphotungstic acid ($H_3PW_{12}O_{40}$), TiO_2, persulfate ions, and in aqueous periodate solution. Presence of mediators has also been shown to suppress the formation of the undesired perflourocarboxylic acids byproducts. However, when exposed to UV-C in the presence of hydrogen peroxide, the decomposition rate was further decreased (Cao et al., 2010; Hori et al., 2004; Vecitis et al., 2009; Wang et al., 2008). These experiments, however, are laboratory based, and not much research has yet been done under environmental conditions.

2.6.2 Adsorption

Many wastewaters contain organic compounds that create unsightly coloration, unpleasant odors and taste, and effervescence or foaming, as a result of contacts with various industrial or household materials. These organic compounds are often resistant to both biological degradation and conventional physiochemical treatment means, such as sedimentation, coagulation, filtration and ozonation. In removal of undesired organic compounds from wastewater, adsorption is one of the most important methods (Cooney, 1998).

Adsorption is the binding of organic compounds onto the surface of adsorbents. There are two chemical mechanisms through which adsorption can be achieved, physisorption, binding through Van der Waals forces, or chemiosorption, binding through covalent bonds; some adsorption can be a combination of both. The rate at which an adsorbate can be adsorbed onto an adsorbent i.e. adsorption rate (R_{ads}) is governed by the Arrhenius equation, where E_a is the activation energy, A is the frequency factor, R is the ideal gas constant and x represents the order of the reaction (Nix, 2003).

$$R_{ads} = Ae^{\frac{-E_a}{RT}}P^x \qquad \text{(Equation 4)}$$

It can therefore be considered that rate of adsorption is controlled by: 1) how fast an adsorbent arrives at the adsorption site; and 2) how frequent such incident adsorption processes take place (Nix, 2003). The first factor is determined by the chemical nature of the binding between the adsorbate and the adsorbent, while the second factor is largely affected by surface diffusion, the rate at which an adsorbate jumps to a neighboring adsorption site to allow for the adsorption sites in the immediate contact area to be available for more adsorptive uptake.

Therefore, when selecting adsorbent materials for adsorbing organic compounds, the two most prominent factors are adsorbing affinity and surface capacity. High surface capacity can be further understood as high surface area for maximized adsorptive uptake and high porosity for maximized diffusion transfer.

Three are a variety of adsorbents for bench and industrial use, but they generally can be categorized as oxygenous adsorbents, carbonaceous adsorbents, and polymeric adsorbents. In this project, activated carbon and zeolites were used as adsorbents of PFOA-containing water. They are carbonaceous and oxygenous adsorbents, respectively.

Activated Carbon as an Adsorbent

Figure 6: Granular Activated Carbon (TradeKorea Global Marketplace, 2000)

Activated carbon, or activated charcoal, is a form of carbon processed to attain high porosity and thus high surface area. The surface of activated carbon is mostly non-polar, which gives it high affinity for other non-polar molecules, including most organic compounds. Its high porosity and high adsorbing affinity makes activated carbon a commonly-used solid adsorbent to remove organic compounds from water in treatment facilities. Adsorption by activated carbon is praised for being effective, economical, and versatile. (Valeria & Reyes, 2008)

Zeolites as an Adsorbent

Zeolites are aluminosilicate minerals that exhibit micro porous crystal structures. Zeolites have uniformly sized pores throughout its crystal structure. While all naturally occurring zeolites are hydrophilic, exhibiting high affinity for polar molecules, de-aluminizing zeolites makes them hydrophobic, exhibiting high affinity for non-polar molecules, including organic compounds. Zeolites are 20 times more costly than activated carbon, but they demonstrate higher stability, meaning potentially lower operation and maintenance costs (United States Environmental Protection Agency, 1999).

Adsorption Isotherms

The United States Geological Survey (USGS) classifies an isotherm as a “graphical representation of the relationship between the bulk activity of adsorbate and the amount adsorbed at constant temperature” (USGS, 2011). An isotherm can be generated from equilibrium data obtained during an adsorption process at constant temperature. Adsorption Isotherm models are pertinent, in this project, to the experimental analysis of the data obtained during the activated carbon treatment as well as treatment with zeolites. The isotherm models which will be used to analyze the gathered data from the experiments are:

- The Freundlich Model
- The Langmuir Model

These models which were developed 70 years ago, are still very useful, and can be easily adapted to most experimental analyses conducted nowadays. The main reason for this is because the parameters for both models can be easily calculated since both equations need only two adjustable parameters each. The parameters can be easily estimated by graphical means or linear regression which is simplified when used in Excel. The original data is transformed and plotted accordingly to the respective models being used (Kinniburgh, 1986).

The Freundlich Model

This model is known as such because Freundlich first created this equation in 1909 and used it to represent the "isothermal variation of Adsorption of a quantity of gas adsorbed by unit mass of solid adsorbent with pressure" (Xamplified: Free Online Education Resource, 2010). The Freundlich model equation is as follows:

$$q_e = K_f C_e^{\frac{1}{n}} \qquad \text{(Equation 5)}$$

Where: q_e = uptake of contaminant adsorbed per unit adsorbent (mg/g)
C_e = Equilibrium concentration (mg/L)
K_f = Freundlich Coefficient
n = empirical coefficient

When fitted into logarithmic form, the equation yields the following:

$$\log(\mathrm{q_e}) = \log(\mathrm{K_f}) + \frac{1}{\mathrm{n}}\log(\mathrm{C_e}) \qquad \text{(Equation 6)}$$

The experimental data is transformed according to Equation 6 and plotted in Excel. Using linear regression, the values for the Freundlich Coefficient and the Empirical Coefficient are obtained. A new graph is then plotted using these coefficients and values for the equilibrium concentration that represents the range of concentrations being investigated.

The Langmuir Model

Similarly to the previous model, this model was named after Irving Langmuir, the scientist who created it in 1916. For the adsorption data to fit Langmuir's model, they have to obey certain assumptions: "a uniform surface, a single layer of adsorbed material, and constant temperature. In addition, the rate of attachment to the surface should be proportional to a driving force times an area. The driving force is the concentration in the fluid, and the area is the amount of bare surface" (Bungay, 2000). The Langmuir model depends on the rate at which molecules cover the surface of the adsorbent and the rate at which other molecules leave the surface. If the steady state condition is taken in consideration, both rates should be equal such that the rate of molecules covering the surface equals the rate of molecules leaving the surface.

$$\text{Rate at which surface is covered} = \mathrm{k_1 C_e}(1-\theta)$$

$$\text{Rate leaving surface} = \mathrm{k_2}\ \theta$$

At equilibrium, the Langmuir model can be described by:

$$\mathrm{k_1 C_e}(1-\theta) = \mathrm{k_2}\ \theta \qquad \text{(Equation 7)}$$

Where: k_1 and k_2 = rate coefficients
C_e = Equilibrium concentration (mg/L)
Θ = Fraction of covered surface

Making θ the subject of the formula, results in

$$\theta = \frac{(\mathrm{k_1 C_e})}{(1-\mathrm{k_2})\mathrm{C_e}} \qquad \text{(Equation 8)}$$

By dividing both the numerator by k1 and if θ is proportional to q, obtaining

$$q_e = \frac{q_m K_L C_e}{1+K_L C_e} \qquad \text{(Equation 9)}$$

Where: K_L = Langmuir coefficient
$q = q_m$ for a single layer

The equation is then transformed so that it can be plotted through perform linear regression. The equation to be plotted is as follows:

$$\frac{1}{\mathrm{q}} = \frac{1}{q_m} + \frac{1}{K_L q_m \mathrm{C_e}} \qquad \text{(Equation 10)}$$

When $1/q$ is plotted versus $1/C_e$, a straight line is obtained with $1/(K_L q_m)$ and y-intercept $1/q_m$.

2.6.3 Traditional Oxidation as a Treatment Method

Oxidization is a common way to degrade compounds for the treatment of water. This decomposition frequently leads to products that are more biodegradable than the parent compound. Therefore, oxidization can result in a more complete removal of substances. The following are common substances that are oxidized in wastewater: ammonia, cyanide, sulfides, phenols, hydrocarbons, and some pathogens. (Eckenfelder, 2006)

The literature states that highly fluorinated compounds, such as PFOA, are very resistant to traditional oxidation methods. However, there is little to no information on any experiments done on PFOA with such oxidation methods. This study aims to fill that gap.

Four oxidizing agents, calcium hypochlorite, sodium persulfate, potassium permanganate, and potassium ferrate, were chosen to attempt the degradation of PFOA in water. They were chosen based upon availability in the laboratory and on their history as an oxidizing agent. The reduction potential E_0 for each agent has been tabulated in the follow sections. The reduction potential is a measure of a substance's ability to gain electrons. High reduction potentials indicate strong oxidizing agents.

Hypochlorite

The hypochlorite ion has been found as an effective oxidizing agent for various inorganics such as MnO_4^{2-} , IO^{3-}, and Fe^{3+}. Additionally, it has been found to be successful in oxidizing organic such as aliphatics, aromatics, and heterocyclics. Hypochlorite can be used for disinfection such as in drinking water. It can also be used for BOD reduction and odor control in sewage and wastewater treatment facilities. The chlorine in hypochlorite has an oxidation state of +1. The half-reaction and reduction potential for hypochlorite is given in Equation 11. (Wojtowicz, 2004)

$$\mathrm{ClO^- + H_2O + 2e \rightarrow\ Cl^- + 2OH^-} \qquad \mathrm{E^0\ =\ 0.81\ V} \qquad \text{(Equation 11)}$$

Persulfate

The persulfate ion is known as one of the strongest oxidizing agents. The sulfur in persulfate has an oxidation number of +6. Reactions with persulfate ions are typically slow around room temperature, and can be sped up through heat, light, gamma rays, or transition metals. The persulfate anion can be activated through the aforementioned methods, where it is turned into a sulfate radical that is even more reactive than the persulfate anion. Persulfate has been found to successfully oxidize organics such as: phenols, aromatic amines, and alkyl aromatics among others. Other uses for persulfate include shock treatment of swimming-pool water and wastepaper recycling. The half-reactions and respective reduction potentials for persulfate are given in Equation 12 and Equation 13. (Steiner & Eul, 2001)

$$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^- \qquad E^0 = 2.01\ \mathrm{V} \qquad \text{(Equation 12)}$$

$$S_2O_8^{2-} + 2H^+ + 2e^- \rightarrow 2HSO_4^- \qquad E^0 = 2.12\ \mathrm{V} \qquad \text{(Equation 13)}$$

Permanganate

Manganese exists in the +7 oxidation state in permanganate, making it a good oxidizing agent. Permanganate can be used to oxidize both inorganic and organic substances in the water industry. Some of its primary uses include oxidizing iron and manganese to remove them from water and oxidizing taste and odor contaminants found in wastewater. It is also used to lessen the amount of disinfection by-products (DBPs) by oxidizing any organic precursors. The half-reactions and their respective reduction potentials for permanganate are given by Equation 14, Equation 15, and Equation 16. Equation 14 and Equation 15 occur in acidic conditions while Equation 16 occurs in alkaline conditions. (EPA, 1999)

$$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O \qquad E^0 = 1.68\ \mathrm{V} \qquad \text{(Equation 14)}$$

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O \qquad E^0 = 1.51\ \mathrm{V} \qquad \text{(Equation 15)}$$

$$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^- \qquad E^0 = 0.60\ \mathrm{V} \qquad \text{(Equation 16)}$$

Ferrate

Ferrate is another strong oxidizing agent; it has been said that ferrate is even stronger than permanganate. The iron in ferrate exists in the +6 oxidation state, which is high when compared to iron's common oxidization state of +2 or +3 in water. Ferrate can oxidize NH_3 to N_2 and water into oxygen at room temperature. (Stolzenberg, 2004) It has been proven to successfully oxidize organics such as phenols, anilines, amines, and olefins. Ferrate is currently being investigated to be used in the removal of phosphates in water treatment, and it has proven to be viable so far (Lee et al., 2009). The half reaction and its respective reduction potential for ferrate are given in Equation 17.

$$FeO_4^{2-} + 8H^+ + 3e^- \rightarrow Fe^{3+} + 4H_2O \qquad E^0 = 2.20\ \mathrm{V} \qquad \text{(Equation 17)}$$

2.6.4 Chemical Oxidation Demand (COD) test

The COD test is an analytical technique used to measure the amount of organic compounds in water. This test has been popularly used in determining the quality of water in wastewater plants as well as surface water. All organic compounds can be fully oxidized to carbon dioxide in the presence of appropriate oxidizing agents and by measuring the amount of carbon before and after the treatment, the quality of the treatment method can also be evaluated.

Oxidants used in the COD test are inorganic and the most common one is a mixture of dichromate and sulphuric acid with silver sulphate as the catalyst (Haandel & Lubbe, 2007). The half reaction and reduction potential for dichromate is given below:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \quad E^0 = 1.232\ V \qquad \text{(Equation 18)}$$

The COD of a given chemical after the oxidation is complete can be evaluated through titration or a spectrophotometer. Stoichiometric calculations can be employed to calculate a theoretical COD value for a given chemical compound. If the experimental value matches the theoretical value, it can be concluded that the oxidation is complete and successful. The following redox reaction for a compound with a structural formula $C_xH_yO_z$ is used for the same (Haandel & Lubbe, 2007).

$$\text{Oxidation: } C_xH_yO_z + (2x - z)H_2O \rightarrow xCO_2 + (4x + y - 2z)H^+ + (4x + y - 2z)e^- \qquad \text{(Equation 19)}$$

$$\text{Reduction: } e^- + H^+ + \frac{1}{4}O_2 \rightarrow \frac{1}{2}H_2O \qquad \text{(Equation 20)}$$

$$\text{COD (Theoretical)} = 8(4x + y - 2z)/(12x + y16z)\text{g COD per g of } C_xH_yO_z.$$

The International Standard Organization (ISO) has prescribed a standard method for performing the COD test (ISO 6060, 2012).

2.7 Summary

This background and literature review section provided the appropriate information to design treatment methods for the removal of PFOA from water. These methods are outlined in the next chapter which also gives an overview of the experimental portion of the report.

Chapter 3: Methodology

3.1 Sample Preparation for Standard Curve Analysis

In order to develop a standard curve for analyzing results of various treatment techniques, 5.25 grams of PFOA in powder form was purchased from Sigma-Aldrich. A literature review and experimental analysis suggested the use of four different concentrations of PFOA solution in water to establish the standard curve. These concentrations had to be above 75 mg/L since below this concentration, the spectrophotometer could not accurately detect the absorbance of the samples and any data obtained was inaccurate as well as constantly varying. Thus, solutions of 100 mg/L, 200 mg/L, 300 mg/L, and 400 mg/L of PFOA powder in E-pure water were prepared by weighing 100 mg, 200mg, 300 mg, and 400 mg of PFOA respectively and adding each to one liter of water in a beaker.

The solutions were then mixed overnight on a magnetic stirrer and after 24 hours of stirring, the pH of each solution was adjusted to 7 through the drop addition of a dilute base, NaOH (since the original solutions were highly acidic). After the four samples were prepared, their absorbance was measured with the Varian Cary UV-Vis spectrophotometer in the Environment Engineering lab. Varian quartz cuvettes were used to analyze the samples and the spectrophotometer was operated at a wavelength of 205 nm. The correlation between the known concentrations of the prepared samples and their measured absorbance was used to develop the standard curve relationship by plotting this data in Microsoft excel.

3.2 Ultraviolet (UV) Degradation Treatment

PFOA in solution was exposed to ultraviolet waves to determine the effectiveness of UV-degradation as a remediation technique for PFOA. Approximately 6 mL of a 400 mg/L solution of PFOA was pipetted into a glass laboratory scale photochemical reactor. The PFOA solution was neutralized prior to being placed in the reactor. A small UV pencil lamp was placed inside an immersion well, which was then submerged into the PFOA solution. A general setup of the apparatus can be seen below.

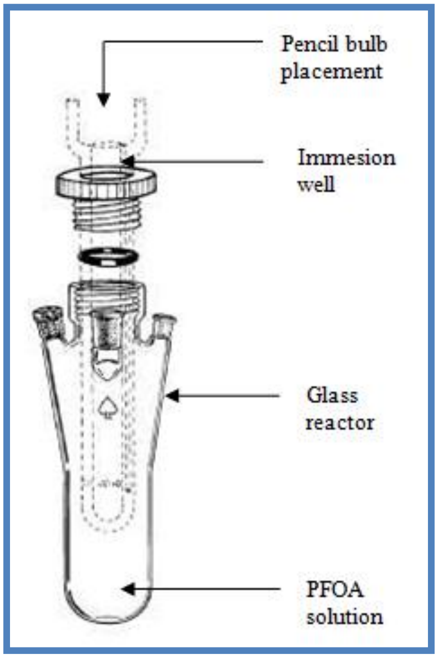


Figure 7: Setup of UV treatment apparatus (Ace Glass Incorporated, 2012)

The PFOA solution was treated with two different lamps for 60 minutes each, to determine the effects of UV wavelength on the degradation process. The first, an ACE Pen Ray 5.5 watt low pressure lamp, which emits short wave UV at 254 nanometers (nm); and a Spectroline 36 – 380 pencil lamp, that emits long wave UV at 365 nm. The experiment was repeated with exposure times of 30 and 75 minutes, to determine effect of exposure time on degradation. Treated samples were then analyzed by the spectrophotometer to determine the final absorbance of the solutions, at the previously specified wavelength. Absorbance scans of each sample were done across the UV spectra, and any emerging peaks were noted.

3.3 Adsorption Treatment

3.3.1 Activated Carbon

The activated carbon adsorption experiments were carried out to analyze the adsorptive uptake of PFOA in equilibrium. The active carbon absorbent used was FILTRASORB 200 granular activated carbon. For each experimental trial, varying amounts of activated carbon were added to glass vials containing 10 mL of PFOA solutions in varying concentrations. The pH values of all PFOA solutions were adjusted to approximately 7.0. The different activated carbon amounts under investigation were 0.007 g, 0.013 g, 0.020 g, 0.025 g, 0.050 g, and 0.075 g. The different PFOA concentrations under investigation were 200 mg/L, 300 mg/L, 400 mg/L, 500mg/L, 600 mg/L, and

1000 mg/L. After adding the activated carbon into the PFOA solutions, the glass vials were then capped, and placed into a rotator rotating at 15 rpm to maintain uniformity in the mixing and adsorption process.

In the equilibrium experimental trials, sufficient contact time of 48 hours between activated carbon and PFOA solutions were allowed to ensure the maximum adsorption of PFOA, where the rate of adsorption equaled the rate of desorption, and no more mass amount of PFOA was adsorbed by activated carbon. After maximum adsorption occurred, the samples were removed from the rotator and centrifuged at 2500 rpm for 20 minutes. After centrifugation, the treated PFOA solutions were then separated from activated carbon by a qualitative paper filter. The treated PFOA solution appeared as a clear liquid after centrifugation and filtration.

Lastly, the treated PFOA solutions were analyzed by UV-Vis spectrophotometry to determine absorbance. The absorbance was then compared to the previously-determined standard concentration curve to determine the PFOA concentration.

3.3.2 Zeolites

The zeolite adsorption experiments were carried out to analyze the adsorptive uptake of PFOA in equilibrium. The zeolite absorbent used was ZSM-5. For each experimental trial, varying amounts of zeolites were added to glass vials containing 10 ml of PFOA solutions in varying concentrations. The pH values of all PFOA solutions were adjusted to approximately 7.0. The different zeolite amounts under investigation were 0.025g, 0.050g, and 0.075g. The different PFOA concentrations under investigation were 200 mg/L, 300 mg/L, and 400 mg/L. After adding the zeolites into the PFOA solutions, the glass vials were then capped, and placed into a rotator rotating at 15 rpm to maintain uniformity in the mixing and adsorption process.

In the equilibrium experimental trials, sufficient contact time of 48 hours between zeolites and PFOA solutions were allowed to ensure the maximum adsorption of PFOA, where the rate of adsorption equaled the rate of desorption, and no more mass amount of PFOA was adsorbed by zeolites. After maximum adsorption occurred, the samples were removed from the rotator and centrifuged at 2500 rpm for 20 minutes. After centrifugation, the treated PFOA solutions were then separated from zeolites by a 0.22 micron syringe-driven filter. The treated PFOA solution appeared as a clear liquid after centrifugation and filtration.

Lastly, the treated PFOA solutions were analyzed by UV-Vis spectrophotometry to determine absorbance. The absorbance was then compared to the previously-determined standard concentration curve to determine the PFOA concentration after maximum zeolite treatment.

3.4 Chemical Oxidation

Chemical oxidation was performed with four oxidizing agents: calcium hypochlorite, potassium permanganate, potassium ferrate, and sodium persulfate in an attempt to oxidize PFOA in water. Solutions with 1:1, 5:1, and 10:1 molar ratios of oxidant to PFOA were prepared. The formula used to calculate the volume of each oxidant and PFOA for every molar ratio set is:

$$\text{Volume of Oxidant} = \frac{(\text{Volume of PFOA})(400)(\text{Molecular Weight of Oxidant})}{(\text{Molecular Weight of PFOA})(500)} \qquad \text{(Equation 21)}$$

The Volume of PFOA for each molar ratio was first chosen and the above formula was applied to obtain the appropriate volume of each oxidant. The following table lists the volume of PFOA and oxidizing agent used to prepare solutions with varying molar concentrations.

