



**COMPARISON OF THE PFAS ADSORPTION CAPABILITIES OF A
COCONUT SHELL BASED GRANULAR ACTIVATED CARBON AND A
BITUMINOUS COAL BASED GRANULAR ACTIVATED CARBON**

THESIS

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Abstract

This research compares the ability of two granular activated carbons (GAC) from different material sources to adsorb perfluoroalkyl substances (PFAS) in deionized water. A bottle study design was used to conduct the research, which measured the reduction in perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS). The carbons used were the bituminous coal based Calgon Filtrasorb 600 (F600) and the coconut shell based Evoqua AquaCarb 1230CX (AC1230CX). Additionally, the research focused on the rates at which the two contaminants were removed and compared them to previous research conducted with different forms of GAC. Results showed that both GACs were capable of reducing the concentration >95% for both PFOS and PFOA, and that the more sustainable and cheaper Evoqua AC1230CX was able to compete with a bituminous coal based carbon. Additionally, PFOS was removed more quickly than PFOA, showing a preference to perfluoroalkane sulfonic acids (PFSA) over perfluorocarboxylic acids (PFCA) similar to that which has been observed in previous research.

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COMPARISON OF THE PFAS ADSORPTION CAPABILITIES OF A COCONUT SHELL BASED GRANULAR ACTIVATED CARBON AND A BITUMINOUS COAL BASED GRANULAR ACTIVATED CARBON

I. Introduction

General Issue

Per- and polyfluoroalkyl substances (PFAS) make up a class of anthropogenic, or man-made, chemicals that have been utilized for a wide variety of industrial processes since their development in the 1940s (EPA, 2018a). Their use in textile manufacturing, non-stick coatings, and stain resistant materials, among other applications, has led to their ubiquitous presence in environmental media throughout the world. This presence has resulted in significant contamination of water supplies in areas that are home to the manufacturing or use of these products. In addition to these commercial uses, PFAS compounds, most prevalently perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS), have been identified as reliable components of high-intensity fire suppressants. This quality has led to manufacturers of the firefighting agent aqueous film forming foam (AFFF) to include PFAS in their blends. This characteristic is due to the chemical composition of PFAS. A PFAS molecule has two parts: a head and a tail. The tail of the molecule is composed of carbon-fluorine bonds and is hydrophobic (repulsed by water). The makeup of the head is dependent on the type of PFAS concerned but is made of a functional group. This functional group is hydrophilic (attracted to water). This composition can be seen in Figure 1-1, specifically of a PFOA molecule. This molecular makeup makes PFAS particularly useful against Class-B hydrocarbon fires. The combination of the hydrophilic and hydrophobic qualities, as well as the surface tension lowering qualities of the surfactants, cause the

AFFF to move to the air-liquid interface and effectively suffocate the fire (Pabon & Corpart, 2002; Korzeniowski, Buck, Kempisty, & Pabon, 2018).

Despite the obvious desirable qualities of a compound that is capable of providing

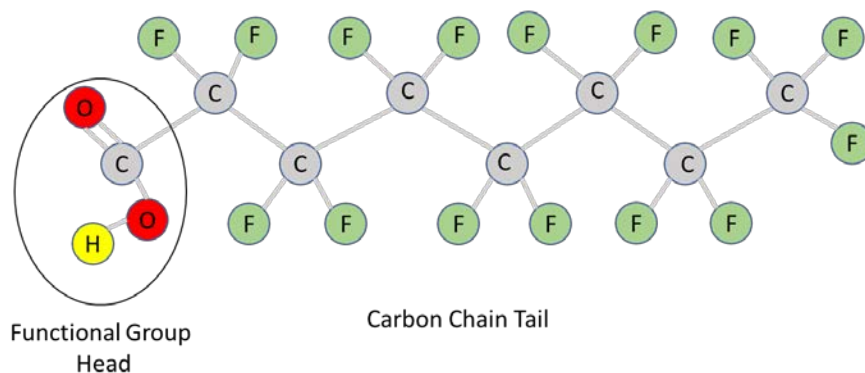


Figure 1-1: Diagram of a PFOA Molecule

such wide-ranging benefits, PFAS present several problems that have come under significant scrutiny. The first is that PFAS are bioaccumulative. This means that the compounds accumulate in organisms because they are persistent and do not readily decompose. They can easily enter the body and they are expelled slowly. This characteristic increases with the length of the carbon chain so that long-chain PFAS are more worrisome than short chain variants (Dauchy, 2019; ATSDR, 2018). Long chain PFAS are defined by the type of PFAS. Perfluoroalkane sulfonic acids (PFSAs, such as PFOS and perfluorohexane sulfonic acid (PFHxS)) with a carbon chain length of six or more are considered long-chain. On the other hand, perfluorocarboxylic acids (PFCAs, such as PFOA) with a carbon chain-length of eight or more are deemed long-chain (FluoroCouncil, 2019). Studies showing that apex predators within food chains, such as polar bears, had the highest concentrations of PFAS also indicate that these compounds biomagnify, increasing the risk of toxicological effects to these species (ATSDR, 2018). This is consistent with the bioaccumulation issue identified.