Table 4: Volume of oxidant and PFOA for various molar ratios

Molar Ratio (Oxidant to PFOA)	1:1	5:1	10:1
PFOA	21.0 mL	9.0 mL	5.50 mL
Calcium Hypochlorite	5.80 mL	12.43 mL	15.19 mL
Potassium Ferrate	8.04 mL	17.22 mL	21.04 mL
Sodium Persulfate	9.66 mL	20.69 mL	25.29 mL
Potassium Permanganate	6.41 mL	13.74 mL	16.79 mL

A 400 mg/L solution of PFOA in water was prepared and left to mix overnight. The pH of this solution was adjusted to 7 before using it as the stock for making the oxidation samples. Next, the appropriate volume of each chemical was measured and stored in amber vials which were then mixed overnight in the mechanical rotator. The absorption of all twelve samples was measured through the use of the UV-Vis spectrophotometer at time intervals of 24 hours, 48 hours, and 72 hours. All samples were centrifuged for thirty minutes and filtered prior to measuring their absorbance. The data thus obtained was recorded. Additionally, a control sample with pure oxidant was prepared for all four oxidant by mixing oxidant with E-pure water in 1:1, 5:1, and 10:1 molar ratios. The control samples were also mixed overnight before being measured for absorbance. The absorbance for each control sample was measured and subtracted from the absorbance of the PFOA and oxidant samples to remove any discrepancies in the result due to chemical interference of the oxidant. The final absorbance data thus obtained was plotted on excel spreadsheets and the standard curve was used to determine the extent of treatment.

3.5 Standard Curve for COD

Samples of 100, 200, 300, and 400 mg/L of PFOA in water, with pH adjusted to approximately 7, were prepared. Then 2.5 mL of each concentration of PFOA was added to standard range (20-900 mg/L) dichromate COD vials obtained from Bioscience, Inc. Additionally, one blank sample containing 2.5 mL of deionized water was prepared in a COD vial. The vials were shaken and then heated to 150°C for 2 hours. The vials were removed and given time to cool to room temperature and for any solid particles to settle. Spectroscopy was performed on each vial at a wavelength of 600 nm to measure the absorbance of Cr^{3+} which gives an indirect measurement of the amount of PFOA. The water/blank sample was used as the zero. The absorbance of each sample was recorded and plotted in Excel to generate a standard curve.

Chapter 4: Results & Discussion

4.1 Overview

In order to complete this section, extensive experimental analyses were performed in the environmental laboratory. Data were gathered for the standard curve to establish the foundation for the treatment techniques. All of the experimental investigations were conducted at a constant temperature and the pH was adjusted to 7 for each trial. Overall, the experimental portion of this project enabled the gathering of more knowledge about the complex chemical and laid out the basis for future research for the complete removal of PFOA from the environment.

4.2 General Findings

In brief, the numerous analyses made with PFOA reinstated the fact that it is a chemical which has a unique behavior towards the common treatment techniques which are usually effective on others. For instance, it was found that PFOA is unresponsive to any type of UV treatment. On the other hand, positive results were collected when conducting the experiments with activated carbon as well as with zeolites which are both commercial adsorbents. Additionally it was discovered that treatment by chemical oxidation with potassium dichromate, a strong oxidizing agent, did not yield any conclusive results. The following sections provide detailed descriptions of the results along with thoughts as to why PFOA behaves the way it does.

4.3 Standard Curve

Thorough experimental analysis suggested that any solution with a concentration less than 75 mg/L of PFOA in water yielded inconsistent results. Thus, four solutions, of 100 mg/L, 200 mg/L, 300 mg/L, and 400 mg/L of PFOA in E-pure water were analyzed using the Varian Cary spectrophotometer at 205 nm in order to develop the standard curve. While the spectrophotometer can be run within a range of 190 nm to 500 nm, 205 nm was chosen since PFOA, like any other aliphatic carboxylic acid in vacuum spectra, shows absorption maxima at this wavelength (Mukerjee et al., 1990). The actual average absorbance of each sample was compared with the theoretical absorbance for each sample obtained from a research study conducted at the University of Wisconsin in 1990 (Mukerjee et al., 1990). The actual absorbance of each sample was within a 2.5% error when compared to the theoretical absorbance and thus, this data was plotted in Microsoft Excel in order to develop the standard curve. This data can be found in Appendix I.

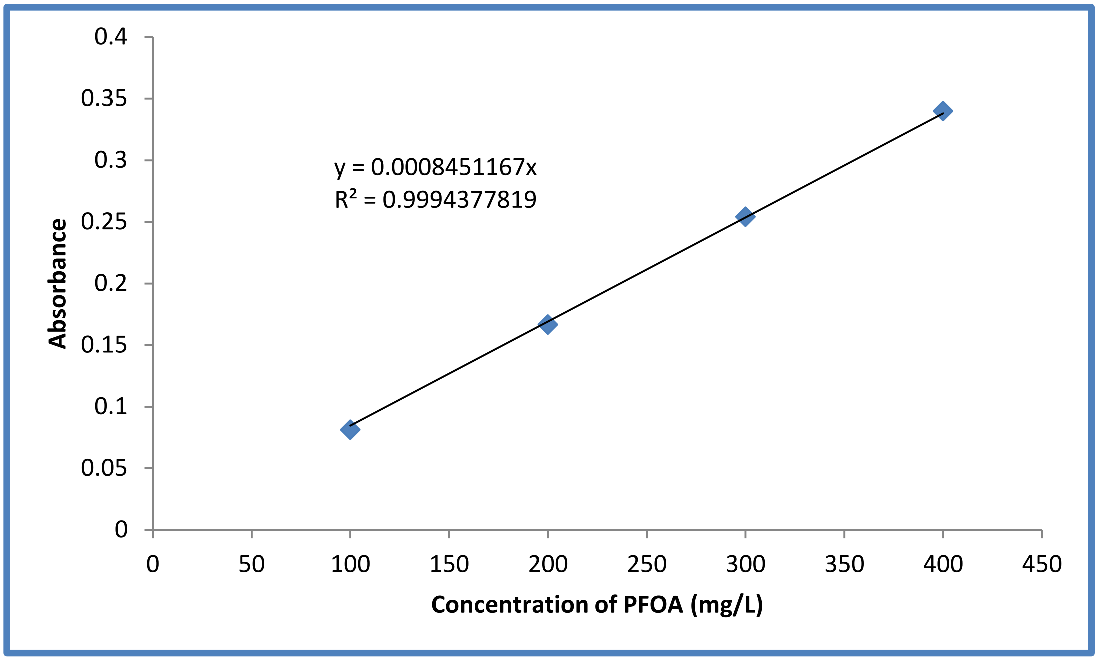


Figure 8: Standard Curve for PFOA in water at a wavelength of 205nm

As can be seen from Figure 8, the absorbance data obtained for the four chosen concentrations has a linear trend with a slope of 0.0008. Regression lines are useful in visually depicting the relationship between the two independent variables, absorbance and concentration of the samples that have been plotted in Figure 8. The straight line obtained depicts a linear trend in the data which means that the equation describing the line is a first order equation. The accuracy of the data fitting is measured in terms of the correlation coefficient. The closer R_2 is to 1.00, the better the fit. In this case, a linear regression analysis yielded a correlation coefficient, $R_2 = 0.9994$. Thus, it was concluded that the standard curve developed by the team was accurate and could be used to analyze the results of the various treatment methods being used to remove PFOA from water.

4.4 UV Treatment

UV treatment was conducted to remove PFOA from water using UV light of 365 nm and 254 nm wavelengths for varying time durations. Table 5 below shows the UV-Vis spectroscopy measurements of PFOA samples before and after 60 minutes of treatment.

Table 5: Absorbance at 205 nm after 60 minutes of treatment

Sample	**Untreated PFOA**	**Exposed to 365 nm**	**Exposed to 254 nm**
Absorbance	0.3455	0.3790	0.8417
	0.3459	0.3787	0.8316
Avg. Absorbance	0.3457	0.3789	0.8367

As seen in the table above, the absorbance of the PFOA sample increased after exposure to both UV wavelengths. There was a small increase in the absorbance of the solution that was exposed to the 365 nm; however, the absorbance of the samples treated with UV light of 254 nm wavelength was significantly increased, more than doubling the absorbance of the initial 400 mg/L PFOA solution. Since no PFOA was added to the system over time, the most reasonable explanation for this observation is that the degradation of PFOA formed byproduct(s) that absorbed UV light at a wavelength of 205 nm, causing interference to the analysis.

To understand this observation further, and to get some insight as to the interactions within the solution during exposure, a scan of absorbance across the entire UV spectra for each sample was taken. This is presented in Figure 9 below, after an exposure time of 60 minutes. Information for exposure times of 30 and 75 minutes can be seen in Appendix II.

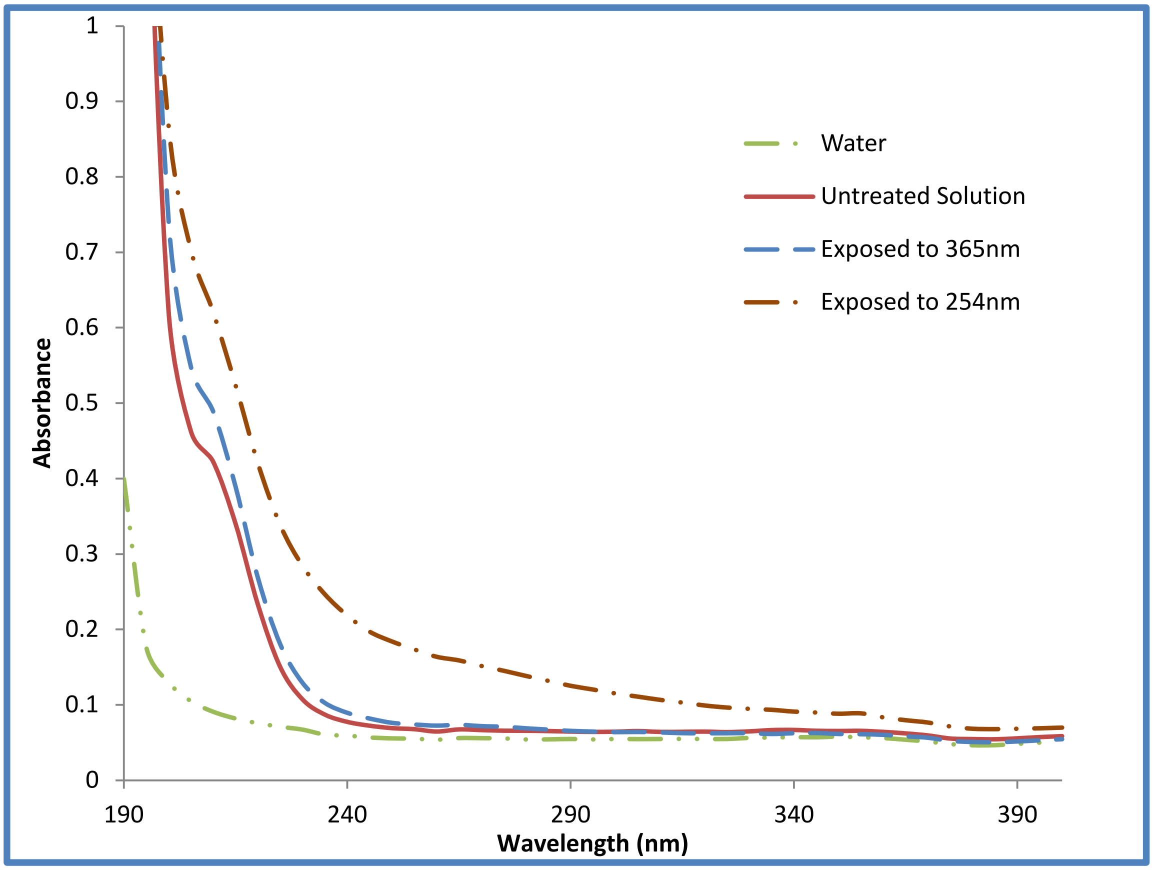


Figure 9: Absorbance of PFOA samples across UV spectra after 60 minutes of UV exposure.

From Figure 9, it can be seen that for the sample exposed to 254 nm light the shape of the absorbance curve over the UV range changed after treatment. This is in keeping with the previous hypothesis that the composition of the sample is changing as it interacts with UV, likely from the degradation of PFOA. However, the absorbance of the sample exposed to the longer 365 nm wavelength light only changed slightly, which would suggest this wavelength of UV has little to no effect in degrading PFOA.

The effect of exposure time on UV degradation of PFOA was also a parameter that was investigated. Figure 10 below compares the absorbance scan across the UV spectra for an untreated solution of PFOA, with solutions exposed to 365 nm wavelength light for 30, 60 and 75 minutes.

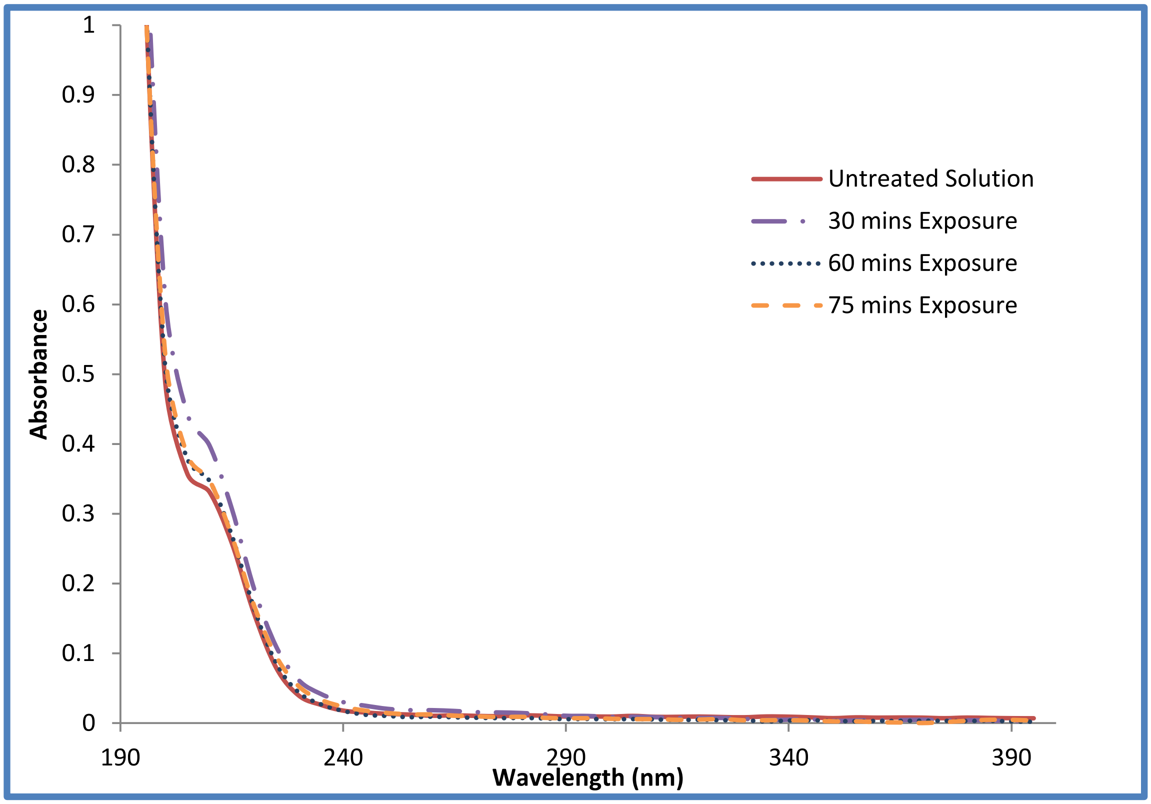


Figure 10: Comparison of varying exposure time for treatment of PFOA using 365nm wavelength light (without absorbance by water)

The graph confirms the hypothesis that negligible degradation of PFOA occurs when exposed to 365 nm wavelength, even for increased time periods. This is probably due to the fact that PFOA does not absorb UV at longer wavelengths. This observation can also be seen in the shape of the graph for the untreated solution above: practically no absorbance is seen from wavelengths around 300 nm and longer.

The same comparison was made for PFOA with solutions exposed to 254 nm wavelength light for the same time intervals, as shown in Figure 11.

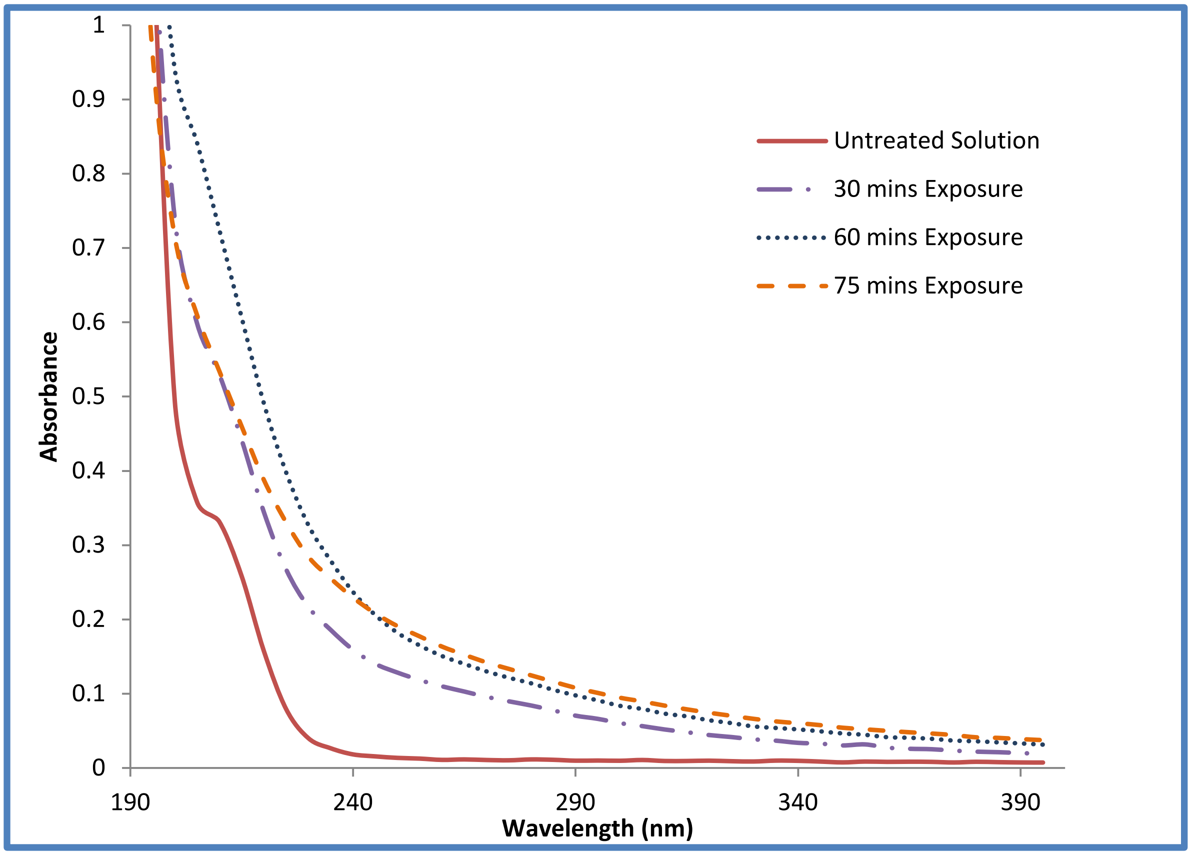


Figure 11: Comparison of varying exposure time for treatment of PFOA with 254 nm wavelength light (without absorbance by water)

Again the presumption that the shorter 254 nm wavelength degrades PFOA has been confirmed by the graph. It can be seen that increased exposure from 30 to 60 minutes increases the absorbance fairly equivalently across the spectra, suggesting that the concentration of a particular byproduct(s) increased the increased exposure time. However, a further increase of exposure time to 75 minutes changes the absorbance curve across the spectra, which is possibly evidence that the byproduct(s) formed from PFOA degradation are being degraded with further exposure to 254 nm wavelength UV light.

4.5 Treatment by Adsorption

Adsorption isotherm was developed to understand the contaminant-adsorbent interactions and to evaluate the adsorption capacity of FILTRASORB 200 granular activated carbon and ZSM-5 zeolite. Langmuir and Freundlich isotherm models were applied to establish empirical correlations against the experimental data obtained in the laboratory. The Langmuir and Freundlich isotherm correlation equations used are described in the Adsorption Isotherm Model section in the Background chapter.

4.5.1 Activated Carbon Adsorption

The treatment with F200 granular activated carbon yielded good results compared to the UV treatment technique. Activated carbon offers a large surface area for adsorption due to its porous surface which makes it a desired material for treatment and removal of contaminants. The data obtained during the experimental analysis is tabulated below, where C_e is the equilibrium concentration of PFOA after treatment.

Table 6: Experimental Data for F200 Treatment

Initial C_{PFOA} [mg/L]	M_{F200}[g]	C_e [mg/L]	% removal
200	0.0265	30.06	0.85
200	0.0514	19.83	0.90
200	0.0753	6.32	0.97
300	0.0240	116.64	0.61
300	0.0488	53.59	0.82
300	0.0769	63.98	0.79
400	0.0255	202.25	0.49
400	0.0526	179.59	0.55
400	0.0754	154.49	0.61
500	0.0077	426.68	0.15
600	0.0134	467.12	0.22
600	0.0218	366.95	0.39
1000	0.0120	868.04	0.13
1000	0.0195	851.88	0.15

Table 6 shows that varying degree of PFOA removal was achieved using F200 granular activated carbon as the adsorbent. Higher percentage of removal was achieved with larger mass amounts of F200 activated carbon and lower initial concentrations of PFOA, and vice versa. A linear regression was performed on the experimental data tabulated above to fit to the Langmuir and Freundlich models. This is to better understand the adsorbate-adsorbent interactions between PFOA granular activated carbon as well as to quantitatively evaluate the adsorption capacity of F200 granular activated carbon.