Bioaccumulation of PFAS in organisms is concerning due to the evidence of toxic effects surrounding these chemicals. Toxicological data for PFAS compounds has been gathered for some time now, with studies dating as early as 1980. After over 70 years of use in various industries, it is becoming increasingly evident that some PFAS compounds readily absorb into the tissues of humans in a manner similar to the other mammals studied (Whittaker & Heine, 2018). The focus of many of these studies is currently on long-chain PFAS that break down and metabolize at slower rates, as compared to the short-chain PFAS which, although they persist in the environment, are not thought to accumulate in mammals to the extent of the long-chain variants (Klein & Braun, 2018; Rice, 2018; Whittaker & Heine, 2018; ATSDR, 2018). Many of the studies have focused on the effects identified in laboratory rodents and other mammals, although some epidemiological studies have been conducted on humans as well. While the epidemiological studies are able to focus on the effects borne out in humans without the uncertainty of extrapolation from rodents to humans, the rodent toxicological studies can identify and isolate the effects thought to be caused by PFAS exposure with fewer confounding factors. The human body systems that are of most concern, according to the Agency for Toxic Substances and Disease Registry (ATSDR), are the liver and immune systems, as well as effects on the development of young children. Additional effects are suspected in the reproductive system and the thyroid. Finally, there is concern over the carcinogenicity of PFAS compounds (Klein & Braun, 2018; Rice, 2018).

While water treatment plants are able to remove many organisms and chemicals from drinking water supplies, PFAS compounds are not effectively removed through conventional water treatment techniques. These techniques include coagulation,

flocculation, activated sludge, sedimentation, ultraviolet (UV) technology, and others. Their low reactivity, which makes PFAS so useful in numerous applications, is responsible for this quality. It is also this characteristic that makes them so persistent in the environment (Darlington, Barth, & McKernan, 2018). This attribute has made it particularly difficult for public water systems (PWS) to eliminate PFAS to the level of newly instituted Health Advisory Levels (HALs) imposed by the United States Environmental Protection Agency (EPA). A HAL is non-regulatory in nature and is an attempt to institute some form of limit on emerging contaminants. This intermediate step is necessary to give guidance and protect the public during the lengthy process which is taken to impose final regulatory limits, called Maximum Contaminant Levels (MCLs).

Although they are non-regulatory, HALs often affect the mindset of the relevant population in a similar manner, and populations typically expect their PWS to take action to reduce the contaminant anyway. Additionally, government authorities may still take action to prevent further harm to populations affected by the contaminant, as illustrated by the case of PFOS and PFOA contamination at Wright-Patterson Air Force Base. In the case of these two chemicals, final HALs were established on May 19, 2016. The next day, the Ohio EPA sent a letter to Wright-Patterson Air Force Base mandating immediate shut down of several wells that were known to be contaminated with PFOS and PFOA, in addition to other actions such as the provisioning of other sources of water and issuance of a drinking water advisory (Brannon, 2018).

Other agencies have also promulgated alternative levels to the EPA's 70 parts per trillion (PPT). These alternative levels are not inconsequential, such as the ATSDR's Minimum Risk Level (MRL) of 7 ppt, a reduction that is one-tenth of the EPA's HAL

(ATSDR, 2018). While it should be noted that this MRL is still in draft form and awaiting further review, this sharp reduction in one agency's recommended level is indicative of the ongoing research and the uncertainty surrounding effects of PFAS on human health.

These issues of low-reactivity and new guidelines present an obvious problem for PWSs, regulators, or anyone concerned about drinking water supplies being contaminated with these compounds. If conventional methods do not work, what will? Much research has been conducted looking at Granular Activated Carbon, or GAC. GAC is a common adsorbent used to treat a wide variety of contaminants in water. These can include both natural and synthetic organic compounds, and compounds that cause taste or odor in the water. Adsorption is a process by which the chemical and physical properties of the adsorbent attract another compound. This causes the targeted compound to accumulate on the surface, or at the interface between the solid and liquid phases. GAC is commonly used due to its porosity, and therefore large surface area, lending itself to accumulate high amounts of contaminants (EPA, 2007).

GAC is produced by numerous companies but is typically produced in a similar fashion. Utilizing materials that contain high carbon content (i.e. wood, peat, coal, coconut, etc.), the producer slowly heats the source with little oxygen. This process allows for the material to be dried out, as well as removes any impurities that are left in the carbon. The result is a material known as char. At this point, char is processed using various chemical and physical processes which increase the surface area and the adsorption capacity of the carbon. These processes also increase the binding capability of

the GAC and can be modified for specific contaminants that are present in the targeted water (Oxbow, 2015).

Problem Statement

PFAS presence in the environment and humans is prolific throughout the United States and globally. According to the EPA, between 1999 and 2001, a study using a sample population indicative of the United States population at large found that 99% of the people tested had detectable levels of PFOS and PFOA in their blood serum (EPA, 2019a). Due to the low reactivity of PFAS and the inefficiency of conventional water treatment techniques, alternative methods to purifying PFAS-contaminated water have been researched, to include GAC.

Other research has focused on comparing the efficiencies of different types of GAC. Because GAC can be derived from a variety of sources, characteristics such as the porosity, pore size, and surface area can vary between specific GACs. This makes some GACs more suitable to removing specific compounds (Water Quality Association, 2013). Past research has shown that virgin bituminous coal based GAC is more effective at removing PFAS from water than GACs derived from other sources. Specifically, Calgon Filtrasorb ® 600 was shown to outperform three other GAC products in the adsorption of PFOS (Schmidt, 2017).

Two of the main issues that arise when selecting a GAC to proceed with in a water treatment system are cost and renewability of the resource. The cost of the selected GAC is something that will affect the water treatment system on a recurring basis as the carbon must be replaced when it becomes saturated and fouled. This fact affects the financial bottom line of any system, whether it is a private or government run entity.

Therefore, the most cost-effective GAC that can still perform well is likely to be preferable.