Freundlich Modeling

The data was first transformed and modeled according to the equation below where K_f is the Freundlich coefficient and n the empirical coefficient.

$$q = K_f C_e^{\frac{1}{n}} \qquad \text{(Equation 22)}$$

The equation above was transformed to obtain a linear representation for modeling the empirical data. The linear representation is depicted by the equation below and plotted in Figure 12.

$$\ln q = \ln K_f + \frac{1}{n}\ln C_e \qquad \text{(Equation 23)}$$

A linear regression yielded the following trend line for Freundlich isotherm, as depicted below in solid line in Figure 12:

$$y = 0.265x + 2.78\ (R^2 = 0.585) \qquad \text{(Equation 24)}$$

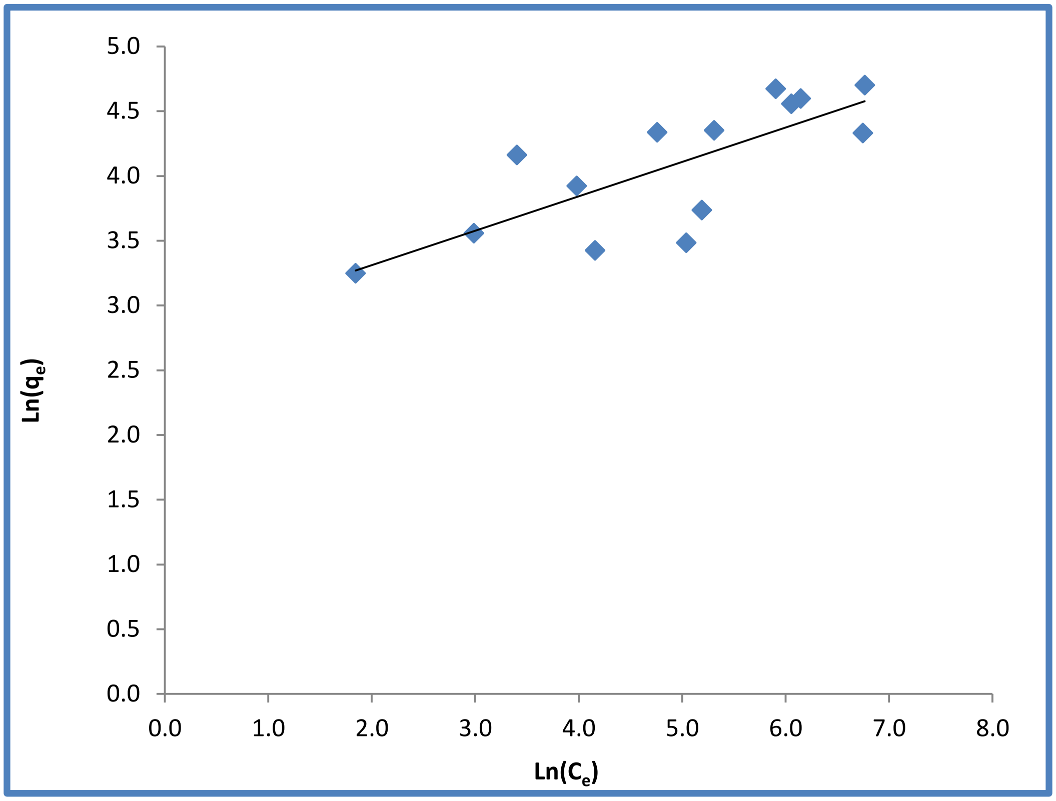


Figure 12: Freundlich Modeling of PFOA on F200 granular activated carbon after 48 hours of adsorptive uptake

Langmuir Modeling

The Langmuir modeling equation listed below was used where q is proportional to the fraction of the adsorbent covered. K_L represents the Langmuir coefficient while q_m accounts for the singularity of the adsorbent layer in the model.

$$q = \frac{q_m K_L C_e}{1 + K_L C_e} \qquad \text{(Equation 25)}$$

The linear transformation used to analyze the experimental data yielded the equation, as plotted in Figure 13:

$$\frac{1}{q} = \frac{1}{q_m} + \frac{1}{K_L q_m C_e} \qquad \text{(Equation 26)}$$

Using the Langmuir isotherm model in Equation 26, a trend line was found from the experimental data obtained using F200 as adsorbent for PFOA, as depicted by the solid line in Figure 13:

$$y = 0.161x + 0.0156 \ (R^2=0.452) \qquad \text{(Equation 27)}$$

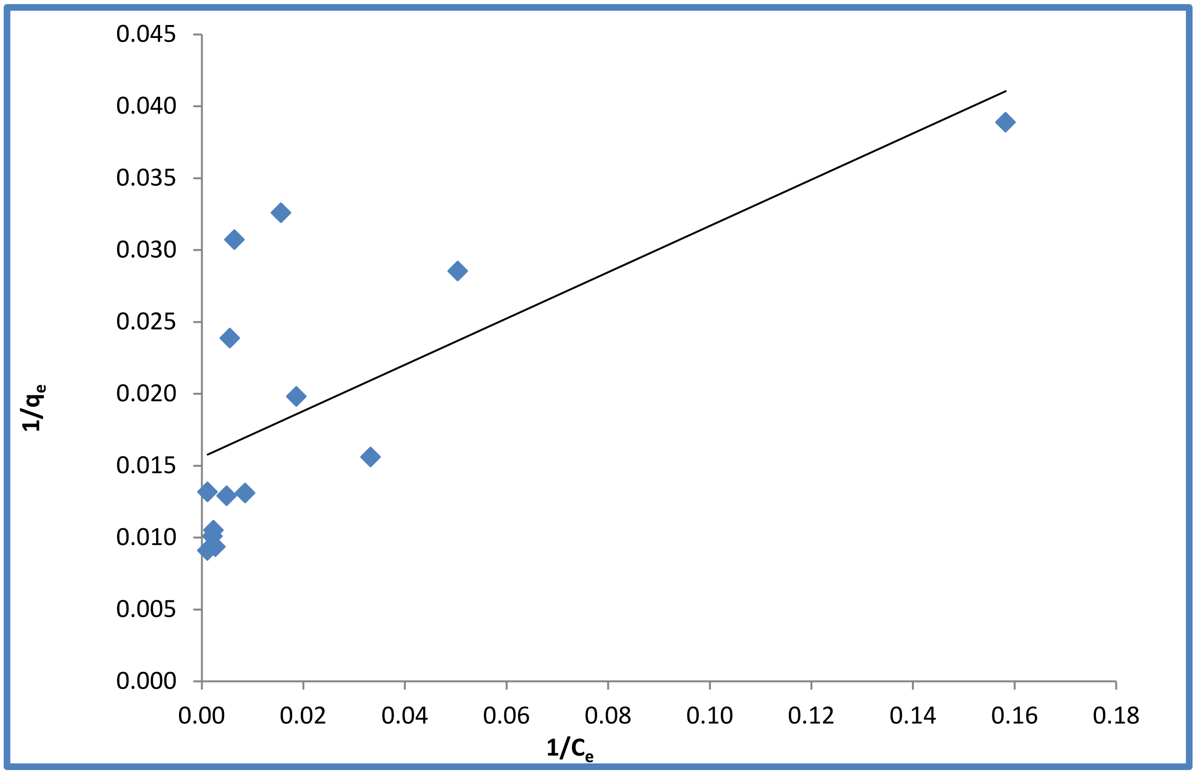


Figure 13: Langmuir Modeling of PFOA on F200 granular activated carbon after 48 hours of adsorptive uptake

From Figures 12 and 13 shown above, experimental data showed quotes deviation from the Langmuir model than from the Freundlich model. In addition, the R^2 value for the Langmuir model is lower than Freundlich model. This suggests that the Freundlich model seems more appropriate.

Activated Carbon Adsorption Models

Figure 14 displays the equilibrium adsorption amounts (q_e) of PFOA on granular activated carbon at different equilibrium concentrations (C_e). The adsorption isotherm of PFOA on granular activated carbon was better fitted into the Freundlich model than the Langmuir model. Because the Freundlich model demonstrated a multilayer adsorption with a heterogeneous energetic distribution of active sites, the good fitting result suggested that the multilayer adsorption of PFOA on granular activated carbons possibly occurred; it also suggested that the adsorbent, granular activated carbon, exhibited heterogeneous surface properties. Such heterogeneity can be due to the nonuniformity of the microporous structure of activated carbon; or it could be due to the variability of the functional groups formed on the external surface of activated carbon during its activation process (Jaroniec & Gilpin, 1991).

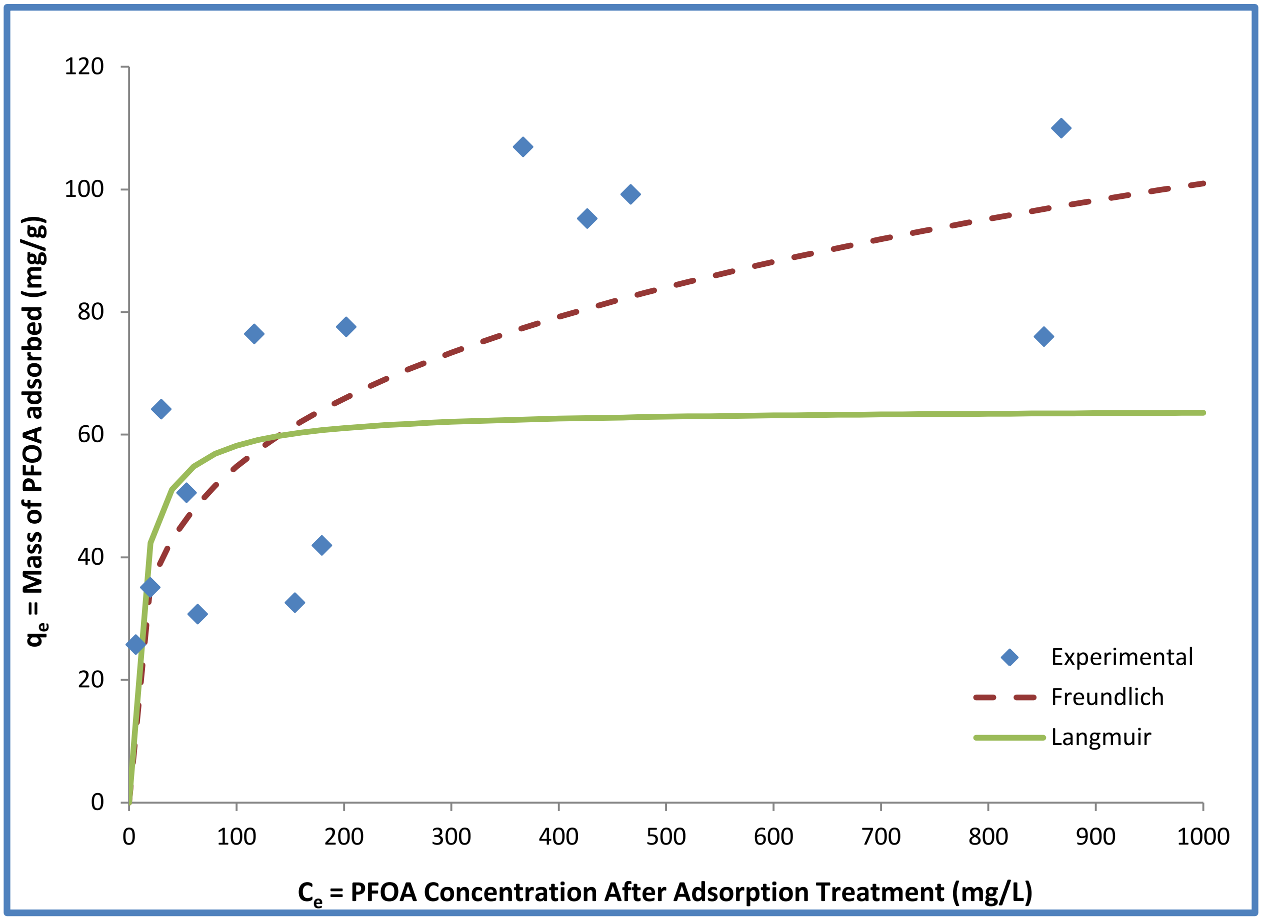


Figure 14: Adsorption isotherms of PFOA on F200 granular activated carbon and modeling using Freundlich and Langmuir equations. The F200 treatment was conducted for 48 hours.

Table 7 presented the calculated equilibrium constants using the Langmuir and Freundlich isotherm modeling. According to the calculated value for 1/n, an indicator of linearity varying between 0 to 1 with 1 being the most linear (Cynthia, 2008), the adsorption isotherm exhibits relatively non-linear property, which can also be attributed to the adsorbent site heterogeneity explained above. The nonlinearity can also be attributed to the adsorbent-adsorbate attractions and repulsions occurred during adsorption processes.

Table 7: Calculated equilibrium constants using the Langmuir and Freundlich modeling equations for adsorption of PFOA onto F200 activated carbon

Adsorbent	**Adsorbate**	**Langmuir constants**			**Freundlich constants**		
Granular activated carbon	PFOA	q_m	K_L	r^2	K_f	$1/n$	r^2
		$mg\ g^{-1}$	$L\ mg^{-1}$		$(mg/g)(L/mg)^{1/n}$		
		64.23	0.097	0.452	16.15	0.265	0.585

In terms of the adsorption capacity of granular activated carbon, the Langmuir coefficient q_m and Freundlich coefficient K_f will be compared to the corresponding coefficients obtained for zeolite adsorption in the Zeolite Adsorption section.

4.5.2 ZSM-5 Zeolite Adsorption

The same procedure for the analysis of collected data with activated carbon was conducted on zeolites as both techniques involve adsorption. The results for the data gathered in the laboratory are shown in the Table 8 below.

Table 8: Experimental Data for ZSM-5 Treatment

Initial C_{PFOA} [mg/L]	**M_{ZSM-5}[g]**	**C_e [mg/L]**	**% removal**
200	0.0250	118.68	0.41
200	0.0500	86.23	0.57
200	0.0750	49.73	0.75
300	0.0250	159.55	0.47
300	0.0500	143.14	0.52
400	0.0250	178.77	0.55
400	0.0500	126.00	0.69

The correlation between the initial concentration of PFOA, the mass amounts of ZSM-5, and the percentage of PFOA removal is more ambiguous than the experimental data for F200 treatment. Comparing to the experimental data for F200 treatment, at the same PFOA initial concentration and adsorbent mass amounts, higher percentage removal was achieved with F200 activated carbon treatment than with ZSM-5 zeolite treatment. Similarly, a linear regression was performed on the experimental data tabulated above to fit to the Langmuir and Freundlich models.

Freundlich Modeling

Using the same method as outlined in the Activated Carbon Adsorption section, a trend line was obtained for the ZSM-5 treatment data using the Freundlich model:

$$y = 0.827x - 0.834\ (R^2 = 0.443) \qquad \text{(Equation 26)}$$

Figure 15 shows the plot and the trend line obtained when using the empirical data to perform the linear regression.

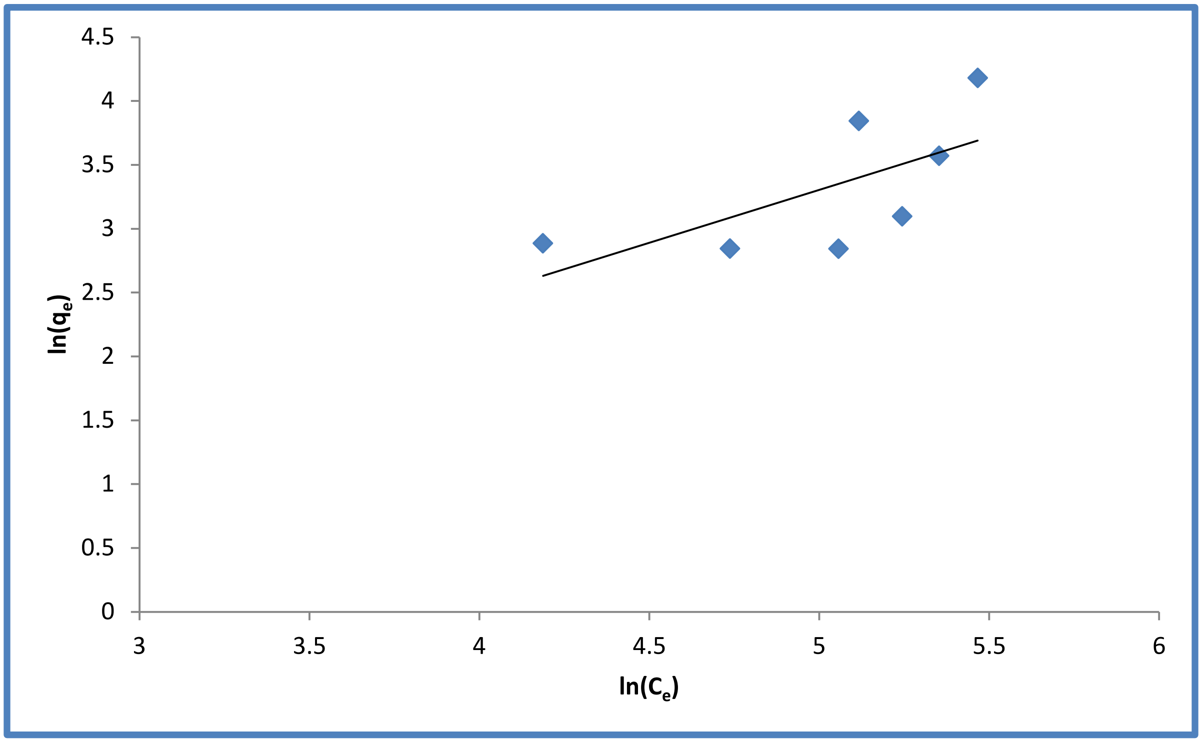


Figure 15: Freundlich Modeling of PFOA Adsorption on ZSM-5 zeolite after 48 hours of adsorptive uptake

Langmuir Modeling

Using the same method as outlined in the Activated Carbon Adsorption section, a trend line was obtained for the ZSM-5 treatment data using the Langmuir equations:

$$y = 2.93x - 0.0192\ (R^2 = 0.366) \qquad \text{(Equation 27)}$$

Figure 16 shows the plot and the trend line obtained when using the empirical data to perform the linear regression.

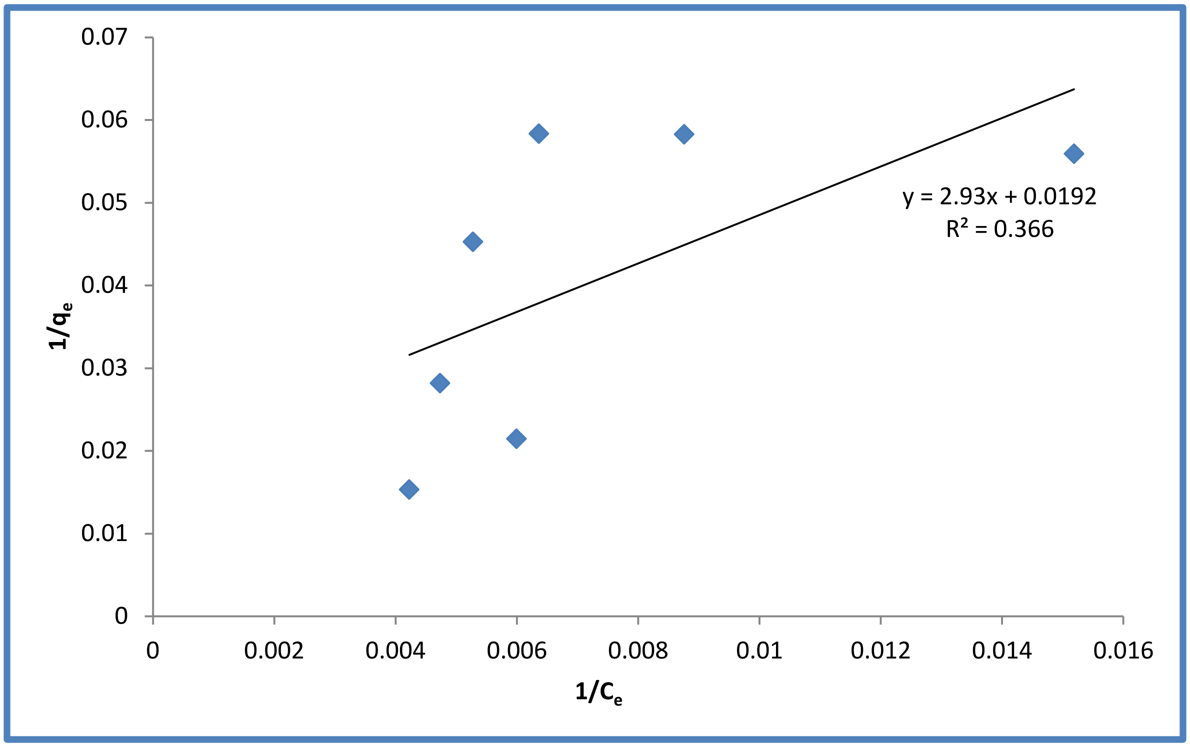


Figure 16: Langmuir Modeling of PFOA Adsorption on ZSM-5 zeolite after 48 hours of adsorptive uptake

When looking at the linear plots obtained from both models, it was observed that the R^2 values are both very low. This implies that the linear regressions performed to obtain the coefficient values were not accurate enough due to scattered data. However, when analyzing both plots above, it can be seen that the points generated using empirical data for the Freundlich model were closer to the trend line than the Langmuir model. An explanation for this would be because the adsorption of PFOA on zeolites does not follow the assumptions for monolayer assumptions for the Langmuir model.

ZSM-5 Adsorption Models

Finally, the coefficients obtained for the Freundlich and Langmuir models were used with the equilibrium data to generate the isotherm plots shown in Figure 17. The graphs were obtained by plotting the mass of PFOA adsorbed against the concentration of PFOA after treatment. The experimental data followed the Freundlich model closer than the Langmuir model. This implies that the adsorption of PFOA on ZSM-5 obeyed the Freundlich model. Similarly to the activated carbon model, this could be accounted by the fact that the ZSM-5 demonstrated heterogeneity at the surface in contact with the solution of PFOA.