In addition to the question of cost, the renewability of a resource is increasingly becoming a significant aspect of decision making. As citizen groups and leaders continue to focus on the effects that certain activities and the use of resources have on the environment and sustainability, research should focus on finding solutions that fit within the boundaries of what is sustainable. Therefore, in the search for the most effective and efficient GAC, research should focus efforts on GAC that is sustainable.

This research will compare two different types of GAC: one produced from coconut shell, and one from bituminous coal. This research differs from the past research done by Schmidt because of the use of the newly enhanced coconut shell-based carbon from Evoqua, AC1230CX. The broad marketing claim from Evoqua suggests that its product is capable of competing with the traditionally more efficient coal-based carbons when it comes to purifying water contaminated with organic compounds, such as PFAS (Evoqua, 2017). This may have effects in future research and application due to the sustainability of coconut based GAC versus coal based GAC, as well as the cost of implementing a GAC system.

Methodology

This study utilized a bottle study setup to determine the effectiveness of two different GACs on two PFAS compounds. Solutions consisting of PFAS and deionized water were placed into centrifuge tubes, along with GAC, and rotated on an automatic tumbler. At various time intervals, the tubes were removed from the tumbler and centrifuged to separate the solution from the GAC. The remaining solutions were

decanted to separate the solution containing the analyte from the carbon. Experiments were designed to determine the effectiveness of the GAC's adsorption capability on the reduction of PFAS in the water at time intervals ranging from 15 minutes to 24 hours.

Samples from the bottle studies were transported to the Environmental Protection Agency (EPA) laboratory in Cincinnati, Ohio. There, they were analyzed for concentration of PFAS and compared to the starting concentration, or C_0 , which was also analyzed. The analysis of the samples followed the EPA's Method 537, which is the process of determining concentrations of select PFAS in water. Specifically, this method uses solid phase extraction and liquid chromatography/tandem mass spectrometry (LC/MS/MS) to determine concentrations (Shoemaker & Tettenhorst, 2018).

Research Objectives and Hypotheses

This research is focused on understanding the capabilities of coconut-based GAC compared to a bituminous coal based GAC that has been utilized in earlier studies (Schmidt, 2017). There are three research objectives associated with this study.

Research Objective One

The first research objective is to determine whether one carbon is more efficient at reducing the amount of PFAS in a deionized water source. The hypothesis associated with this research objective is that there will not be a significant difference between the coconut shell-based Evoqua AC1230CX and previously more efficient Calgon Filtrasorb® 600. While Schmidt found that the F600 outperformed the other GACs in his study, AC1230CX was not available at that time and was not tested (Schmidt, 2017). Evoqua claims that this newly enhanced carbon is capable of competing with traditional bituminous coal-based carbons in the adsorption of organic compounds (Evoqua, 2017).

This research will compare the concentration at different time intervals with the initial concentration (C/C_0) for both carbons and with both PFAS compounds to determine if there is significant difference.

Research Objective Two

The second research objective is to determine whether the PFOS or PFOA is removed at a more rapid rate. The hypothesis is that the PFOS will be removed at a more rapid rate due to previous research. Multiple studies have shown that PFOS sorbs to GAC at a higher rate, potentially due to the sulfonic functional group of the PFSA creating a greater electrostatic effect when compared to the carboxylic functional group found on the perfluorinated carboxylic acid PFOA. This electrostatic effect generates a higher attraction between the PFAS compound and the carbon adsorbent when compared to the Van der Waals forces typically associated with adsorption (Appleman et al., 2014; McCleaf et al., 2017).

This research objective leads to another hypothesis regarding the removal of the compounds when they are mixed into one solution. Based on the aforementioned research, the hypothesis is that a higher rate of removal will be seen for the PFOS in the mixture. Due to the competition between the two compounds for adsorption sites, this will likely decrease the amount of PFOA removed when compared to the solution with just PFOA (Appleman et al., 2014; McCleaf et al., 2017).

Assumptions, Scope, and Limitations

This study assumed that the results from the methods used will be applicable to a full-scale treatment system. There are differences in kinetics of a full-scale system and a bottle study. This has much to do with the fact that in a full-scale, fixed bed system, the

carbon is packed together. This reduces the amount of surface area. The assumption is that this change would affect both carbons equally, and thus the results from this bottle study will still apply. Results of the tests, and comparisons between the Calgon Filtrasorb-600 bituminous coal-based GAC and Evoqua AC1230CX coconut shell-based GAC, can therefore be carried forward with future research into PFAS treatment and remediation. Additionally, this study utilized one source of water, which was deionized. Future research should be mindful of this fact with future studies that involve water sources with different matrices. These sources will not be as pure and may have co-contaminants in them which will likely compete with the PFAS for adsorption sites.

The scope of this study focused solely on water treatment techniques. While the contamination of water, in particular drinking water, is of great concern to the community of researchers investigating the problem, PFAS is also a contaminant of concern in soils and air worldwide (EPA, 2019b). This research was also focused on the evaluation and comparison of two GAC sources: the bituminous coal-based Calgon Filtrasorb-600 and the coconut shell-based Evoqua AC1230CX. Filtrasorb 600 was chosen due to a study conducted by Christopher Schmidt in 2017 which showed that it outperformed three other GAC sources in remediation of PFOS and AFFF. On the other hand, the coconut-based carbon was chosen due to new innovations in its design that are reported by Evoqua to have drastically increased its ability to adsorb various organic contaminants (Evoqua, 2017). Finally, while there are numerous PFAS present in soil, water, and air, this study focused on the ability of the two selected GACs to adsorb two of the more prevalent PFAS: PFOS and PFOA. Each of these is considered a long-chain PFAS, which are persistent in the environment, bioaccumulative, and toxic to humans. These are also two

of the common PFAS in legacy, military standard (MILSPEC) AFFF, and are thus the focus of significant attention within the DOD (ITRC, 2018).