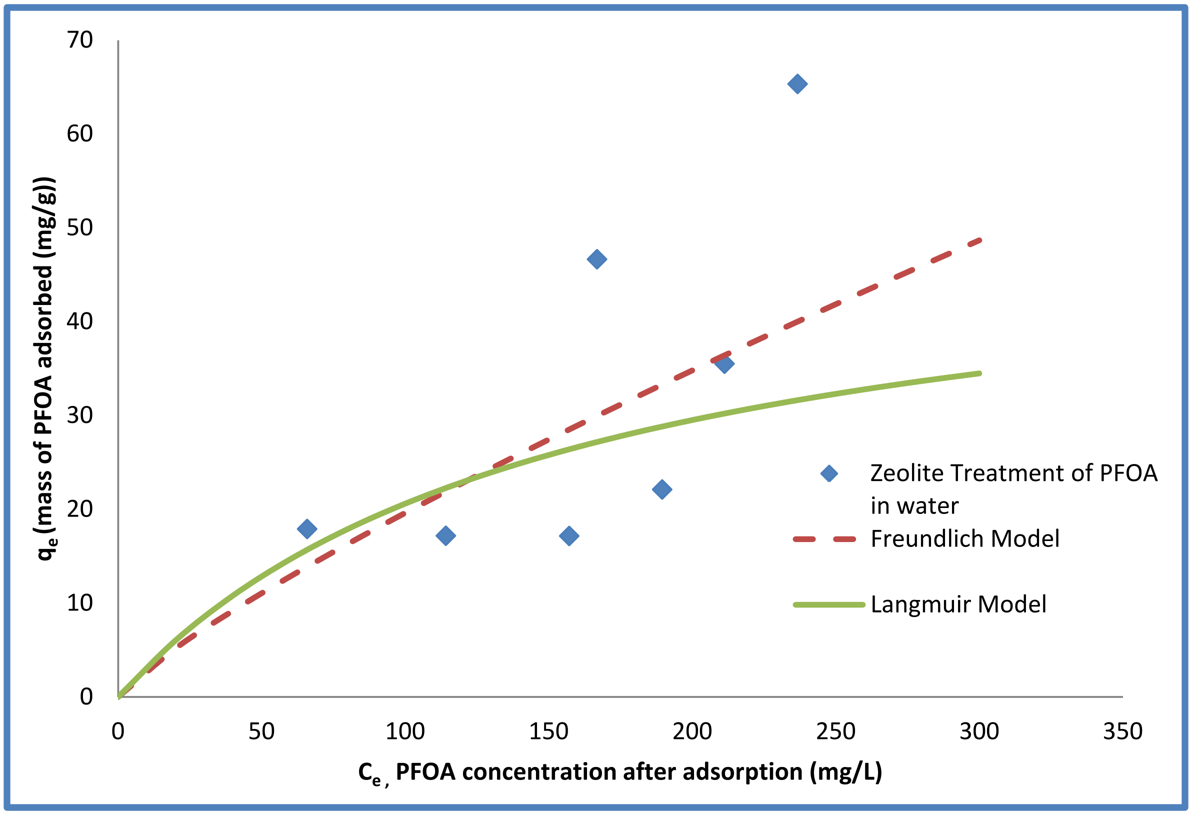


Figure 17: Adsorption isotherms of PFOA on ZSM-5 zeolite and modeling using Freundlich and Langmuir equations. The ZSM-5 treatment was conducted for 48 hours.

Table 9 shows the equilibrium constants obtained using Langmuir and Freundlich modeling. From the value of 1/n, a larger degree of linearity was observed; this suggested that adsorption using ZSM-5 was a better fit for the Freundlich Model. However, this is not necessarily an indication of the homogeneity of the adsorption site surfaces. This can be accounted for by the insufficient amount of data for ZSM-5 treatment.

Table 9: Calculated equilibrium constants using the Langmuir and Freundlich modeling equations for adsorption of PFOA onto ZSM-5

Adsorbent	Adsorbate	Langmuir constants			Freundlich constants		
ZSM-5 Zeolite	PFOA	q_m	K_L	r^2	K_f	1/n	r^2
		mg g^{-1}	L mg^{-1}		$(mg/g)(L/mg)^{1/n}$		
		52.03	0.00656	0.366	0.43	0.827	0.434

4.5.3 Comparison of Adsorbents

During the analysis of the results obtained for adsorption, it was observed that greater adsorption was achieved using F200 granular activated carbon compared to ZSM-5. The table below compares the Freundlich and Langmuir coefficients for both adsorption techniques used in this project.

Table 10: Comparison of Adsorption Capacities between F200 Granular Activated Carbon and ZSM-5 Zeolites

	Freundlich Coefficient (K_f)	Langmuir Coefficient (q_m)
Granular Activated Carbon	16.15	64.23
Zeolites	0.434	52.029

Both the Freundlich and Langmuir coefficients were greater for F200 granular Activated Carbon than ZSM-5 zeolites for the adsorption of PFOA showing greater adsorption capacity. This implies that single component adsorption using F200 granular activated carbon was more effective than using ZSM-5 zeolites under the same conditions of temperature, pressure as well as the pH used.

Previous studies have shown that in general, zeolites and activated carbon behave differently during adsorption. Though they both are widely used commercial adsorbents, activated carbon is usually preferred over zeolites. The reason for this is because activated carbon does not require specific optimum conditions for the adsorption process. Studies have shown that zeolites are temperature dependent and work best over a restricted range of pHs compared to activated carbon (Payne & Abdel-Fattah, 2004).

Another way to account for the differences in adsorption capacities is to look at the differences in the active surface areas of activated carbon and zeolites. Generally, activated carbon has a S_g value of 300-1200 m^2/g, while zeolites have a S_g value of 200-500 m^2/g. The larger surface area of activated carbon contributes to a greater degree of mass transfer, and thus greater efficiency of F200 granular activated carbon in treating PFOA.

4.6 Chemical Oxidation

The experimental results from chemical oxidation of PFOA show unrealistic change in the concentration of PFOA before and after treatment. Figure 18 contains an example plot of treatment of PFOA by potassium ferrate. The plot shows that the concentration of PFOA increases with time, which is not possible since no PFOA was added over the duration of treatment. This trend is not limited to the treatment by potassium ferrate. In fact, all of the plots regarding the treatment of PFOA by chemical oxidants (e.g., sodium persulfate, potassium permanganate, and calcium hypochlorite, which can be found in Appendix IV) show the same unrealistic increase in PFOA concentration as shown in Figure 18.

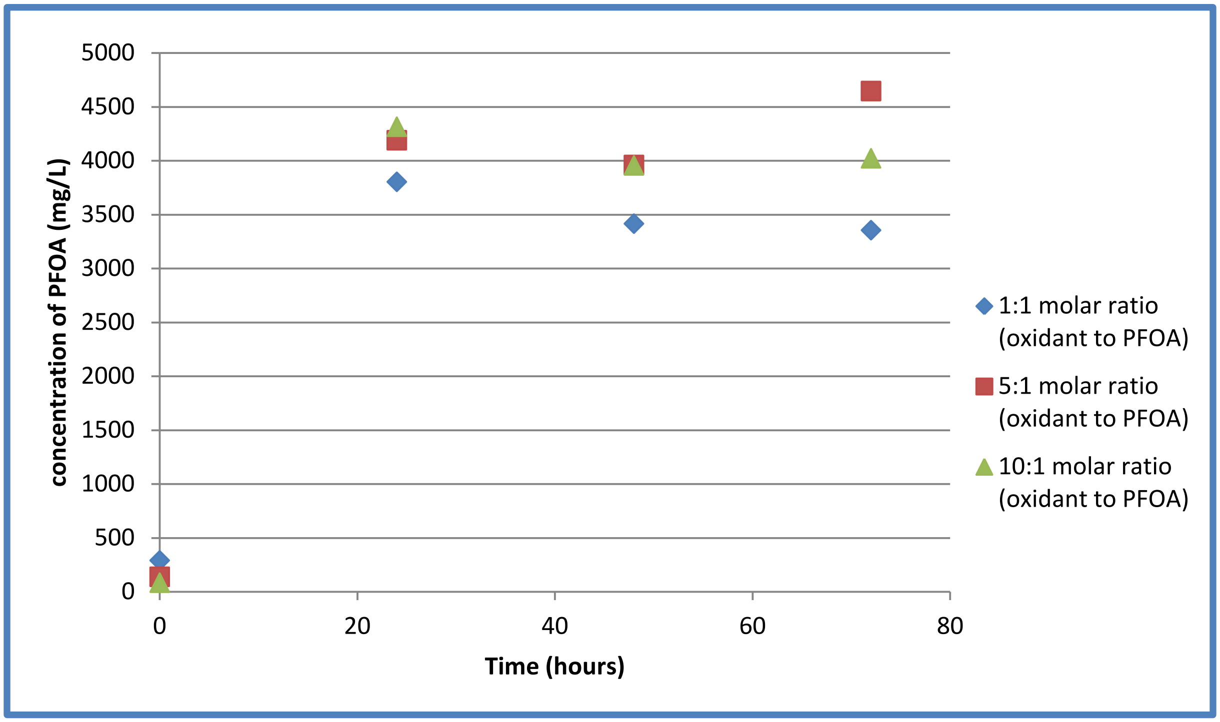


Figure 18: Treatment of PFOA by potassium ferrate over time. Data collected at 205 nm with varying oxidant to PFOA molar ratio

The increase in concentration was thought to be caused by the formation of oxidation byproducts. Some byproducts were removed through centrifugation and filtration, but the apparent increase in the concentration of PFOA, persisted (Figure 19).

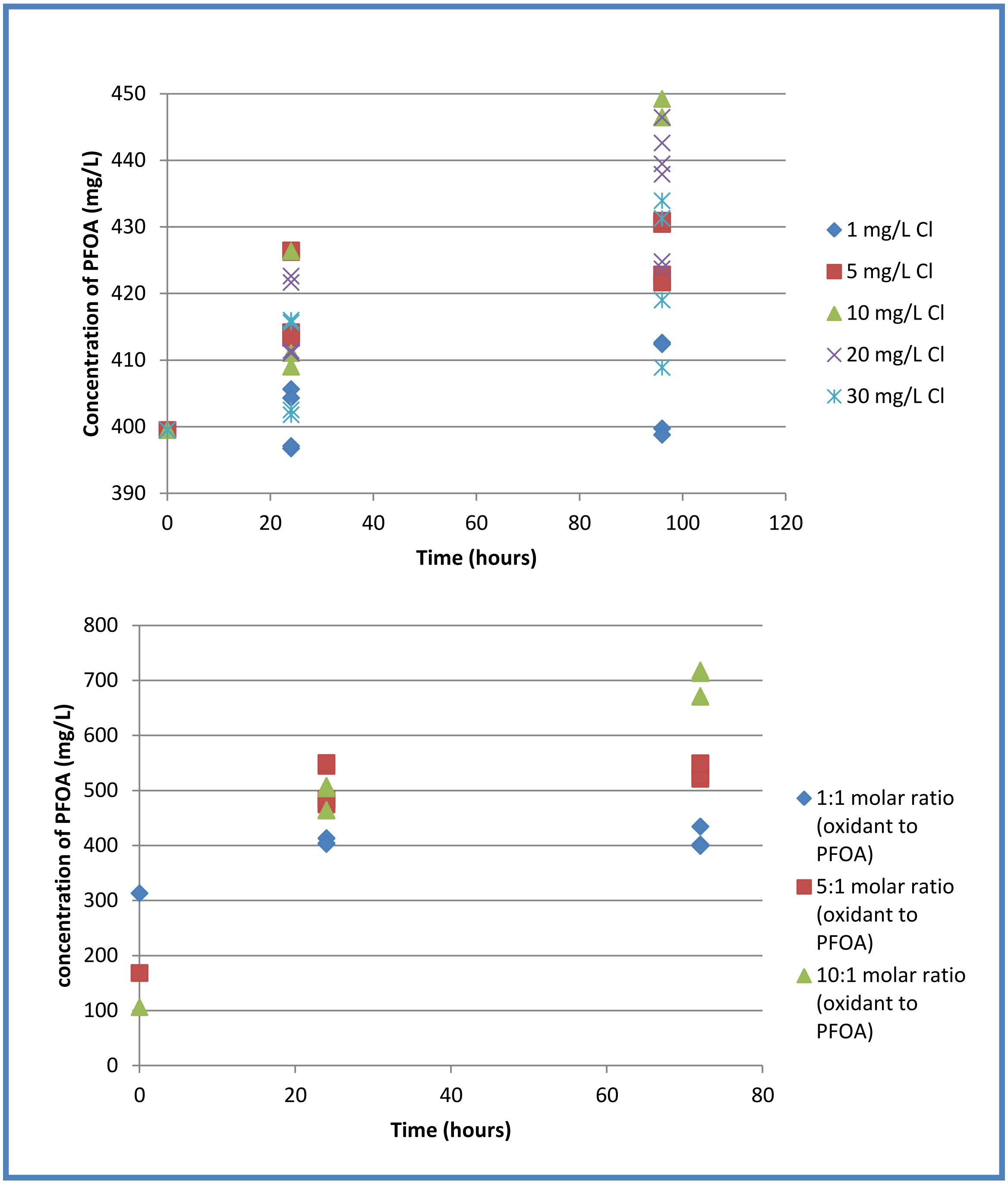


Figure 19: Apparent increase in PFOA concentration without centrifugation and filtration (top) and with centrifugation and filtration (bottom)

It was hypothesized that the oxidizing agents themselves could be causing interference in the readings, therefore UV-Vis spectra were obtained for the oxidizing agents over the range of 190-250 nm (Figure 20). The same centrifugation and filtration processes as in the treatment experiments were performed.

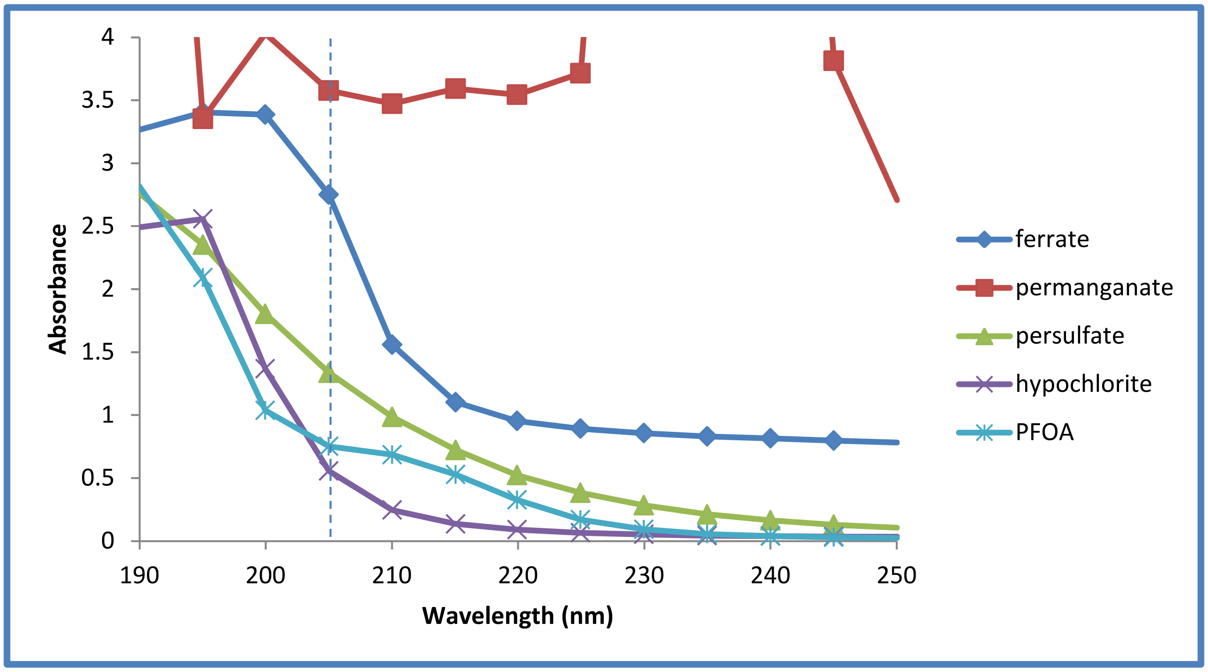


Figure 20: UV Spectra of PFOA and oxidizing agents from 190-250nm. The dotted line represents 205 nm. The concentration of PFOA is 400 mg/L in water and the concentration of the oxidizing agents is 500 mg/L in water

The scan shows significant interference for each oxidizing agent at 205 nm, which is the wavelength used for spectroscopy measurements throughout the study. Therefore, it is believed that the interference is caused by each respective oxidizing agent. Due to time constraints, the interference was unable to be removed.

4.7 COD Standard Curve

A standard curve was generated from the measured UV-Vis absorbance of Cr^{3+}, the product of chemical oxidation in COD testing. The absorbance obtained is used as an indirect measurement of the concentration of PFOA. The COD standard curve plot shows a slope of approximately 0, meaning that almost no Cr^{3+} was present. The absence of Cr^{3+} indicates that dichromate was not able to oxidize PFOA. As a result, COD analysis cannot be used to measure the presence of PFOA. Thus, UV-Vis spectroscopy must be used to directly measure the absorbance of PFOA.

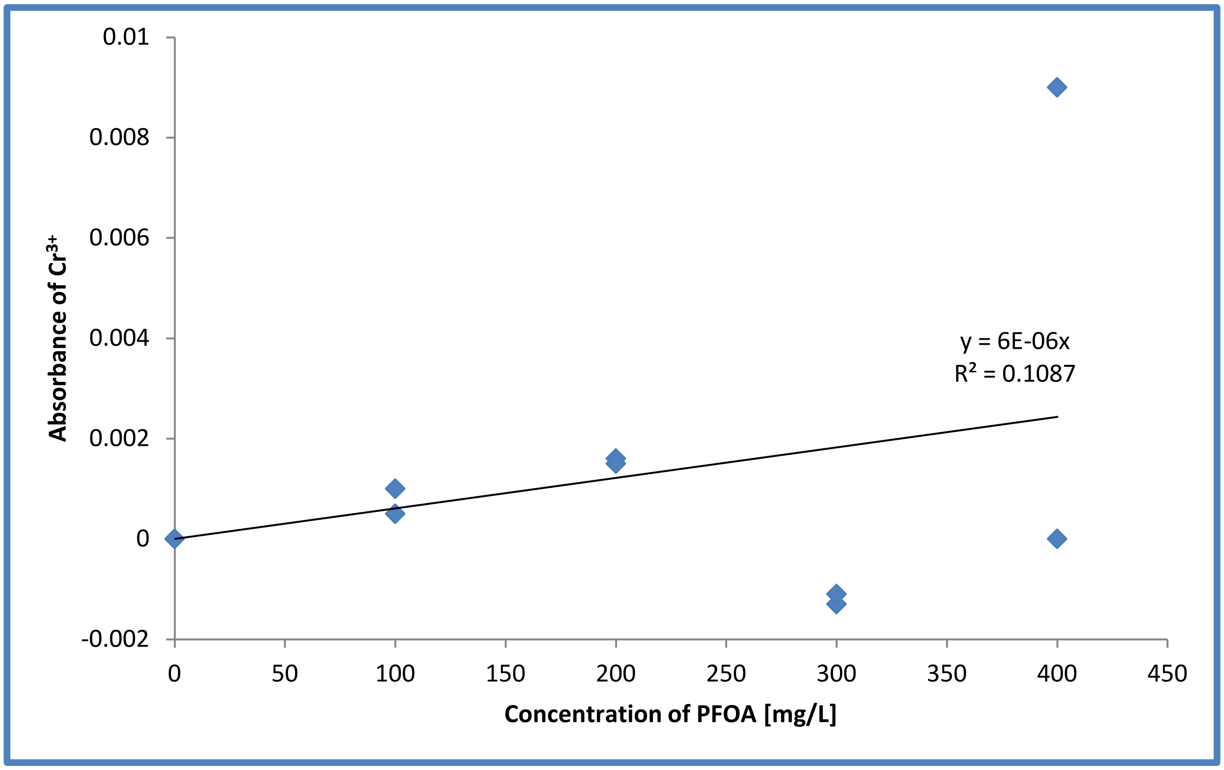


Figure 21: Standard curve for PFOA using COD, at a wavelength of 600nm, to measure the presence of Cr3+

The oxidation resistance of PFOA can be attributed to its chemical structure. Perfluorinated compounds are known to be highly resistant to oxidation due to the abundance of carbon-fluorine bonds. The C-F bond is one of the strongest known covalent bonds to carbon. Fluorine is highly electronegative which correlates with increased bond polarity. Also, there is no steric hindrance in the molecule, due to the perfluorination. This creates a shielding effect on PFOA. Another factor that contributes to the recalcitrance of PFOA is fluorine's high reduction potential (Equation 3). The reduction potential indicates that it is thermodynamically unfavorable for fluorine to lose electrons and oxidize. Several of the reasons why PFOA is chemically stable lead back to the background section of this document titled, Chemical Stability of Fluorosurfactants. (Kissa, 2001)

Chapter 5: Conclusions and Recommendations

This project enabled the gathering of much knowledge about the behavior of perfluorooctanoic acid, PFOA as a contaminant. Till now, resources were being mostly allocated towards determining the environmental and health risks associated with the chemical. The project was aimed at finding possible effective treatment techniques for the removal of PFOA from water.

The analysis led to the conclusion that adsorption using F200 granular activated carbon under constant room temperature and at an adjusted pH of 7 was the most effective treatment. Nonetheless, further investigation of other types of activated carbon is recommended to find more possible effective treatment techniques. While adsorption using zeolite ZSM-5 yielded somewhat positive results, due to limited time constraints for the project completion, the effects of modifying the pH or temperature on the zeolite treatment were not investigated. Conducting further experiments in the future with varying pH and temperatures to find the optimum conditions for zeolite treatment are recommended.