Finally, this study faced some inherent limitations due to the equipment and substances used. While these limitations will be discussed in detail in Chapter Four, a broad understanding of them here will be useful to the reader. The first limitation came from errors induced by the equipment. Although each piece of equipment used to measure volume or mass was within its calibration period, the allowable ranges of precision and accuracy led to various levels of potential error. This was compounded by the fact that the volumes and masses of GAC and PFAS were small, and therefore the error could have been a larger percentage.

Other error was introduced by the substances themselves. In particular, the PFOS that was used was a technical grade PFOS (T-PFOS) obtained from Sigma-Aldrich. A substance that is labeled as “technical grade” has a specified range of purity that is allowable. In this instance, the certificate of analysis (COA) obtained from the Sigma-Aldrich website states that the range of concentration for their T-PFOS is 35%-45% weight-to-weight in water (Sigma-Aldrich, 2018). For the purposes of this study, the midpoint of the range was used, and the concentration was assumed to be 40%. Measurements were made accordingly. In contrast, the study used a form of PFOA that was 96% concentration and not considered technical grade.

Summary

Chapter one introduced the concept of PFAS, its various uses, and the issues presented by the ubiquitous presence of PFAS in the environment. These issues include problems of bioaccumulation and toxic effects associated with the uptake of these

compounds. This chapter also introduced GAC as a popular treatment technique for water contaminated with PFAS. The research will focus on two forms of GAC and their adsorption ability with respect to PFOS, PFOA, and a combination. Additionally, the assumptions made in the study and analysis were discussed, along with the scope and the limitations of the research. Chapter two presents previous research that has been conducted regarding PFAS, its presence, effects, and treatment. Later chapters detail the conduct of the study, its results, and conclusions that were drawn by the researcher.

II. Literature Review

Overview

The majority of chapter two is a review of the literature surrounding poly- and perfluoroalkyl substances (PFAS). The body of research surrounding PFAS is extensive and continues to grow. This research includes topics such as their presence in the environment, their toxicological properties, and the various treatment methods available that are effective in the removal of these substances. Understanding these different subjects and furthering the research into them is important due to the evidence that PFAS are bioaccumulative and toxic to numerous species, to include humans (ATSDR, 2018). Agencies focused on the health of the environment and humans should prepare to continue efforts aimed at remediating PFAS contamination due to past, present, and future manufacturing and use of these compounds. The necessity of long-term planning for remediation of environmental media affected by these compounds is due to the stable nature of PFAS produced by the strong bond between the carbon and fluorine atoms (Crone et al., 2019). Therefore, even with more stringent regulations and a focus on reduction in the use of PFAS, environmental officials will continue to have to contend with the effects for many years to come.

This thesis focuses on the treatability of perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) (sometimes referred to as perfluorooctane sulfonate and perfluorooctanoate respectively). Therefore, the majority of this literature review includes studies conducted using these two compounds. Some studies have also included work with other PFAS such as perfluorohexanesulfonic acid or perfluorohexane sulfonate (PFHxS), perfluorobutanesulfonic acid or perfluorobutane sulfonate (PFBS), and

perfluorobutanoic acid or perfluorobutanoate (PFBA). To show the scope of these authors' works, as well as some of the differences between various forms of PFAS, these comparisons were included in the literature review. These occur in the toxicological data and treatment methods sections.

Key Terms

PFAS: Per- and polyfluoroalkyl substances

PFOS: Perfluorooctanesulfonic acid

PFOA: Perfluorooctanoic acid

Effluent: Water discharged after treatment

Health Advisory Level: Non-regulatory numerical quantity of a contaminant that the EPA considers detrimental to the health of humans (Brannon, 2018)

Presence of PFAS

Various industries have utilized poly- and perfluoroalkyl substances in different ways since the substance was developed in the late 1940s. PFAS is produced by stripping hydrocarbons of their hydrogen atoms and replacing them with fluorine atoms. This process creates a new chemical structure that is a highly stable molecule. This molecule has properties that include a stronger acidic molecule, higher surface activity, and water and oil repellant features. Regulatory agencies around the world have begun to understand the ramifications that the stability and toxicity of these chemicals represent. Due to this understanding, these agencies have started regulating the different types of PFAS and the amounts allowed in various industries. The main focus of these regulations has been placed on long-chain PFAS such as PFOS and PFOA. Still, the legacy use of these substances, as well as their precursors, presents an issue of remediation that is likely

to last well into the future. Although researchers have conducted numerous studies on PFOS and PFOA, there are many more PFAS varieties that scientists have not studied. Because industry is replacing long-chain PFAS such as PFOS and PFOA with these substitutes, PFAS will continue to occur in the environment (Wang, Dewitt, Higgins & Cousins, 2017).

In one study conducted by Kaboré et al. (2018), the researchers measured the occurrence of multiple PFAS in drinking water around the world. Countries that were studied included Canada, United States, Burkina Faso, Chile, Ivory Coast, France, Japan, Mexico, and Norway. Researchers took 97 samples, with triplicates run on each sample. The study found that 86% of the tap water samples contained detectable levels of PFOA while 85% contained detectable levels of PFOS. The study also found that the maximum level for PFOA and PFOS were 4.9 ng L^{-1} and 4.1 ng L^{-1} respectively. Both of these levels are well below the EPA's Health Advisory Level (HAL) of 70 ng L^{-1} (Kaboré et al., 2017). Although these are below the limits, due to the small sample size, proliferation of PFAS in other countries, and the fact that the locations tested were not necessarily in close proximity to manufacturing sites, researchers should still be concerned. Additionally, this level may be concerning to sensitive populations such as young children, pregnant women, and elderly adults.

Other studies have focused on areas that are relatively close to PFAS discharge points. One such study was conducted by researchers in northern France near an industrial wastewater treatment plant that treats raw sewage coming from a manufacturer of various PFAS. The study investigated the river, as well as three drinking water treatment plants located downstream in order to understand the effectiveness of their

systems on PFAS removal. This study found significant amounts of compounds which are precursors to a class of PFAS called perfluorocarboxylic acids, or PFCAs. This is important because PFOA is a part of the PFCA class. Precursors are not as stable as PFCAs or PFSAAs, but their ability to breakdown into more stable varieties is concerning to regulators and researchers. While the study did not find that PFOA was the most significant contaminant, the presence of multiple precursors, some of which have not been well researched, could present issues in the future (Boiteux et al., 2017).

PFAS is also a large contributor of contamination at Department of Defense (DOD) sites. This is especially true at air bases and other installations that conduct frequent firefighting training. Legacy aqueous film forming foam (AFFF) has been in use since the 1960s as an additive to water that effectively controls large hydrocarbon fires. Although the characteristics of PFAS that control these fires are beneficial, the stability of the compounds, as well as the lack of options to remediate environmental media that is impacted, has caused high levels of contamination at these sites. Studies have indicated high levels of long-chain PFAS in multiple environmental media (soil, surface water, groundwater, etc.) at air bases and fire training areas (FTAs) (Baduel, Mueller, Rotander, Corfield & Gomez-Ramos, 2017); (Anderson, Long, Porter & Anderson, 2016).

Numerous other studies throughout literature describe similar occurrences of PFAS in environmental media. The studies discussed above suggest that the major problems and concentrations tend to occur closest to manufacturing and/or discharge sites. Although this may be the case, it is evident that the compounds are transported throughout the environment and are still found in environmental media in areas that are not in close proximity to these types of places. Although many studies find levels that are

lower than current advisory levels, the state of the science is still evolving, and PFAS is still prolific around the globe. Additionally, as toxicological and epidemiological studies become more advanced, and regulatory agencies continue to refine recommended contaminant levels, limits may dip below levels observed in studies of the general environment causing more concern for even some of the lower levels observed in historical research.

Toxicological Data

Toxicological data for PFAS compounds has been gathered for some time now, with some studies dating as early as 1980. After over 70 years of use in various industries, it is becoming more evident that some PFAS compounds readily absorb into the tissues of humans and other mammals. Compounding the problem is the fact that PFAS bioaccumulate to levels that are concerning to toxicologists and epidemiologists (Whittaker & Heine, 2018). The focus of many of these studies is currently on long-chain PFAS that break down and metabolize at slower rates when compared to short-chain PFAS which, although they persist in the environment, are not thought to accumulate in mammals and cause health concerns to the extent of the long-chain variants (Klein & Braun, 2018; Rice, 2018; Whittaker & Heine, 2018; Agency, 2018). Many of the studies have focused on the effects identified in laboratory rodents and other mammals, although some epidemiological studies have been conducted on humans as well. Both types of study present advantages and disadvantages. Epidemiological studies are able to focus on the effects borne out in humans, without the uncertainty of extrapolation from rodents or other laboratory animals to humans. However, toxicological studies that use laboratory animals can identify and isolate the effects thought to be caused by PFAS exposure with

fewer confounding factors. According to the Agency for Toxic Substances and Disease Registry (ATSDR), the liver, immune, and child developmental systems are at most risk for negative effects from PFAS exposure. Additional effects are suspected in the reproductive and thyroid systems. Finally, there is concern over the carcinogenicity of PFAS compounds (Klein & Braun, 2018; Rice, 2018). The following paragraphs will summarize the observed effects on these organ systems.

According to the ATSDR's PFAS Toxicological Profile, studies show that various PFAS compounds have significant effects on the health of the liver in rodents. Exposure to PFOS and PFOA correlated with increased liver weights, hepatocellular (liver cell) hypertrophy, and decreases in serum cholesterol and triglyceride levels. The profile also indicates that the risk of liver effects increases with the length of the carbon chain, up to a length of ten, with most of the studies involving PFOS and PFOA (Agency, 2018). Despite these findings in the majority of studies done on rodents, epidemiological studies of humans have found less correlation between PFAS exposure and these effects. Additionally, an increase in serum cholesterol was found in some humans, as opposed to the decrease found in rodents. As such, the effects on humans remain unclear for liver health (Rice, 2018)

Indicators of immunotoxicity, such as thymic and splenic atrophy, were observed in laboratory studies involving rodents and monkeys. While both rodents (rats and mice) experienced some level of atrophy, mice exhibited symptoms at a higher rate than rats. Additionally, T-dependent antibody response (TDAR) was inhibited at levels as low as 0.05 mg PFOS/kg in male mice. Epidemiological studies of humans have also observed a

suppression of the immune system, making this one of the major areas of concern in the toxicological and epidemiological communities (Agency, 2018; Rice, 2018).