On the other hand, the data presented for the UV treatment is only sufficient enough to draw the conclusions that 254 nm wavelength UV light degrades PFOA, and possibly some of its byproducts, in water, while longer wavelengths, such as 365 nm, does not. Due to the fact that the byproduct(s) produced have similar UV absorbance as PFOA, UV-Vis spectroscopy cannot produce quantitative result for the degradation of PFOA. As such, the effectiveness of UV treatment using short wave 254 nm light cannot be determined unfortunately with the analytical method utilized in the project. Further investigation into the use of short wave UV light as a possible treatment option is suggestion, using a more appropriate analytical method, preferably one that separates PFOA from the forming byproducts.

For the oxidation treatment, there was a large amount of interference in the plots. This is believed to be caused by the oxidizing agents. The interference could not be removed from the oxidation plots due to time constraints. However, the literature states that traditional oxidation methods do not work on PFOA. This resistance to oxidation was observed during COD testing, where potassium dichromate could not successfully oxidize PFOA. As a result, COD is not a viable method to detect to the presence of PFOA. UV spectroscopy is the better alternative for monitoring the presence of PFOA.

If the recommendations presented above are taken into consideration, the treatment of water contaminated with PFOA could be implemented on a large scale in the near future.

Chapter 6: Limiting Exposure of PFOA

6.1 Addressing PFOA

Fire suppressants are mainly used to prevent and extinguish fires but many contain toxic chemicals that can be easily ingested from water contamination if treatment is not sought. Fire suppressing chemicals such as perfluorooctanoic acid (PFOA) have recently emerged as an environmental pollutant of concern due to their world-wide distribution, environmental persistence, and bioaccumulation potential. Many of these chemicals have become increasingly present in water treatment facilities and wells around the world. Fire suppressing chemicals, like PFOA, have been used to provide protective coating for cookware, textiles, and plastics and are commonly found in firefighting foams. These chemicals may enter the drinking water supply when products containing these chemicals are used by industry or consumers or discharged to the environment from landfill sites where products that contain these chemicals are disposed. Fire suppressing chemicals like PFOA are expected to persist in the human body because of their stable and recalcitrant traits. There is limited information available regarding health effects to humans from ingestion; however, some of these chemicals have been found in human tissues and fluids (Agency for Toxic Substances and Disease Registry, 2011). Laboratory studies on animals who had ingested PFOA linked the chemical to several adverse health effects including carcinogenicity, reproductive toxicity, and neurotoxicity (Miller, 2011).

Because PFOA is an emerging contaminant that is currently under-regulated, there is no simple way to address the problem of PFOA in water. This chapter will introduce the problems with PFOA and investigate many different ways to limit exposure of PFOA to humans. It will then propose a final solution to best limit exposure of PFOA in drinking water.

6.2 Firefighting Foams

Firefighting foams are foams that are used to suppress fire by blocking air supply to the fire. These foams are a stable mass of bubbles and have a density lower than that of water and most flammable liquids. Firefighting foams consist of three main components: water, solvents, and surfactants. Additionally, corrosion inhibitors and preservative dyes are added to further enhance the fire retardant action of these foams. The surfactants constitute 17% of the concentrate and 0.52% of the foam solution. Attention has been given to the environmental impact of surfactants used in the foams (Ruppert et al., 2011). While most foam manufactured today are claimed to be nontoxic and biodegradable, they may actually take years to biodegrade if at all and thus pose toxicity threats to the aquatic life and human health for the duration that they are present in water.

There are various different kinds of firefighting foams that are used in the industry today. The most common foams include protein foams, fluoroprotein foams, film forming fluoroprotein foams, aqueous film forming foams, and alcohol resistant foams, and synthetic detergent foams. Film forming fluoroprotein foams are those fluoroprotein foams that are designed to form a film on the surface of the hydrocarbon once released onto the fire. Aqueous film forming foams (AFFFs) consist of synthetic foaming agents in addition to fluorochemical surfactants. (Kiddle Fire, 2011)

Two main foams are used to fight fires: carbonaceous foams and hydrocarbon or fuel foams. Carbonaceous foams are typically used when there is a wood fire. On the other hand, hydrocarbon or fuel foams are usually used when there is a fuel fire. These foams are much stronger than carbonaceous foams and can combat fires that carbonaceous fires cannot; however, hydrocarbon/fuel foams are much more toxic over time and tend not to degrade. (Framingham, Massachussetts Fire Department, 2012)

When foams are discharged into the environment, they will typically make their way to a surface water body and might make their way to a wastewater treatment facility. When a foam is in water, it removes oxygen killing aquatic life and contaminates the water. When it enters a wastewater treatment plant, it not only foams more from all of the mixing, but it disrupts the mechanical devices and causes “sludge bulking” and Froth. Because it removes oxygen, it kills microorganisms used to treat sewage contaminates the water. Foam should be avoided in wastewater treatment plants. (Ruppert)

6.3 Exposure of PFOA to Humans

PFOA in its pure form is a white powdery substance. It is commonly found as a substrate on materials to make them fire resistant and is also a main component of firefighting foams. When PFOA is discharged from firefighting foam, contaminated landfills, or releases into the air, it can enter the environment through leachates from landfills and run-off. The degradation of other fluorocarbon compounds can also lead to the release of PFOA. Because PFOA is heat, chemically, and biologically stable, it persists in the environment and can make its way to surface waters and eventually to drinking water plants. As a result, exposure of PFOA to humans usually comes from releases into the environment as a saturated chemical in water. The technology in drinking water utilities is currently not sufficient enough to remove PFOA to an acceptable level, so PFAO will likely transpire into drinking water sources as shown in case studies.

The release of PFOA is typically from AFFF firefighting foams, used to suppress fuel fires, or leaching from fire retardants on solid materials. PFOA contamination can usually be traced back to its place of release and therefore can be considered a point-source contaminant. One might argue that it comes from a non-point source since contaminants such as fertilizers which are released in a certain area are usually categorized as non-point source. Although non-point source pollution tends to come from run-off, PFOA contamination is typically released and then carried with run-off, rather than being picked up as a pollutant during run-off.

PFOA, the surfactant in AFFF firefighting foams, constitutes 17% of the foam concentrate which is a main component of firefighting foams (Ruppert et al., 2011). According to a PFOA Material Safety Data Sheet, PFOA is toxic when ingested or contacted with skin at extremely high concentrations (Sigma Aldrich, 2012). PFOA is essentially non-volatile and therefore exposure is unlikely via inhalation (Bull & Foxall, HPA Compendium of Chemical Hazards PFOS + PFOA, 2009). "PFOA is not metabolized in the body; its tissue distribution in humans is unknown, but studies in rats suggest it is likely to be present primarily in the liver, kidney, and blood" (Steenland et al., 2010). When a person drinks water or eats food that is contaminated with PFOA, it bioaccumulates in their blood and increases health risks.

PFOA accumulates in the blood from inhaling PFOA in its original powder state or drinking water contaminated with PFOA. The estimated biological half-life of PFOA in human blood is two to four years on average. In 2000-2001, blood from the United States general population was analyzed based on a blood bank sampling. The study concluded that the average American contains about 5 parts per billion (ppb) of PFOA in their blood. Workers who come into contact with PFOA have an elevated concentration of less than 20 parts per million (ppm) in their blood. (Environment Canada Health Canada, 2010)

6.4 Regulations

PFOA did not become a public area of concern until the late 1990's when EPA began raising awareness of its toxicity. By May 2000, the increasing health risks associated with the chemical caused 3M to stop manufacturing PFOA. Following these studies, EPA started taking legal actions against DuPont for continuing the manufacture of PFOA despite being aware of its health and environmental issues (George Washington University School of Public Health and Health Services, 2011). “In April 2003, the EPA completed preliminary risk assessments on PFOA, and later that year took the first steps towards developing an enforceable consent agreement for PFOA and related fluoropolymers” (Encyclopedia of Earth, 2011). In an effort to encourage the decrease in use of PFOA, EPA also developed a program which aimed at eliminating PFOA use by 2015. Several such studies are increasingly being encouraged to detect the presence of PFOA in water bodies. Currently the EPA is also trying to find alternatives to the use of the PFOA or any similar chemicals (Environmental Protection Agency, 2010).

EPA has established a provisional drinking water health advisory for PFOA of 0.4 ppb which is only intended for short-term exposure. Several states have established a groundwater limit of PFOA. For example, West Virginia must be provided with alternative drinking water when PFOA levels exceed 0.5 ppb, Minnesota has a limit of 0.3 ppb, and North Carolina has proposed a limit of 1.6 ppb in groundwater. PFOA is not currently analyzed or treated for at public drinking water utilities. (State Water Resources Control Board, 2010)

The Safe Drinking Water Act does not regulate PFOA or any aqueous film forming foams (AFFF) (Ruppert). PFOA is not a Comprehensive Environmental Release, Compensation, and Liability Act (CERCLA) recognized hazardous (U.S. EPA, 2001). However, “Owner/operators can still be held liable under CERCLA for clean-up costs or damages used by a release of AFFF… even though the release itself is not reportable” (Ruppert et al., 2011).

6.5 Fluorosurfactant Spill Remedial Process

Typically, perfluorinated foam is not used to treat a fire unless it is a fuel or hydrocarbon fire for many reasons including cost and vulnerability of contamination to the environment. When firefighting foam is used to treat a fire, fire fighters try to contain the foam the best they can by only releasing the smallest amount of foam possible and calling the hazardous material team to clean the foam after. Only ten gallons of foam are stored in one fire truck, but after 50 gallons are used, there is a definite problem regarding contamination. The hazardous material team will clean up the foam by putting sand, pad, and/or absorbent around the area to prevent discharge into catch basins. The fire fighters and hazardous material team wear extreme protective gear to ensure that they do not come into direct contact with the foam. Firefighting foam is extremely expensive as well, so fire fighters try to limit the use of foams unless it is absolutely needed. (Framingham, Massachussetts Fire Department, 2012)

When PFOA is released into the environment in large quantities, for instance from the discharge of foams from sprinkler systems in buildings or at airports, the state health and environmental protection agency and/or EPA's emergency response team is notified. Typically, the agencies will become involved immediately as a consultant to the potentially responsible party (PRP). The agency's main goal is to prevent exposure of PFOA and other harmful constituents to humans. The PRP is responsible for cleaning up the site and paying for all remedial costs. If the PRP does not have enough funds to clean the spill, then EPA will step in and provide preliminary assistance in remediation and funding. The PRP can take out loans and, according to the National Contingency Plan, the PRP must act quickly or the state agency or EPA can take over. The state or EPA will sue the PRP for the costs if the PRP cannot pay. The PRP has to remediate from a spill and EPA must verify proper treatment is sought. (Hearn, 2012)

6.6 Overview of Treatment of PFOA in Water

There is very limited information regarding treatment of PFOA in water in the literature. Because PFOA is extremely stable and recalcitrant, it does not degrade in water and persist indefinitely. However, one reference suggests PFOA can be treated using reverse osmosis, nano-filtration and activated charcoal (State Water Resources Control Board, 2010). Because information on treatment of PFOA is so limited and PFOA is such a harmful chemical, evaluation of the removal of PFOA from water through various oxidation and adsorption treatment methods was sought as described in this report. Treatment by chemical oxidation was performed with dichromate, calcium hypochlorite, sodium persulfate, potassium permanganate, potassium ferrate, and UV light. Adsorption with FILTRASORB 200 granular activated carbon and ZSM-5 zeolite was also attempted. Results showed that none of the oxidation methods presented coherent results due to strong interference of the oxidant with the PFOA solution. Nonetheless, adsorption proved to be a successful and promising technique for removing PFOA from water as compared to oxidation techniques. All PFOA solutions were adjusted to pH of 7 through the dropwise addition of dilute base, NaOH.

6.7 Limiting Exposure of PFOA to Humans

PFOA is extremely recalcitrant and harmful to humans when ingested. Because of its ability to transpire in drinking water supplies, it is imperative to find solutions to limit this chemical from being exposed to humans and the environment. This section will investigate and propose solutions to limit PFOA exposure.

6.7.1 Limit or Eliminate Fluorosurfactant Foam

One possible way to limit exposure of PFOA from firefighting foams is to severely limit the use of foams with perfluorinated surfactants. Instead of using fluorosurfactant foams on fires other than hydrocarbon and fuel fires, less harmful foams should be used. Such foams could be those used to fight carbonaceous fires. These foams are much less expensive than fluorosurfactant foams used to fight hydrocarbon fires and are much less harmful than foams used to fight carbonaceous fires. Only small doses of fluorosurfactant foams as a last resort should be used when fighting hydrocarbon and fuel fires.

An argument for using foams that fight carbonaceous fires is that some of these foams are more acutely toxic than fluorosurfactant foams. Because of this acute toxicity, environmentalists tend to want to steer away from these foams since they might be toxic to the aquatic environment initially. Although, fluorosurfactant foams have a more toxic long-term impact to the aquatic environment and humans compared to foams used to fight carbonaceous fires. (Klein, 2009)

There are foams created to fight fuel fires that are completely fluorosurfactant free and satisfy industrial standards. Other options include using foams with a fluoropolymer which, according to the manufacturer, is environmentally benign. This, however, does not mean that it is safe for humans to ingest. In addition, alternative types of fire suppressants can be used to replace AFFF firefighting foams in some cases. Examples include water mist or fog, compressed air foam systems, hydrophilic gels, or free-radical chain-breaking powders. A combination of foam and alternatives can also be a way to fight fires while limiting fluorosurfactant foams. (Klein, 2009)

EPA is enforcing a manufacturing ban of PFOA although foams containing PFOA will probably still be around for decades. It would be great to see fluorosurfactant foams banned from use since there are many alternatives than using fluorosurfactant foams. Also, if foam containing fluorosurfactants must be used, there should be a limit on the concentration allowed to be discharged. Even if foam with PFOA is banned, PFOA is so recalcitrant that it will be in the environment for many years.

6.7.2 Mitigate Immediately On-Site

Of course, the most objective when there is a fire is to put it out, but firefighters must be conscious of the toxic contamination from foams. There are multiple response techniques that can be used if there is a firefighting foam spill containing PFOA. Mechanical containment or recovery techniques using booms, barriers, and/or skimmers, can be used “to capture and store the spilled material until it can be disposed of properly." Chemical and biological methods can be used such as dispersing and gelling agents. Physical methods such as oxidation and on-site treatment techniques can also be employed. Using these techniques could reduce costs in the end if long-term remediation can be avoided. (U.S. EPA, 2008)

When there is a spill, run-off should be contained for subsequent treatment and disposal when possible. Access to drainage systems should be minimized by adding barriers such as sand and hay barrels. For large-scale spills using fluorosurfactant foams, such as those used to fight motorway incidents, aircraft crashes, petrol station fires, fires involving shipping, or harbor facilities, alternative clean up strategies must be sought (Klein, 2009).

6.7.3 Increase Industrial Protocols

When fluorosurfactant foams must be used in drainage pipes in the case of a fire in industrial buildings, storage techniques should be investigated. "Good bunding of storage areas, with bund volumes calculated to take all the stored volume of fuel plus the foam used to control the fire, together with drainage systems that can be isolated, provide one solution." This technique will make sure that there is enough foam to suppress a fuel fire, although it will not discharge more foam than necessary. Foam for long-term storage should not be allowed in a building and there should be a limit on the amount of storage of fluorosurfactant foams corresponding to the amount of fuel on site. (Klein, 2009)

To reduce the likelihood of an accidental release of foam, fire suppression systems in buildings should be inspected at least once a year, in accordance with Title 20 of the Code of Federal Regulations under the United States Department of Labor (U.S. Department of Labor). Firefighting foams should be stored properly in steel, glass reinforced plastic, or high density polyethylene tanks and discarded after surpassing shelf life (Angus Fire).

In buildings that have fluorosurfactant foam, there should be remedial techniques on-site in the case that foam has to be used. Options could include catch basins for the foam, treatment equipment, and barriers to reduce run-off. This would reduce the chances of contamination and save the company money over time from not having to remediate more in the end.

6.7.4 Require Pollution Liability Insurance

Contractors and businesses currently have the option of buying pollution liability insurance if they have risks of a pollution incident. The insurance "… helps protect these companies from the liability and financial loss that can result when a covered operation results in a pollution incident"

(Chubb Group of Insurance Companies, 2012). It would be beneficial for a company that uses firefighting foam with fluorosurfactants to have pollution insurance in case there is a significant discharge of firefighting foam into the environment. A company with liability insurance is more likely to properly and quickly remediate contamination from PFOA than a company that does not have the liability insurance because they do not have to worry as much about money and the insurance provider will assist wotj the remediation for the company. Requiring insurance would the beneficial to the public although it is costly for businesses.

6.7.5 Update Clean Water Act

The EPA has recently formed a fluorosurfactant action group to decide how to regulate PFOA and other fluorosurfactants. Because PFOA is not regulated in the Clean Water Act (CWA), drinking water facilities are not mandated to test for PFOA. PFOA should be regulated in the Clean Water Act with a maximum contaminant level (MCL) of 0.4 ppb. This is currently the suggested limit as set by EPA for drinking water. The problem with changing the Clean Water Act and requiring drinking water utilities to treat water for PFOA is that this regulation would take years to enforce.

6.7.6 Treat at Drinking Water Utilities

Public drinking water utilities have the responsibility of providing clean drinking water to consumers. There are numerous contaminants regulated by the CWA, all which are tested and treated for at drinking water facilities. PFOA should be a regulated contaminant under the CWA and therefore should be tested and treated to 0.4 ppb in drinking water utilities (as suggested by the EPA). The results from the laboratory experiments described in this report show that F200 activated carbon is a preferred treatment technique to remove PFOA in water. Drinking water facilities should test for PFOA and if the PFOA concentration is above 0.4 ppb then the utility must treat the water. This can be done using an activated carbon reactor. Activated carbon is fairly inexpensive and extremely available so it is very suitable for drinking water facilities. A private drinking water facility should sample and treat for PFOA although it is the consumer's preference whether they want to treat for PFOA or not. PFOA does not need to be regulated in wastewater since it usually does not enter the drinking water supply.

6.7.7 Treat In-Home

As mentioned above, adsorption with F200 activated carbon was the most successful treatment technique to remove PFOA in water. If drinking water in a home is contaminated with PFOA (with a concentration above 0.4 ppb), a possible solution is to implement a small activated carbon system for each fixture that would be used for drinking. The amount of activated carbon needed to remove PFOA from one fixture (i.e. a sink) is extremely small and the filter would not have to be replaced until at least one year. The most optimal system would include two cylinders in series, each with activated carbon. The first cylinder would be the main filter whereas the second would be there in case the first malfunctioned. There should be a valve at the bottom of the first cylinder to sample water that passes through the filter and make sure the filter is working properly. If it needs to be changed, other valves can be turned to reroute the water to only go through the second filter. The second filter could be changed as well.

6.8 Conclusions

There are many options to consider when trying to decide what should be done to limit exposure of PFOA to humans. There seem to be three common themes: liability, treatment, and limiting the use of foams. It seems as though in order to significantly reduce the risk of being exposed to PFOA, at least one action within each category must be sought. It is important to reduce the risk of contamination via PFOA by properly storing and maintaining foam with PFOA, require insurance for businesses with large amounts of foam on site, and make regulations more stringent. Discharges of foam should be contained at the spill site so that PFOA is not released into surface waters. In order to reduce the risk of drinking contaminated water with PFOA, the contaminated water must be treated. This could happen in a home or at a drinking water facility. The most optimal treatment method is using F200 activated carbon. Finally, limiting and/or banning fluorosurfactant foams and PFOA would be ideal so that contamination would be significantly reduced although it would take years to see reduced concentrations in drinking water.

The problem of PFOA exposure to humans is an emerging problem that needs to be addressed. The government should be responsible for responding to this problem mainly because they can enforce standards like regulating PFOA in the CWA. This, in turn, would require public drinking water utilities to monitor and treat PFOA in water and would allow for safe drinking water. The government could also ban foams and materials consisting of PFOA which would reduce exposure to humans. A combination of these two efforts from the government would eventually phase out PFOA in water.

For the short-term, an in-home filer would be the most optimal solution. It would completely remove PFOA in water so there would be no need to worry about drinking PFOA. Also, it is very small and could fit under a sink. There would be little maintenance and it would only have to be changed at minimum once a year. Finally, it is extremely economic. Activated carbon is very inexpensive and PVC piping and valves that would connect the water line to the filter are inexpensive as well. It would be interesting to find out if a Britta filter works to filter PFOA. If so, a Britta filter would be an ideal short-term fix since it is very inexpensive and very available.

Chapter 7: Design of a Granular Activated Carbon System

7.1 Background and Assumptions

FILTRASORB 200 (F200) granular activated carbon (GAC) is commonly used as a filter in households to remove harmful chemicals and bacteria in water. PFOA was removed from water using F200 in the laboratory, so it is possible that PFOA can be removed from an in-home F200 activated carbon system. Because PFOA is not volatile and only dermally harmful at extreme concentrations in water, treatment of PFOA in water is only needed at fixtures where water is being ingested, i.e. sinks (Bull & Foxall, HPA Compendium of Chemical Hazards PFOS + PFOA, 2009).In order for the system to exclusively filter water going to a specific fixture, a system must be implemented at individual fixtures. For houses with small children, a larger system that could treat all of the water coming into a house might be optimal since children tend to drink from other sources than sinks. It might also be more economical to implement one large system to filter all of the influent water rather than to implement multiple systems at different fixtures.