Due to the sensitivity of young children populations to certain contaminants, significant attention has been paid to the effects of PFAS on developmental progress. In fact, these studies have been influential in the development of guidance values and the EPA HALs discussed previously. Rodents exposed to PFAS both *in utero* and through pregnancy have experienced increased instances of low birth weight, neonatal fatality, and developmental delays. According to Klein and Braun, these instances are not dependent on breastfeeding practices, indicating that the fetus may be susceptible *in utero* (2018). Furthermore, studies have observed that PFAS increases the rate at which puberty occurs in rodents at low levels (< 10 mg/kg/day) when compared to the control. However, at a level of 20 mg/kg/day, there was a noticeable delay in male puberty (Klein & Braun, 2018).

In studies involving rodents and exposure to PFAS compounds, the contaminant of most concern in terms of direct effect on the male reproductive system was perfluorododecanoic acid, or PFDODA. Exposure to this contaminant correlated with decreased male fertility and spermatogenesis. This occurred at 105 mg/kg. Although this was the only direct effect, other studies have shown correlations between exposure to PFAS compounds and decreased male hormones in serum, damage to the testes to include atrophy, abnormal sperm, and decreased steroidogenesis. Epidemiological studies for humans are inconclusive at this time although concerns over the above stated effects exist in the toxicological community (Rice, 2018; Agency, 2018). Effects on the female reproductive system are similarly complicated. Some doses of PFDODA and PFOS were

linked to abnormal periods of diestrus. Additionally, PFOA was found to have effects on the mammary gland development in mice that were exposed prenatally. As with the male reproductive system, epidemiological data for exposure to PFAS is inconclusive, yet still of concern due to the possible effects found in rodents. Still, some evidence exists for decreased fertility and increased time to get pregnant. Many of these effects are thought to have potential for being confounded by reverse causality. As such, the classification of PFAS as being toxic to the human reproductive system remains unclear (Rice, 2018; Agency, 2018).

Studies related to thyroid toxicity in laboratory rats are sparser than studies on the previously discussed organ systems. The results have also been mixed in outcomes and significance levels. In a study conducted by Van Otterdijk in 2007, rats administered 2700 mg/kg experienced thyroid follicular cell hypertrophy, which could lead to decreased levels of the thyroid hormones T3 and T4 (Rice, 2018). Other studies have shown that cynomolgus monkeys that were exposed to PFAS experienced decreased levels of T3 and T4, as well as rats that experienced thyroid follicular cell adenoma. In epidemiological studies, results have varied for thyroid effects from finding none to finding direct associations in the general population between serum PFOA levels and thyroid disease. Others have found negative associations between serum perfluorohexanesulfonic acid (PFHxS) levels and free T4. As with other organs, the association is still unclear for human health, and must be investigated further (Rice, 2018).

PFOA and PFOS are the primary PFAS compounds that have been studied for carcinogenic effects. Both compounds have shown tendencies to produce malignancies in

the liver. PFOA has also been linked to tumors in the pancreas and testes, while PFOS is tied to thyroid tumors in male rats. In epidemiological studies of humans, high levels of PFOA exposure have correlated with increased incidence of kidney and testicular tumors. Interactions of these compounds with human body systems can manifest themselves differently than in rats (as with other effects). It is therefore vital that studies continue to determine what levels are safe for humans, and what steps can be taken to mitigate the effects (Rice, 2018).

Treatment Methods

Researchers have conducted numerous studies to understand the physico-chemical properties of PFAS. These properties vary with carbon-chain length (categorized as short and long chain compounds), as well as functional groups (perfluoroalkane sulfonic acids and perfluoroalkyl carboxylic acids) (EPA, 2018c). As of now, the EPA recognizes three different technologies as being effective at treating PFAS: activated carbon, anion exchange resins, and high-pressure membrane filtration (EPA, 2018b). Each of these have their own advantages and disadvantages, depending on the targeted compound and the presence of other contaminants.

Granular Activated Carbon, or GAC, is a common adsorbent used to treat a wide variety of contaminants in water. These include both natural and synthetic organic compounds and compounds that cause taste or odor in the water. Adsorption is a process by which the chemical and physical properties of the adsorbent attract another compound. This causes the targeted compound to accumulate on the surface, or at the interface between the solid and liquid phases. GAC is commonly used due to its porosity and high

surface area. These properties allow carbon to accumulate high amounts of contaminants (EPA, Water Treatability Database: Granular Activated Carbon).

GAC is produced by numerous companies but is typically produced in a similar fashion. Utilizing materials that contain high carbon content (i.e. wood, peat, coal, coconut, etc.), the manufacturer slowly heats the source with little oxygen. This process allows for the material to be dried out, as well as removes impurities that are left in the material. The result is a material known as “char”. Once the char is produced, it is processed using various chemical and physical processes that increase the surface area and the adsorption capacity of the carbon. These processes also increase the binding capability of the GAC and can be modified for specific contaminants that are present in the targeted water (Oxbow, 2015).

Most of the research on GAC adsorption of PFAS has focused on long-chain PFAS compounds, such as PFOS and PFOA. However, several studies have placed some emphasis on short-chain compounds such as perfluorobutane sulfonate (PFBS) and perfluorobutanoic acid (PFBA). These studies have shown a positive correlation between the chain length of the specific PFAS compound and ability of the GAC to adsorb the contaminant. This is typically measured in breakthrough time, or the time that it takes for the adsorbent to lose the ability to adsorb the adsorbate due to saturation (Dickenson & Verdugo, 2018; Inyang & Dickenson, 2017; Carter and Farrel, 2010; McCleaf & et. al, 2017).