The U.S. Environmental Protection Agency has set a maximum contaminant level goal (MCLG) at 0.4 ppb so an F200 system would need to treat PFOA to a concentration below 0.4 ppb. Based on the case studies analyzed in this report, an influent concentration of PFOA in water was assumed to be 25 ppb. This number is higher than the reported concentrations; however, it is important to mitigate for higher concentrations in the case higher concentrations are present. The life of the activated carbon is two years so that there is a sufficient cylindrical volume of activated carbon. Two years also allows for ease of maintenance on the system. A typical household of three people will use one sink for around 15 minutes per day, so the gallons used per day average to be around 45 per faucet. The Freundlich equilibrium isotherm model is used to find the mass adsorbed at equilibrium because this model fit the experimental F200 data best.

This section will design a point-of-use F200 GAC system, based on the removal results obtained in the laboratory.

7.2 Design Explanation

With a PFOA concentration of 25 ppb in the drinking water supply of an average household, in order to remove the concentration of PFOA to 0.4 ppb, an F200 activated carbon system could be installed at each fixture. The volume of F200 activated carbon must be found in order to successfully remove PFOA to 0.4 ppb.

According to the American Water Works Association, an average fixture at a home has a pressure of 35 psi at outlet. For one sink with a ½ inch connection, the flow rate is about 3 gallons per minute (gpm) (American Water Works Association, 1975). If the sink is used for a total of 15 minutes per day, then the average flow rate would be 0.0313 gpm. To design for a system that would need to be replaced every two years, the volume of water that would flow out of one fixture for a total of two years would be 32924 gallons, as found in Equation 28.

$$V_{water} = (Q)(time) \tag{Equation 28}$$

$$Q = 0.0313\ gpm\ for\ one\ sink\ over\ the\ course\ of\ one\ day\ (15\ min.running\ faucet)\ (45\ gpd)$$

$$time = 2\ years = \ 1051897.55\ minutes$$

$$V_{water} = 0.0313\ \frac{gallons}{minute}(1051897.55\ minutes)$$

$$V_{water} = 32924\ gallons$$

Using the Freundlich equilibrium isotherm model derived in the results portion for F200 activated carbon, the mass of PFOA adsorbed at equilibrium (q_e) can be found, as shown in Equation 29. The Freundlich coefficient, K_f, was experimentally found to be 16.15 (mg/g)(L/mg)0.265, C_e is the influent concentration of PFOA which is 0.025 mg/L or 25 ppb, and 1/n is the dimensionless Freundlich constant which was found to be 0.265. The resulting adsorbance at equilibrium (q_e) was calculated at 6.076 mg/g.

$$q_e = (K_f)(C_e^{\frac{1}{n}}) \tag{Equation 29}$$

$$\frac{1}{n} = 0.265$$

$$K_f = 16.15\ \left(\frac{mg}{g}\right)\left(\frac{L}{mg}\right)^{0.265}$$

$$C_e = influent\ PFOA\ concentration = 25\ ppb = 0.025\frac{mg}{L}$$

$$q_e = \ 16.15\ \left(\frac{mg}{g}\right)\left(\frac{L}{mg}\right)^{0.265}(0.025\frac{mg}{L}^{0.265})$$

$$q_e = 6.076\frac{mg}{g}$$

Finally, to find the volume of activated carbon needed, the bed life design approach for GAC can be used, shown in Equation 30. Equation 28 was used to determine the volume of water that would flow out of a household sink fixture in 6 months, which would be around 1397 gallons, or 5289 liters. q_e was found using Equation 29 as 6.076 mg/g. The bulk density for F200 GAC is 0.58 g/cm^3 (Calgon Carbon Corporation, 2009). The influent concentration of PFOA was assumed to be 25 ppb or 0.025 mg/L. Solving equation 30, the volume of F200 activated carbon needed to remove PFOA in water to a concentration below 0.4 ppb is 0.0312 ft^3.

$$V_{GAC} = \frac{V_{water}}{\frac{q_e(\rho_{GAC})}{C_o}} \qquad \text{(Equation 30)}$$

$$V_{water} = 32924\ gallons = \ 124631\ L$$

$$q_e = 6.076\frac{mg}{g}$$

$$\rho_{GAC} = bulk\ density\ of\ F200\ granular\ activated\ carbon = 0.58\frac{g}{cm^3} = 580\ \frac{g}{L}$$

$$C_o = influent\ PFOA\ concentration = 25\ ppb = 0.025\frac{mg}{L}$$

$$V_{GAC} = \frac{124631\ L}{\frac{(6.076\ \frac{mg}{g})(\ 580\frac{g}{L})}{0.025\frac{mg}{L}}}$$

$$V_{GAC} = \ 0.884\ L = .00088\ m^3 = 0.0312\ ft^3$$

Because the volume of F200 GAC needed is so small, the volume of an actual cylinder must be much larger. It would be sensible to design for cylinder with a height of 10 inches and a radius of 3 inches. This would yield a volume of 301.833 cubic inches. This calculation is shown in Equation 31. This type of system is extremely feasible for a fixture at a home or business.

$$V_{cylinder} = \pi r^2 h \qquad \text{(Equation 31)}$$

$$Desired\ radius: 3\ inches$$

$$Desired\ height: 10\ inches$$

$$V_{cylinder} = 3.1415(3\ inches^2)(10\ inches)$$

$$V_{cylinder} = 301.834\ inches^2$$

7.3 Schematic

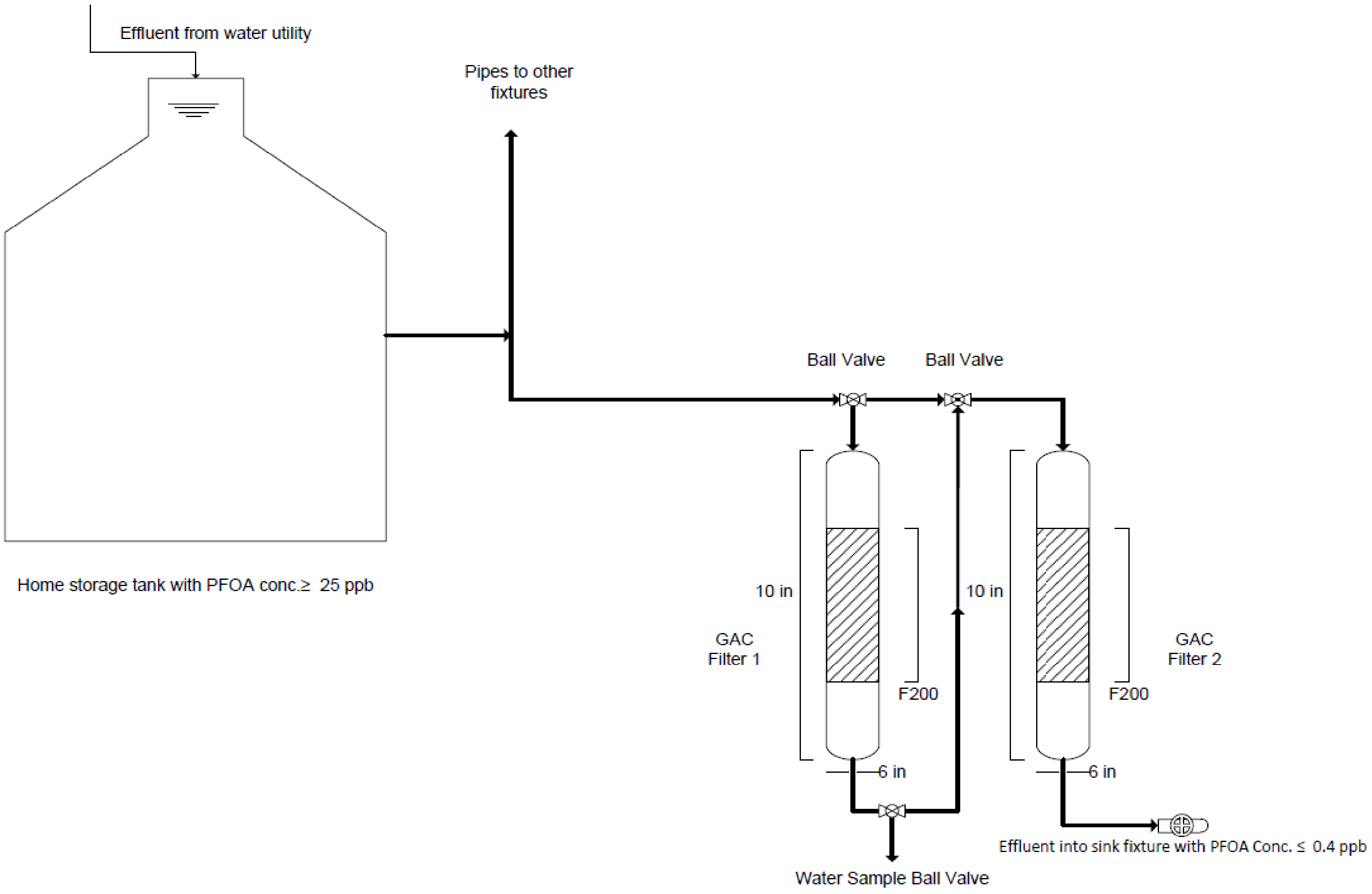


Figure 22: In-home single faucet F200 filter design

The proposed in-home F200 granular activated carbon system is designed to treat water contaminated with PFOA for one single outlet. The water is pumped from a treatment plant into a holding tank where it is then distributed to fixtures. Each drinking fixture, i.e. sink, would contain a filter in series. The water would run through the first F200 cylinder filter and then through the second F200 cylinder filter which would treat the PFOA and discharge out of a faucet. Each cylinder would contain a minimum volume of 0.00088 m^3 of F200. There is a ball valve at the end of the first filter in order for samples to be periodically taken to verify the activated carbon is successfully removing PFOA. If concentrations coming out of the sample after being filtered through the first cylinder have a concentration higher than 0.4 ppb then the ball valve located directly above the first cylinder will be turned so that water will bypass the first filter and into the second. This will allow the water to be filtered using the second cylinder filter while the first filter is replaced. Samples can be tested from the second cylinder only by closing off the first cylinder and sampling water through the faucet. The filters are designed in series to ensure that influent water is always being treated and to allow for a backup filter when the first is out of order.

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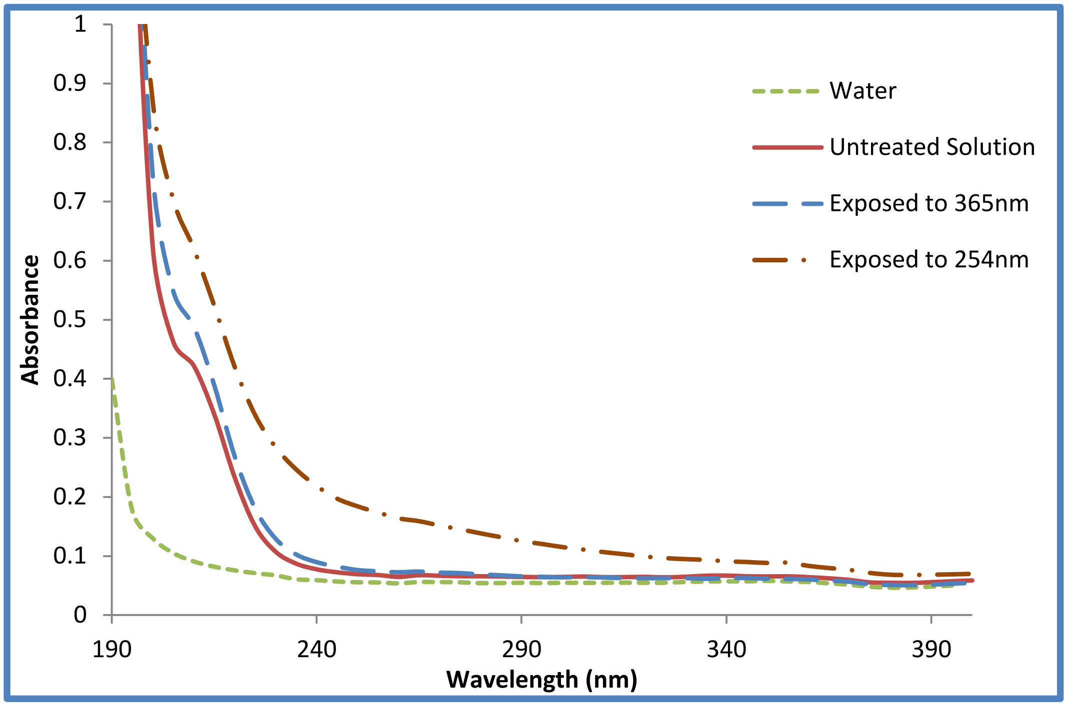
Appendix I

Standard Curve

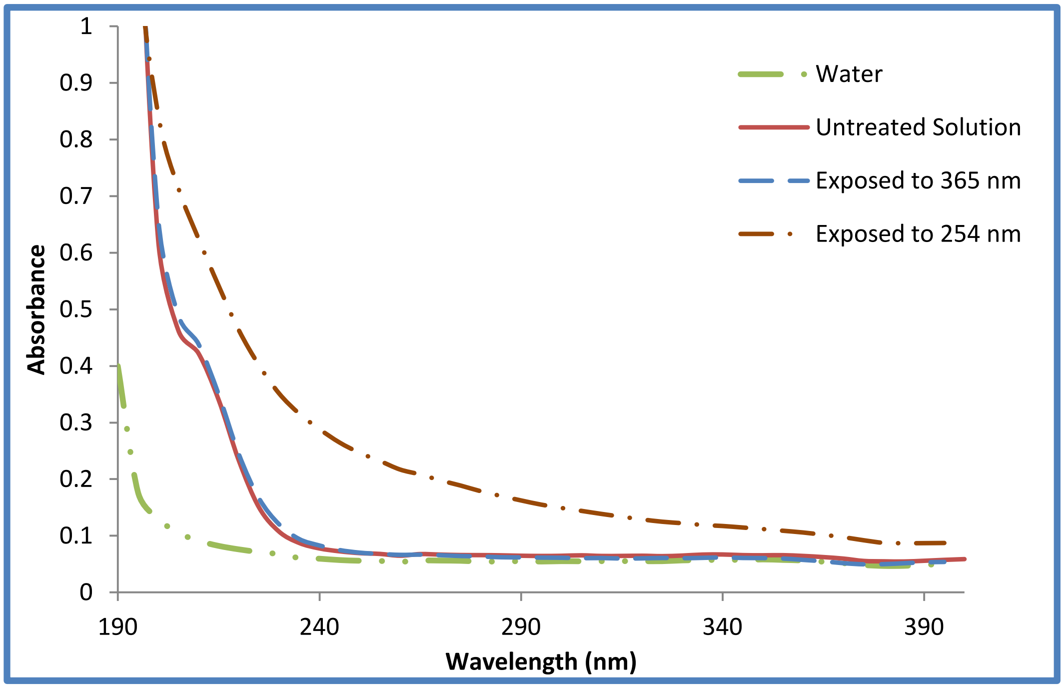
PFOA conc. (mg/L)	*PFOA conc. (mol/L)*	*Theoretical abs*	*Actual abs. [Run # 1]*	*Actual abs. [Run # 2]*	*Average actual abs.*	*Percent Difference*
100	0.000242	0.08307774	0.0812	0.0811	0.08115	2.32
200	0.000483	0.16615548	0.1667	0.1663	0.1665	0.21
300	0.000725	0.24923322	0.254	0.254	0.254	1.91
400	0.000966	0.33231096	0.3381	0.3415	0.3398	2.25

Appendix II

UV Treatment



Absorbance across the UV spectra after 30 minutes of exposure



Absorbance across the UV spectra after 75 minutes of exposure.

Wavelength (nm)	Water	Absorbance in Solution							PFOA Absorbance						
		Untreated	30 mins		60 mins		75 mins		Untreated	30 mins		60 mins		75 mins	
			365 nm	254 nm	365 nm	254 nm	365 nm	254 nm		365 nm	254 nm	365 nm	254 nm	365 nm	254 nm
190	0.3997	2.4500	2.5453	2.2738	2.6070	2.2157	2.4749	1.8625	2.0503	2.1456	1.8741	2.2073	1.8160	2.0752	1.4628
195	0.1769	1.3141	1.4218	1.3324	1.3345	1.4398	1.3078	1.1375	1.1372	1.2449	1.1555	1.1576	1.2629	1.1309	0.9606
200	0.1300	0.6230	0.7434	0.8685	0.6441	1.0700	0.6623	0.8449	0.4930	0.6134	0.7385	0.5141	0.9400	0.5323	0.7149
205	0.1051	0.4630	0.5484	0.7036	0.4841	0.9468	0.4897	0.7148	0.3579	0.4433	0.5985	0.3790	0.8417	0.3846	0.6097
210	0.0910	0.4224	0.4888	0.6207	0.4380	0.8154	0.4391	0.6253	0.3314	0.3978	0.5297	0.3470	0.7244	0.3481	0.5343
215	0.0820	0.3403	0.3893	0.5239	0.3513	0.6886	0.3501	0.5420	0.2583	0.3073	0.4419	0.2693	0.6066	0.2681	0.4600
220	0.0758	0.2331	0.2685	0.4203	0.2404	0.5666	0.2445	0.4636	0.1573	0.1927	0.3445	0.1646	0.4908	0.1687	0.3878
225	0.0711	0.1503	0.1803	0.3385	0.1565	0.4689	0.1666	0.4017	0.0792	0.1092	0.2674	0.0854	0.3978	0.0955	0.3306
230	0.0673	0.1073	0.1291	0.2842	0.1114	0.3941	0.1205	0.3517	0.0400	0.0618	0.2169	0.0441	0.3268	0.0532	0.2844
235	0.0607	0.0872	0.1026	0.2467	0.0877	0.3397	0.0944	0.3159	0.0265	0.0419	0.1860	0.0270	0.2790	0.0337	0.2552
240	0.0593	0.0776	0.0895	0.2186	0.0768	0.2963	0.0831	0.2887	0.0183	0.0302	0.1593	0.0175	0.2370	0.0238	0.2294
245	0.0569	0.0725	0.0819	0.1972	0.0688	0.2628	0.0750	0.2650	0.0156	0.0250	0.1403	0.0119	0.2059	0.0181	0.2081
250	0.0557	0.0693	0.0762	0.1842	0.0659	0.2376	0.0704	0.2467	0.0136	0.0205	0.1285	0.0102	0.1819	0.0147	0.1910
255	0.0553	0.0679	0.0740	0.1737	0.0637	0.2201	0.0681	0.2324	0.0126	0.0187	0.1184	0.0084	0.1648	0.0128	0.1771
260	0.0539	0.0648	0.0725	0.1639	0.0631	0.2045	0.0665	0.2173	0.0109	0.0186	0.1100	0.0092	0.1506	0.0126	0.1634
265	0.0561	0.0676	0.0736	0.1591	0.0643	0.1961	0.0669	0.2085	0.0115	0.0175	0.1030	0.0082	0.1400	0.0108	0.1524
270	0.0560	0.0667	0.0718	0.1518	0.0636	0.1859	0.0659	0.1981	0.0107	0.0158	0.0958	0.0076	0.1299	0.0099	0.1421
275	0.0556	0.0659	0.0710	0.1454	0.0627	0.1770	0.0645	0.1890	0.0103	0.0154	0.0898	0.0071	0.1214	0.0089	0.1334
280	0.0543	0.0658	0.0689	0.1385	0.0617	0.1682	0.0636	0.1790	0.0115	0.0146	0.0842	0.0074	0.1139	0.0093	0.1247
285	0.0544	0.0654	0.0672	0.1320	0.0611	0.1595	0.0623	0.1706	0.0110	0.0128	0.0776	0.0067	0.1051	0.0079	0.1162
290	0.0549	0.0647	0.0655	0.1254	0.0605	0.1525	0.0620	0.1627	0.0098	0.0106	0.0705	0.0056	0.0976	0.0071	0.1078
295	0.0543	0.0643	0.0646	0.1205	0.0603	0.1452	0.0616	0.1553	0.0100	0.0103	0.0662	0.0060	0.0909	0.0073	0.1010
300	0.0549	0.0646	0.0639	0.1153	0.0603	0.1384	0.0614	0.1494	0.0097	0.0090	0.0604	0.0054	0.0835	0.0065	0.0945
305	0.0547	0.0654	0.0641	0.1111	0.0605	0.1340	0.0606	0.1442	0.0107	0.0094	0.0564	0.0058	0.0793	0.0059	0.0895
310	0.0549	0.0643	0.0635	0.1068	0.0601	0.1279	0.0609	0.1388	0.0094	0.0086	0.0519	0.0052	0.0730	0.0060	0.0839
315	0.0550	0.0644	0.0625	0.1032	0.0594	0.1244	0.0600	0.1339	0.0094	0.0075	0.0482	0.0044	0.0694	0.0050	0.0789
320	0.0549	0.0647	0.0623	0.0993	0.0597	0.1190	0.0603	0.1292	0.0098	0.0074	0.0444	0.0048	0.0641	0.0054	0.0743

325	0.0549	0.0640	0.0624	0.0966	0.0590	0.1152	0.0610	0.1251	0.0091	0.0075	0.0417	0.0041	0.0603	0.0061	0.0702
330	0.0563	0.0650	0.0625	0.0949	0.0603	0.1121	0.0606	0.1224	0.0087	0.0062	0.0386	0.0040	0.0558	0.0043	0.0661
335	0.0568	0.0667	0.0614	0.0936	0.0592	0.1105	0.0612	0.1194	0.0099	0.0046	0.0368	0.0024	0.0537	0.0044	0.0626
340	0.0573	0.0669	0.0624	0.0912	0.0610	0.1091	0.0619	0.1175	0.0096	0.0051	0.0339	0.0037	0.0518	0.0046	0.0602
345	0.0572	0.0658	0.0627	0.0900	0.0614	0.1064	0.0610	0.1148	0.0086	0.0055	0.0328	0.0042	0.0492	0.0038	0.0576
350	0.0580	0.0655	0.0614	0.0884	0.0610	0.1043	0.0608	0.1121	0.0075	0.0034	0.0304	0.0030	0.0463	0.0028	0.0541
355	0.0571	0.0657	0.0611	0.0889	0.0599	0.1016	0.0600	0.1091	0.0086	0.0040	0.0318	0.0028	0.0445	0.0029	0.0520
360	0.0561	0.0643	0.0603	0.0835	0.0593	0.0974	0.0576	0.1060	0.0082	0.0042	0.0274	0.0032	0.0413	0.0015	0.0499
365	0.0539	0.0623	0.0583	0.0798	0.0571	0.0944	0.0551	0.1019	0.0084	0.0044	0.0259	0.0032	0.0405	0.0012	0.0480
370	0.0514	0.0596	0.0564	0.0767	0.0548	0.0905	0.0518	0.0977	0.0082	0.0050	0.0253	0.0034	0.0391	0.0004	0.0463
375	0.0481	0.0555	0.0522	0.0715	0.0514	0.0848	0.0498	0.0923	0.0074	0.0041	0.0234	0.0033	0.0367	0.0017	0.0442
380	0.0465	0.0548	0.0508	0.0685	0.0495	0.0823	0.0501	0.0877	0.0083	0.0043	0.0220	0.0030	0.0358	0.0036	0.0412
385	0.0467	0.0545	0.0505	0.0680	0.0501	0.0810	0.0517	0.0871	0.0078	0.0038	0.0213	0.0034	0.0343	0.0050	0.0404
390	0.0484	0.0558	0.0515	0.0685	0.0508	0.0813	0.0533	0.0872	0.0074	0.0031	0.0201	0.0024	0.0329	0.0049	0.0388
395	0.0501	0.0574	0.0530	0.0691	0.0520	0.0814	0.0540	0.0875	0.0073	0.0029	0.0190	0.0019	0.0313	0.0039	0.0374
400		0.0587	0.0545	0.0700	0.0534	0.0819									

Appendix III

Controls for Activated Carbon

Blank controls of activated carbons in water		
V_w [ml]	m_{AC} [g]	Abs
10	0.0074	0.0419
10	0.0132	0.0527
10	0.0205	0.0533
10	0.0245	0.0546
10	0.0495	0.0579
10	0.0756	0.0580

Experimental and Manipulated Data for Activated Carbon

Experimental data of activated carbon adsorption of PFOA												
V_P [ml]	C_P [mg/L]	m_P [mg]	m_{AC} [g]	Absorbance				Avg Abs	Adj Avg Abs	C_e	$\%_{adsorbed}$	q_e [mg/g]
10	200	2	0.0265	0.0752	0.0774	0.0835	0.0822	0.0796	0.0250	30.06	0.85	64.13
10	200	2	0.0514	0.0672	0.0694	0.0802	0.0807	0.0744	0.0165	19.83	0.90	35.05
10	200	2	0.0753	0.0628	0.0618	0.0640	0.0644	0.0633	0.0053	6.32	0.97	25.72
10	300	3	0.0240	0.1495	0.1496	0.1536	0.1533	0.1515	0.0969	116.64	0.61	76.40
10	300	3	0.0488	0.1021	0.1016	0.1031	0.1029	0.1024	0.0445	53.59	0.82	50.49
10	300	3	0.0769	0.1119	0.1118	0.1103	0.1106	0.1112	0.0532	63.98	0.79	30.69
10	400	4	0.0255	0.2279	0.2284	0.2174	0.2168	0.2226	0.1680	202.25	0.49	77.55
10	400	4	0.0526	0.1970	0.1998	0.2172	0.2144	0.2071	0.1492	179.59	0.55	41.90
10	400	4	0.0754	0.1871	0.1882	0.1855	0.1846	0.1864	0.1284	154.49	0.61	32.56
10	500	5	0.0077	0.3973	0.3973	0.3953	0.3956	0.3964	0.3545	426.68	0.15	95.22
10	600	6	0.0134	0.4379	0.4369	0.4447	0.4436	0.4408	0.3881	467.12	0.22	99.16
10	600	6	0.0218	0.3614	0.3636	0.3538	0.3538	0.3582	0.3049	366.95	0.39	106.91
10	1000	10	0.0120	0.7666	0.7642	0.7822	0.7824	0.7739	0.7212	868.04	0.13	109.96
10	1000	10	0.0195	0.7558	0.7586	0.7677	0.7620	0.7610	0.7077	851.88	0.15	75.96

Empirical Data for Freundlich Modeling

Activated Carbon - Freudlich model - empirical data			
C_e [mg/L]	q_e [mg/g]	Ln(C_e)	Ln(q)
30.06	64.13	3.40327	4.16087
19.83	35.05	2.98724	3.55684
6.32	25.72	1.84362	3.24732
116.64	76.40	4.75907	4.33600
53.59	50.49	3.98144	3.92183
63.98	30.69	4.15851	3.42401
202.25	77.55	5.30951	4.35091
179.59	41.90	5.19068	3.73535
154.49	32.56	5.04015	3.48310
426.68	95.22	6.05603	4.55622
467.12	99.16	6.14659	4.59676
366.95	106.91	5.90521	4.67195
868.04	109.96	6.76624	4.70016
851.88	75.96	6.74745	4.33017

Empirical Data for Langmuir Modeling

Activated Carbon - Langmuir model - empirical data			
C_e [mg/L]	q_e [mg/g]	1/C_e	1/q_e
30.06	64.13	0.03326	0.01559
19.83	35.05	0.05043	0.02853
6.32	25.72	0.15824	0.03888
116.64	76.40	0.00857	0.01309
53.59	50.49	0.01866	0.01980
63.98	30.69	0.01563	0.03258
202.25	77.55	0.00494	0.01290
179.59	41.90	0.00557	0.02386
154.49	32.56	0.00647	0.03071
426.68	95.22	0.00234	0.01050
467.12	99.16	0.00214	0.01008
366.95	106.91	0.00273	0.00935
868.04	109.96	0.00115	0.00909
851.88	75.96	0.00117	0.01317

Appendix IV

Control for Zeolite Treatment	
wt. zeolite (g)	abs [avg]
0.025	0.11735
0.05	0.1781
0.075	0.202

Experimental data of zeolite treatment of PFOA										
V_P [ml]	C_P [mg/L]	m_P [mg]	$m_{zeolite}$ [g]	Absorbance		Avg Abs	Adj Avg Abs	C_e	$\%_{adsorbed}$	q_e [mg/g]
10	200	2	0.0250	0.2479	0.2479	0.2479	0.13055	157.142	0.214290138	17.14321
10	200	2	0.0500	0.2727	0.2732	0.27295	0.09485	114.1702	0.429149135	17.16597
10	200	2	0.0750	0.2548	0.2586	0.2567	0.0547	65.84194	0.670790276	17.88774
10	300	3	0.0250	0.2893	0.2964	0.29285	0.1755	211.2479	0.295840262	35.50083
10	300	3	0.0500	0.3425	0.3286	0.33555	0.15745	189.5213	0.368262389	22.09574
10	400	4	0.0250	0.3142	0.3138	0.314	0.19665	236.706	0.408234989	65.3176
10	400	4	0.0500	0.3169	0.3165	0.3167	0.1386	166.8317	0.58292077	46.63366

Zeolite Treatment of PFOA			
C_e [mg/L]	q_e [mg/g]	Ln(C_e)	Ln(q)
157.142	17.14321	5.05715	2.841602
114.1702	17.16597	4.73769	2.842929
65.84194	17.88774	4.187257	2.884116
211.2479	35.50083	5.353032	3.569556
189.5213	22.09574	5.244501	3.095385
236.706	65.3176	5.466819	4.179261
166.8317	46.63366	5.116985	3.842323

Zeolite Treatment of PFOA			
C_e [mg/L]	q_e [mg/g]	$1/C_e$	$1/q_e$
157.142	17.14321	0.006364	0.058332
114.1702	17.16597	0.008759	0.058255
65.84194	17.88774	0.015188	0.055904
211.2479	35.50083	0.004734	0.028168
189.5213	22.09574	0.005276	0.045258
236.706	65.3176	0.004225	0.01531
166.8317	46.63366	0.005994	0.021444

Appendix V

Hypochlorite

1 to 1 molar ratio of oxidant to PFOA

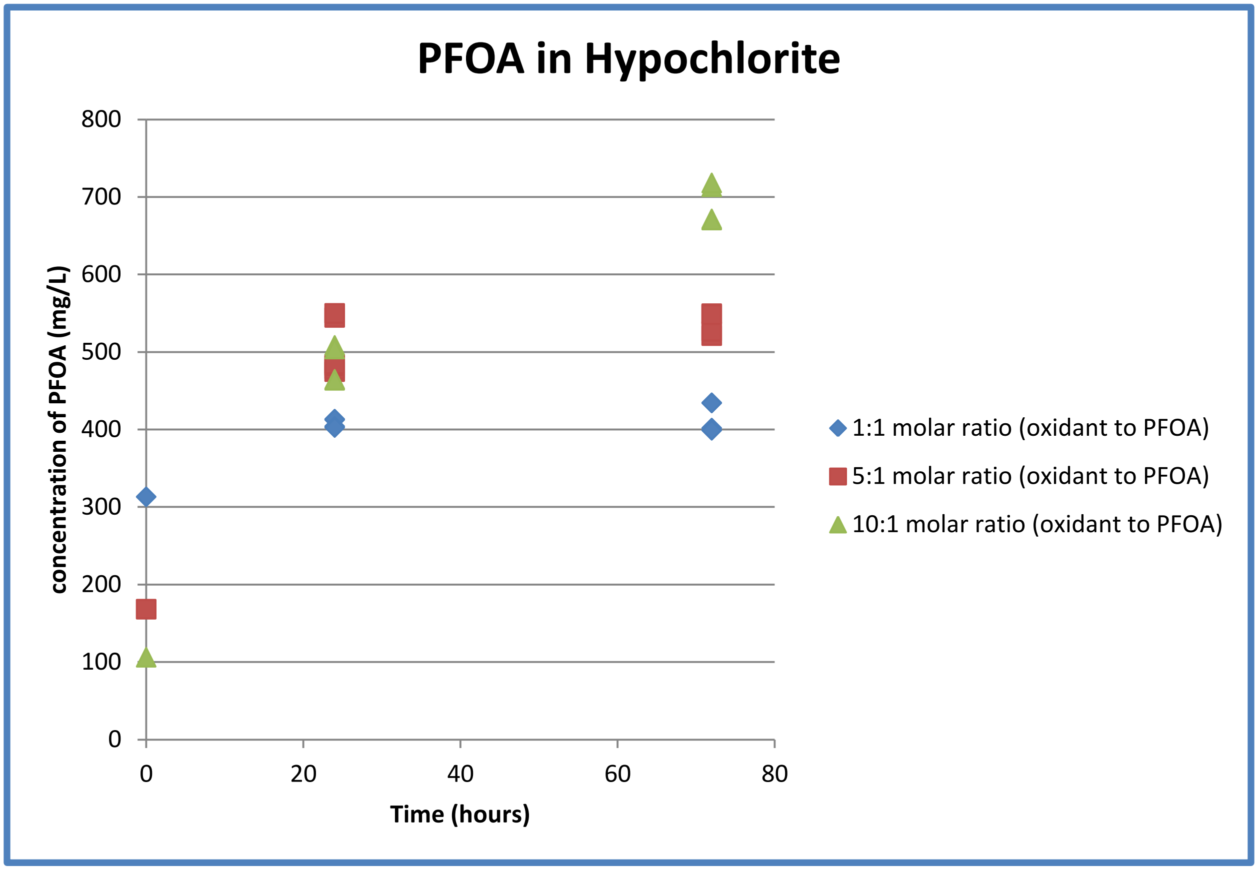
oxidant molar ratio	abs	abs corrected	PFOA conc. (mg/L)	PFOA conc. corrected (mg/L)	time (hours)
0	N/A	0.31821	313	313	0
1	0.3426	0.1239	412	149	24
1	0.3433	0.1246	413	150	24
1	0.3356	0.1169	404	141	24
1	0.3343	0.1156	402	139	24
1	0.3337	0.115	402	138	72
1	0.3313	0.1126	399	136	72
1	0.3608	0.1421	434	171	72
1	0.3606	0.1419	434	171	72

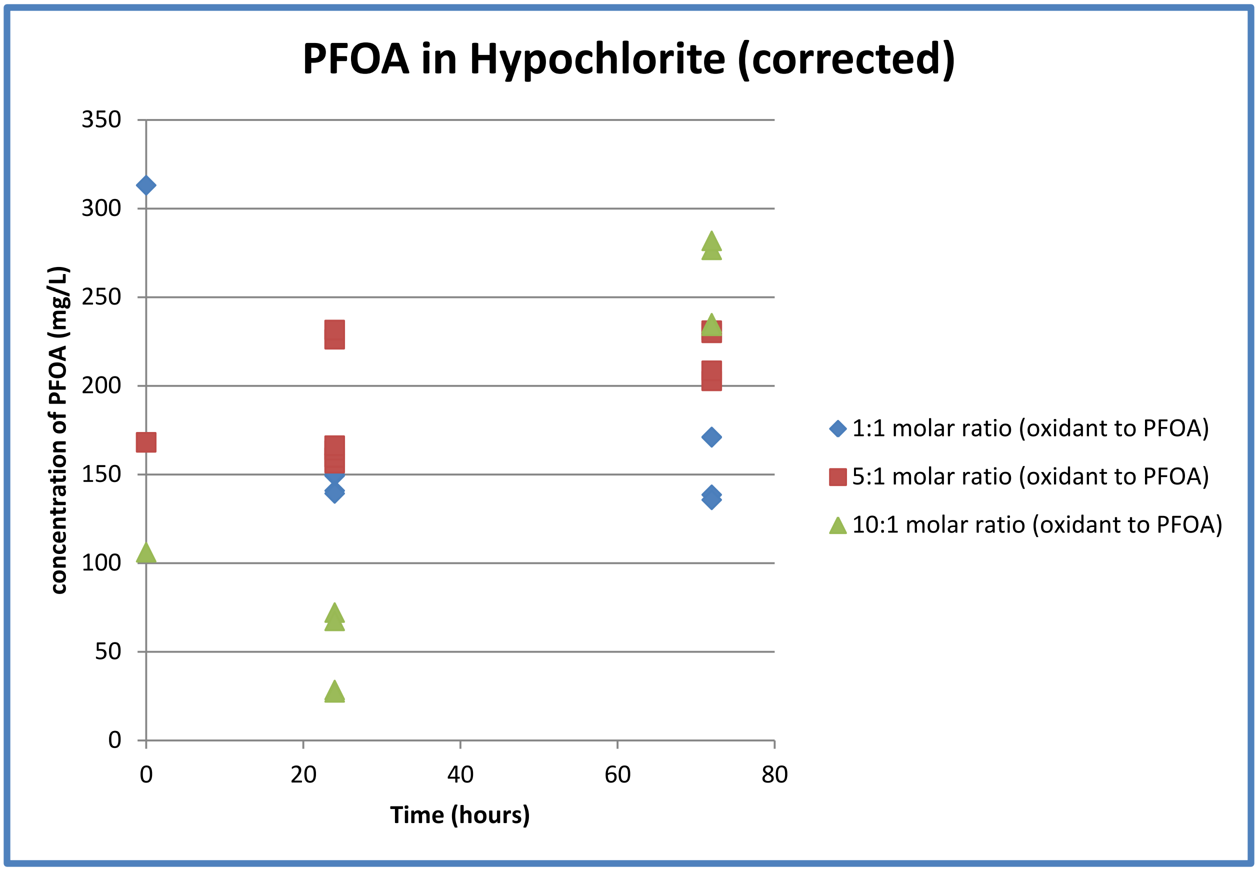
5 to 1 molar ratio of oxidant to PFOA

oxidant molar ratio	abs	abs corrected	PFOA conc. (mg/L)	PFOA conc. corrected (mg/L)	time (hours)
0	N/A	0.31821	168	168	0
5	0.3942	0.1298	474	156	24
5	0.3969	0.1325	478	159	24
5	0.4523	0.1879	544	226	24
5	0.4566	0.1922	550	231	24
5	0.4003	0.1359	482	164	24
5	0.4024	0.138	484	166	24
5	0.4328	0.1684	521	203	72
5	0.4375	0.1731	527	208	72
5	0.4563	0.1919	549	231	72
5	0.4553	0.1909	548	230	72

10 to 1 molar ratio of oxidant to PFOA

oxidant molar ratio	abs	abs corrected	PFOA conc. (mg/L)	PFOA conc. corrected (mg/L)	time (hours)
0	N/A	0.31821	106	106	0
10	0.386	0.0235	465	28	24
10	0.3849	0.0224	463	27	24
10	0.4223	0.0598	508	72	24
10	0.4184	0.0559	504	67	24
10	0.5579	0.1954	672	235	72
10	0.5567	0.1942	670	234	72
10	0.5923	0.2298	713	277	72
10	0.5965	0.234	718	282	72





Persulfate

1 to 1 molar ratio of oxidant to PFOA

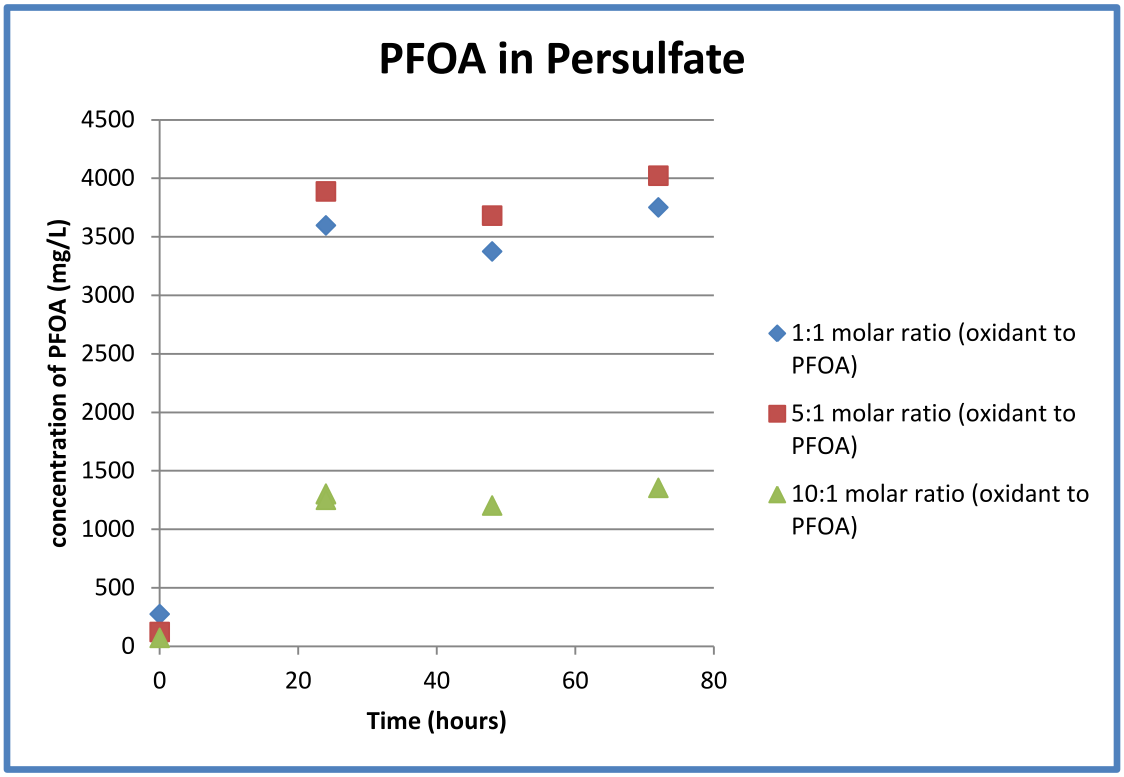
oxidant molar ratio	abs	abs corrected	PFOA conc. (mg/L)	PFOA conc. corrected (mg/L)	time (hours)
0	N/A	N/A	274	274	0
1	2.988	2.5705	3596.631	3094.09	24
1	2.8029	2.3854	3373.828	2871.287	48
1	3.1158	2.6983	3750.463	3247.922	72