One issue with the use of GAC, or of other forms of activated carbon such as powdered activated carbon (PAC) or biochar, is the presence of other types of organic matter. As an adsorbent, activated carbon has different levels of affinity to material based

on certain chemical and physical properties. This property has been noticed in laboratory tests that compare the adsorption capacity of GAC used in various qualities of water. Intuitively, laboratory-grade water, which is already filtered and does not contain noticeable levels of contaminants prior to introduction of contaminants of concern, allows for a higher adsorption rate of PFAS compounds than other types of water such as wastewater. These different levels of affinity for adsorption can be due to the charge of the various contaminants, the hydrophobicity, or other chemical and physical properties of the competing substances (Dickenson & Verdugo, 2018; Roccaro & et. al, 2018). In the Department of Defense, which is a large user of AFFF that contains PFAS, this has created a dilemma due to the many other contaminants contained in AFFF. Some of these contaminants have a higher affinity for adsorption to GAC, and therefore foul the adsorbent before it can effectively remove the PFAS. An example of this is the total organic carbon (TOC) which increases as a result of the use of AFFF. This was one focus of research conducted by Dyson in which a treatment train was designed to reduce the concentration of TOC prior to remediating the PFAS contamination with GAC (Dyson, Schmidt, & Stubbs, 2018). More research is necessary and ongoing to determine the best method for dealing with these issues, to include the ideal size of GAC and treatment trains that optimize the removal of PFAS compounds.

While GAC has been frequently studied as a treatment technology for PFAS due to its well-known adsorptive capabilities for a wide variety of contaminants, recent studies have also focused on the use of anion exchange resins. Ion exchange is a process which removes ions from a solution based on their charge. After removal, the ion is replaced by another ion from the resin or other material. This replacement happens

because of the mobility of the ions that are attached to the immobile functional acid or base group. In anion exchange, which is utilized for removal of PFAS, these ions are negatively charged. Once the capacity of the resin is reached, it is possible to regenerate it using brine, strong acids, or strong bases (EPA, Ion Exchange).

In one study conducted by Zaggia, Conte, Falletti, Fant, and Chiorboli, the researchers found that the ability of the anion resins to exchange with the PFAS compounds was largely dependent on the chain length and the hydrophobicity of the selected anion exchange resin. Utilizing three different resins that had hydrophobicity levels of low, intermediate, and high, the study found that, especially for short-chain PFAS (in this case PFBS and PFBA), the higher the hydrophobicity level of the resin, the higher the equilibrium exchange capacity between the resin and the PFAS. The resins used were Purolite A600E (non-hydrophobic), A520E (fairly hydrophobic), and A532E (highly hydrophobic). For PFBS, a short-chain PFAS with a sulfonate functional group, the equilibrium exchange capacity (C_{eq}) for these resins were as follows: A600E-36.6 mg g⁻¹; A520E-53.8 mg g⁻¹; A532E-109.2 mg g⁻¹. The capacities increase dramatically with a long-chain PFAS with a sulfonate functional group. This study used PFOS, and found C_{eq} of 186.2 mg g⁻¹, 210.4 mg g⁻¹, and 260.5 mg g⁻¹ respectively. The sulfonate groups also had higher C_{eq} than the corresponding carboxylate PFAS (PFBA and PFOA). This study also concluded that anion exchange is more appropriate and effective for removal of trace concentrations of PFAS than GAC, as GAC is less selective and therefore may become saturated with contaminants other than PFAS (Conte, Fant, Chiorboli, Falletti, & Zaggia, 2015). The ability of anion exchange resins to be tailored to specific compounds such as

PFAS, and therefore have increased efficiency from the outset, makes this technology an attractive solution.

Although anion exchange resins are better suited for long-chain PFAS, there has been some success with removal of short-chain compounds via the resins. Dickenson and Verdugo point to a study conducted by Appleman in 2014 which found that Purolite FerrlX A33e ion exchange resin successfully removed PFBS at a rate of 81%. This is in contrast to multiple studies done on breakthrough of GAC by short-chain PFAS compounds. In fact, according to Dickenson and Verdugo, to treat water contaminated with short-chain PFAS compounds via GAC, it is necessary to supplement the treatment with other technologies. These may be ion exchange, nanofiltration, or reverse osmosis (Dickenson & Verdugo, 2018). Necessary considerations for choosing between the technologies include cost effectiveness, specific compounds that are present, and technologies available to the specific site.

The final treatment method that the EPA focuses on is high pressure membrane technology. The effectiveness of high-pressure membranes varies based on the size of the pores in the system. Studies have shown that nanofiltration and reverse osmosis have consistent removals rates of over 93%, and as high as 99.4%. Interestingly, Dickenson and Verdugo cite a 2017 study by Soriano et al. that found 99.4% removal of PFHxA using a DowFilm NF270 nanofiltration membrane (Dickenson & Verdugo, 2018; Soriano et. al, 2017). This is significant as interested parties attempt to understand the differences in removal of long-chain and short-chain PFAS.

In contrast, high-pressure membranes with larger pore sizes have been shown to be significantly less effective than their smaller-pore counterparts. According to

Dickenson and Verdugo, one water treatment plant that attempted to use a microfiltration system alone, with 0.2-micron-rated pore size, did not reduce PFOA or PFOS. Another found that utilizing a microfiltration and ultrafiltration system in series with each other led to small reductions in long-chain compounds only (24-44% removal rates) (Dickenson & Verdugo, 2018).