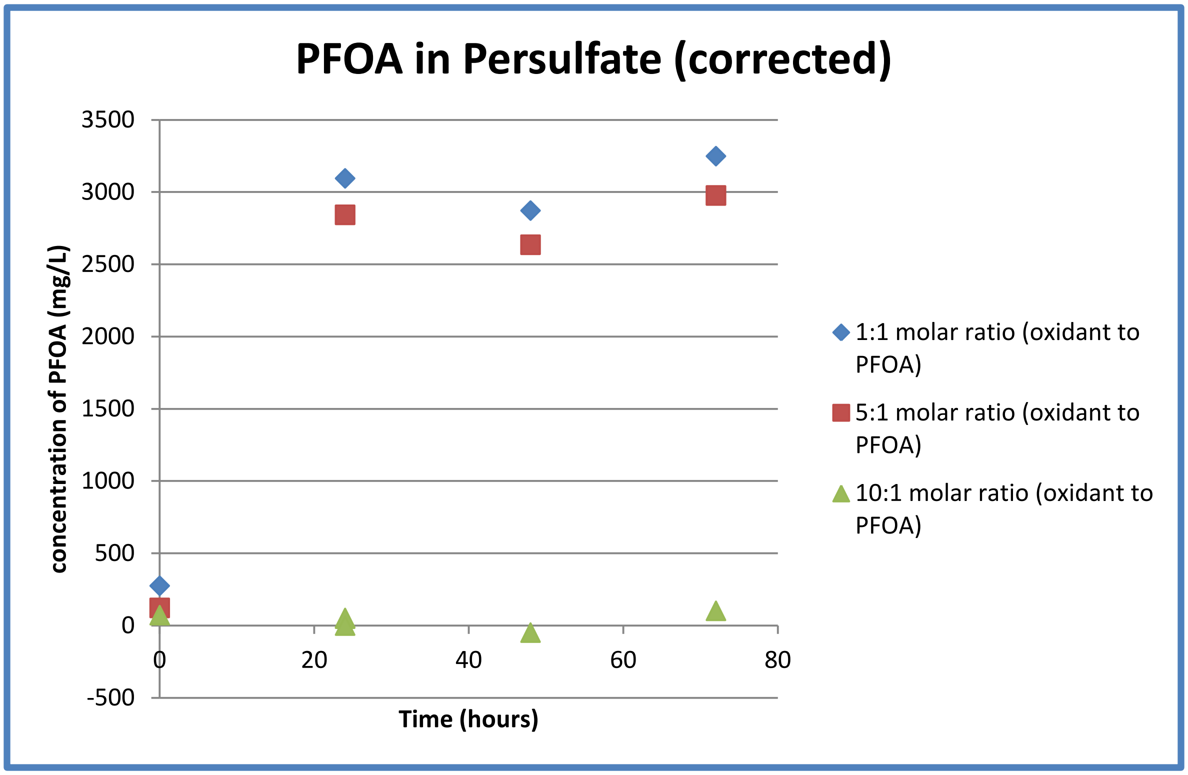
5 to 1 molar ratio of oxidant to PFOA

oxidant molar ratio	abs	abs corrected	PFOA conc. (mg/L)	PFOA conc. corrected (mg/L)	time (hours)
0	N/A	N/A	121	121	0
5	3.2293	2.3609	3887.082	2841.796	24
5	3.0573	2.1889	3680.047	2634.761	48
5	3.3407	2.4723	4021.173	2975.887	72

10 to 1 molar ratio of oxidant to PFOA

oxidant molar ratio	abs	abs corrected	PFOA conc. (mg/L)	PFOA conc. corrected (mg/L)	time (hours)
0	N/A	N/A	71	71	0
10	1.0789	0.0388	1298.663	46.70324	24
10	1.083	0.0429	1303.598	51.63838	24
10	1.0393	-0.0008	1250.997	-0.96295	24
10	0.9989	-0.0412	1202.368	-49.5921	48
10	1.1242	0.0841	1353.19	101.2305	72


PFOA in Persulfate
4500
4000
3500
3000
2500
2000
1500
1000
500
0
concentration of PFOA (mg/L)
0
20
40
60
80
Time (hours)
◆ 1:1 molar ratio (oxidant to PFOA)
■ 5:1 molar ratio (oxidant to PFOA)
▲ 10:1 molar ratio (oxidant to PFOA)


PFOA in Persulfate (corrected)
3500
3000
2500
2000
1500
1000
500
0
-500
concentration of PFOA (mg/L)
0
20
40
60
80
Time (hours)
◆ 1:1 molar ratio (oxidant to PFOA)
■ 5:1 molar ratio (oxidant to PFOA)
▲ 10:1 molar ratio (oxidant to PFOA)

Ferrate

1 to 1 molar ratio oxidant to PFOA

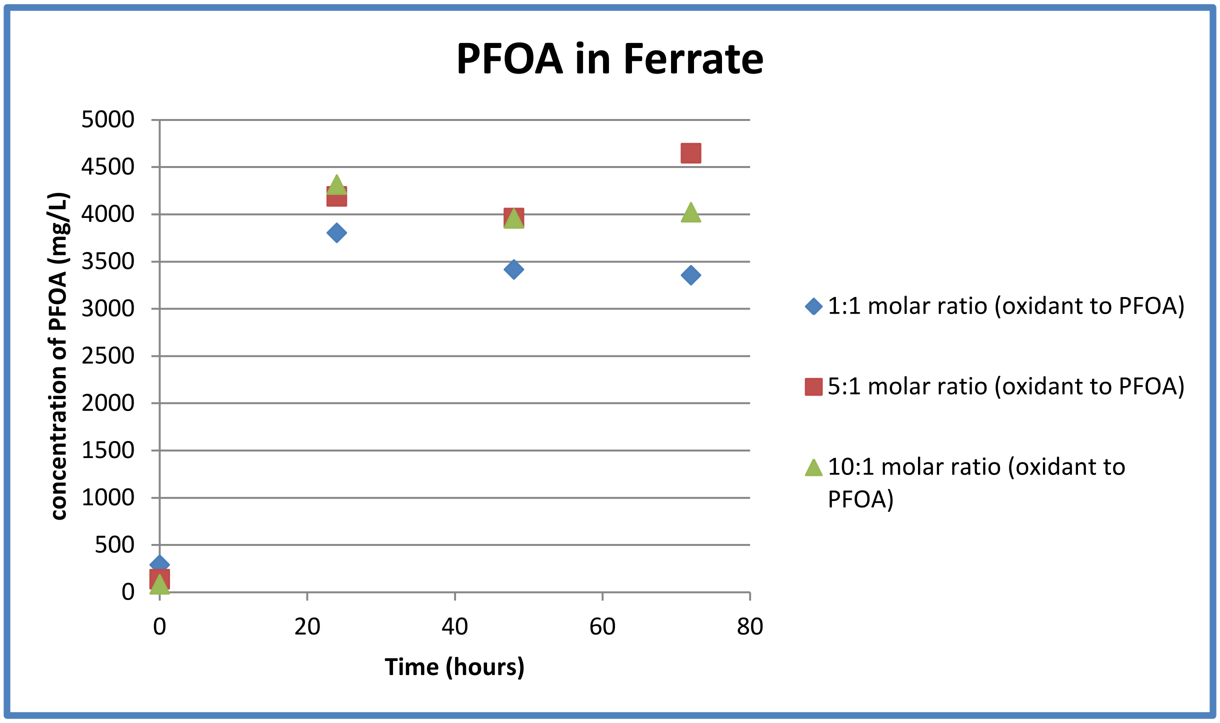
oxidant molar ratio	abs	abs corrected	PFOA conc. (mg/L)	PFOA conc. corrected (mg/L)	time (hours)
0	N/A	N/A	289	289	0
1	3.1593	0.5309	3802.824	639.04	24
1	2.8368	0.2084	3414.633	250.8494	48
1	2.7864	0.158	3353.967	190.1833	72

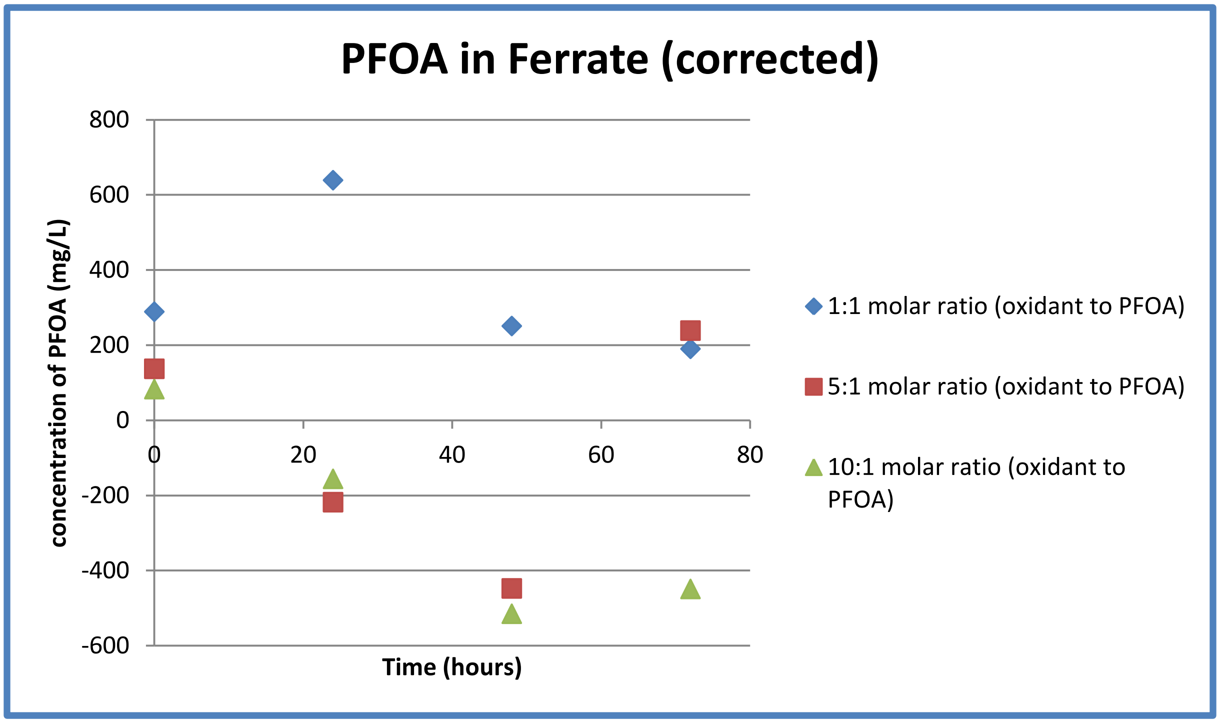
5 to 1 molar ratio oxidant to PFOA

oxidant molar ratio	abs	abs corrected	PFOA conc. (mg/L)	PFOA conc. corrected (mg/L)	time (hours)
0	N/A	N/A	137	137	0
5	3.4798	-0.1812	4188.607	-218.109	24
5	3.2891	-0.3719	3959.063	-447.653	48
5	3.8593	0.1983	4645.408	238.6921	72

10 to 1 molar ratio oxidant to PFOA

oxidant molar ratio	abs	abs corrected	PFOA conc. (mg/L)	PFOA conc. corrected (mg/L)	time (hours)
0	N/A	N/A	83	83	0
10	3.5842	-0.1295	4314.272	-155.878	24
10	3.2858	-0.4279	3955.091	-515.06	48
10	3.3407	-0.373	4021.173	-448.977	72


PFOA in Ferrate
concentration of PFOA (mg/L)
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
0
20
40
60
80
Time (hours)
◆ 1:1 molar ratio (oxidant to PFOA)
■ 5:1 molar ratio (oxidant to PFOA)
▲ 10:1 molar ratio (oxidant to PFOA)


PFOA in Ferrate (corrected)
concentration of PFOA (mg/L)
800
600
400
200
0
-200
-400
-600
0
20
40
60
80
Time (hours)
◆ 1:1 molar ratio (oxidant to PFOA)
■ 5:1 molar ratio (oxidant to PFOA)
▲ 10:1 molar ratio (oxidant to PFOA)

Permanganate

1 to 1 molar ratio oxidant to PFOA

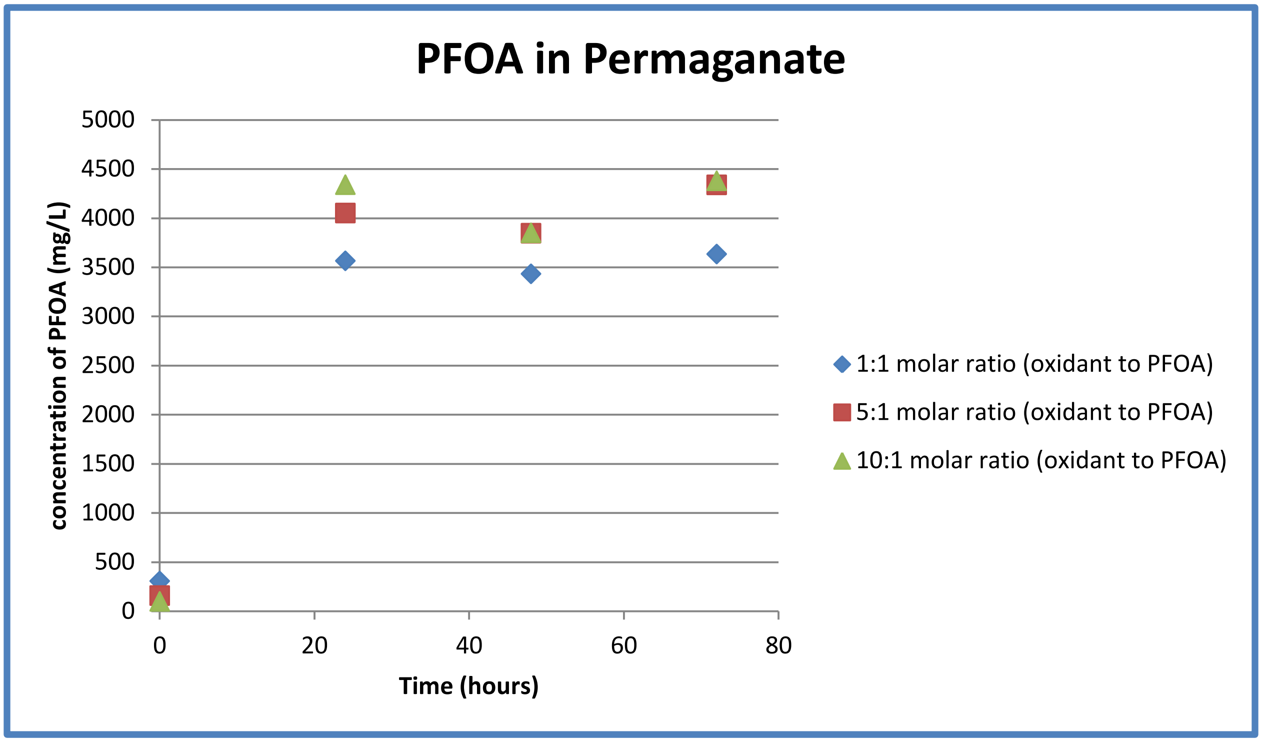
oxidant molar ratio	abs	abs corrected	PFOA conc. (mg/L)	PFOA conc. corrected (mg/L)	time (hours)
0	N/A	N/A	306	306	0
1	2.9615	-0.0858	3564.733	-103.277	24
1	2.8516	-0.1957	3432.448	-235.562	48
1	3.0187	-0.0286	3633.585	-34.4256	72

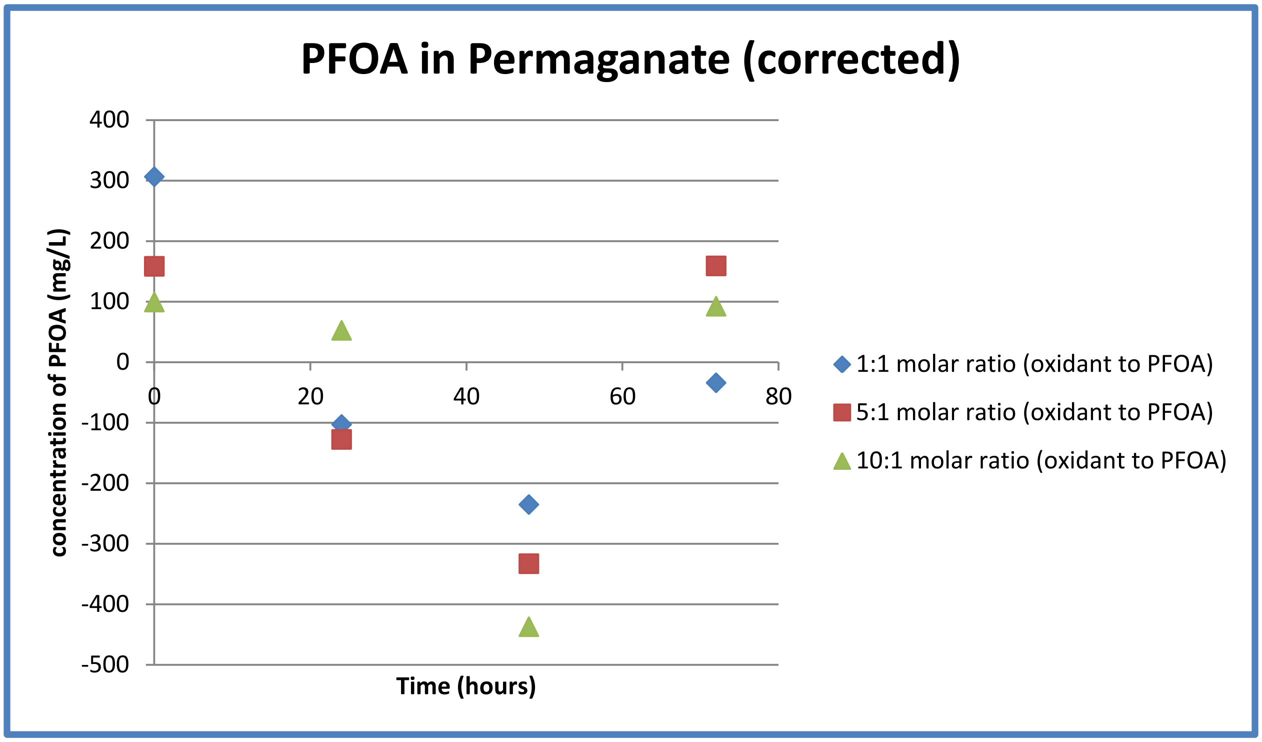
5 to 1 molar ratio oxidant to PFOA

oxidant molar ratio	abs	abs corrected	PFOA conc. (mg/L)	PFOA conc. corrected (mg/L)	time (hours)
0	N/A	N/A	158	158	0
5	3.3656	-0.1063	4051.145	-127.952	24
5	3.195	-0.2769	3845.795	-333.302	48
5	3.6037	0.1318	4337.744	158.6466	72

10 to 1 molar ratio oxidant to PFOA

oxidant molar ratio	abs	abs corrected	PFOA conc. (mg/L)	PFOA conc. corrected (mg/L)	time (hours)
0	N/A	N/A	99	99	0
10	3.6053	0.0434	4339.67	52.24023	24
10	3.1986	-0.3633	3850.129	-437.301	48
10	3.6384	0.0765	4379.512	92.08243	72


PFOA in Permaganate
concentration of PFOA (mg/L)
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
0
20
40
60
80
Time (hours)
◆ 1:1 molar ratio (oxidant to PFOA)
■ 5:1 molar ratio (oxidant to PFOA)
▲ 10:1 molar ratio (oxidant to PFOA)


PFOA in Permaganate (corrected)
concentration of PFOA (mg/L)
400
300
200
100
0
-100
-200
-300
-400
-500
0
20
40
60
80
Time (hours)
◆ 1:1 molar ratio (oxidant to PFOA)
■ 5:1 molar ratio (oxidant to PFOA)
▲ 10:1 molar ratio (oxidant to PFOA)

Scan (190-250nm) of Oxidizing Agents

wavelength (nm)	abs				
	ferrate	permanganate	persulfate	hypochlorite	PFOA
250.0391	0.783563	2.70688	0.106926	0.033594	0.025528
245.0264	0.797088	3.813266	0.129594	0.035895	0.029859
240.0115	0.815568	10	0.163973	0.039887	0.039449
234.9942	0.830724	10	0.211684	0.042914	0.05642
229.9747	0.857119	10	0.284169	0.053229	0.092419
224.9529	0.892694	3.714039	0.383208	0.065643	0.169267
219.9289	0.953618	3.54391	0.524077	0.090283	0.326686
215.0599	1.101779	3.591986	0.723075	0.135296	0.528075
210.0317	1.558856	3.472025	0.985688	0.246369	0.684988
205.0015	2.750622	3.576446	1.335785	0.556008	0.751694
199.9689	3.386068	4.030313	1.80376	1.367884	1.037385
195.0332	3.404201	3.352311	2.353058	2.557755	2.091383
189.9364	3.264445	10	2.765473	2.491041	2.824668

Hypochlorite (without centrifugation and filtration)

24 hrs				
reading #	**Cl conc. mg/L**	**abs**	**PFOA conc. mg/L**	**time (hours)**
zero	N/A	0.0006	N/A	
1	0	0.3319	400	0
2	0	0.3317	399	0
3	0	0.331	398	0
4	0	0.344	414	0
5	0	0.3397	409	0
6	1	0.3296	397	24
7	1	0.3299	397	24
8	1	0.337	406	24
9	1	0.3359	404	24
10	5	0.3541	426	24
11	5	0.3543	426	24
12	5	0.3441	414	24
13	5	0.3434	413	24
14	10	0.3415	411	24
15	10	0.3398	409	24
16	10	0.3542	426	24
17	10	0.3542	426	24
18	20	0.3415	411	24
19	20	0.3418	411	24
20	20	0.3511	423	24
21	20	0.3503	422	24
22	30	0.3344	403	24
23	30	0.3338	402	24
24	30	0.3453	416	24
25	30	0.3456	416	24

96 hrs				
reading #	**Cl conc. mg/L**	**abs**	**PFOA conc. mg/L**	**time (hours)**
zero	N/A	0.0007	N/A	
1	1	0.3321	400	96
2	1	0.3313	399	96
3	1	0.3428	413	96
4	1	0.3426	412	96
5	5	0.3513	423	96
6	5	0.3503	422	96
7	5	0.3576	430	96
8	5	0.358	431	96
9	10	0.3747	451	96
10	10	0.3732	449	96
11	10	0.3709	446	96
12	10	0.3709	446	96
13	20	0.4073	490	96
14	20	0.4071	490	96
15	20	0.3529	425	96
16	20	0.352	424	96
17	20	0.3709	446	96
18	20	0.3677	443	96
19	20	0.3638	438	96
20	20	0.3651	439	96
21	30	0.3481	419	96
22	30	0.3397	409	96
23	30	0.3605	434	96
24	30	0.3583	431	96
25	0	0.3276	394	96
26	0	0.3293	396	96
27	0	0.3403	410	96
28	0	0.34	409	96

UV-Vis Spectroscopy Data for Standard Curve for COD

Concentration of PFOA [mg/L]	**Absorbance**
0	0
100	0.001
100	0.0005
200	0.0016
200	0.0015
300	-0.0013
300	-0.0011
400	0.009
400	0