While nanofiltration and reverse osmosis technologies are effective at the removal of PFAS, there are some very serious downsides to the use of them. One is that, in many instances, it is cost prohibitive and energy intensive. The use of high-pressure membranes carries with it a high capital cost, requires high amounts of energy, and has significant training to operate on a large scale (Speith & et. al, 2018). Additionally, there is an issue with the highly concentrated brine which remains behind after the process is completed. Reverse osmosis and nanofiltration are efficient systems with around 80% of the water fed into the system (feed water) being filtered and usable after the process. However, the other 20%, the brine, presents a significant problem. This water is extremely concentrated with salts and other contaminants, to include PFAS. It is so concentrated that it is not effective to put it through the system again. The issue that arises is the handling and disposal of such a contaminated source of water (EPA, 2018c; Dickenson & Verdugo, 2018). While some concentrates can be treated by various wastewater treatment designs, PFAS is unaffected by conventional water treatment technologies, and thus must be disposed of or treated in other ways (Speith & et. al, 2018). These factors have led to the Environmental Protection Agency suggesting that high-pressure membrane technologies be utilized as a point of use technology for individual homeowners. This would reduce the volume that is being pushed through the membranes, and enable longer lasting, more

efficient membranes to be utilized (EPA, 2018c). Still, this would pose a significant cost, and eventually lead to the same issues of treatability and concentrated contaminants. Additionally, the concern of expertise necessary for operation is not necessarily mitigated by point of source use. If high-pressure membranes were more energy efficient, less costly, and treatment trains were designed to enable the effective treatment of the concentrate that remains, they may be a viable option in the future.

Coal Based and Coconut Based GAC Comparison

Previous studies have shown that bituminous coal based GAC outperformed other types of GAC, including those produced using coconut shell, when adsorbing compounds with larger molecular weights, such as PFAS (Evoqua, 2017; Schmidt, 2017). This is likely related to the increased sorption kinetics observed in GACs that are mesoporous in structure (such as GAC derived from coal) (Du et al. 2014; Evoqua, 2017). However, claims made by Evoqua regarding their enhanced AC1230CX coconut shell based carbon require research into the ability of certain types of biochar based GACs to compete with coal based versions. According to Evoqua, they have been able to create this carbon with the typical microporous structures that allow for adsorption of lower molecular weight compounds, but also an enhanced mesoporous structure that is capable of targeting higher weight contaminants (Evoqua, 2017). With this in mind, some municipalities, such as Kennebunkport & Wells Water District, are upgrading their systems to use this relatively new GAC, showing that there is belief that it may in fact compete with coal based products (Evoqua, 2018).

These issues are important due to the sustainability and cost associated with both. Currently, according to communication with Evoqua in January 2020, AC1230CX is

priced at \$2.50 per pound. In contrast, a 2018 cost estimate by the United States Navy for remediation using Calgon F600 shows a cost of \$2.75 per pound (NAVFAC, 2018). Additionally, the Calgon Corporation plans to increase the cost of many products 10-15%, according to a press release by the company (Calgon, 2019). Furthermore, as concerns continue to rise over the sustainability implications of the use of coal based products in general, coconut and other biochar based products will provide alternatives that are not susceptible to these issues.

Summary

The body of knowledge surrounding PFAS is progressing rapidly. Recent studies have shown that the past use of these compounds has resulted in wide occurrence of environmental contamination throughout the globe. The high stability of many PFAS ensures that its presence in soil, groundwater, and surface water will be a lingering issue for environmental agencies, regulators, and engineers. PFAS presence must be dealt with due to the numerous toxicological problems that the substances present, especially with the level of uncertainty that still exists. This uncertainty is evident in the different values of limits that have been calculated by regulatory agencies. The first provisional health advisory levels (HAL) promulgated by the EPA were 0.2 and 0.4 µg/L for PFOS and PFOA, respectively. Seven years later, the EPA updated these to 0.07 µg/L for a combined concentration (Via, 2019); (EPA, 2016). Meanwhile, a 2018 draft toxicological profile for PFAS by the Agency for Toxic Substances and Disease Registry produced a recommended level of .007 µg/L combined concentration (ATSDR, 2018). These agencies continue to work with industry to phase out certain compounds and remediate areas that have already been contaminated. They are accomplishing this through the use

of novel technologies such as GAC, anion exchange, and high-pressure membranes. Still, the effectiveness of these technologies, as well as their feasibility in regard to cost, must be studied in more depth, especially as new forms come into production. The methodology explained in chapter three will further investigate the capability of two forms of GAC to adsorb PFOS and PFOA.

III. Methodology

Introduction

This chapter describes the procedures followed to answer the research questions of which granular activated carbon (GAC) adsorbs perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) most efficiently and which substance will be removed more quickly. These research questions are important due to the impact that PFOA and PFOS have on the environment and human health. These bioaccumulative substances, along with other varieties of poly- and perfluoroalkyl substances (PFAS), have been linked to numerous toxicological impacts, both carcinogenic and non-carcinogenic. The impacts of PFAS are most readily apparent from exposures to long-chain varieties of PFAS, such as the common PFOA and PFOS (ATSDR, 2018). As municipalities, public water systems, and regulatory agencies continue to remediate drinking and other waters impacted by the presence of PFAS, understanding the answers to these questions will aid in the determination of best practices for improving the levels of PFAS in water. This is most important in locations that are home to fire training areas, aircraft operations, and PFAS manufacturing industries. These areas have the highest concentrations of PFAS due to the proximity, as well as the relatively high discharges of the chemicals (Korzeniowski, Buck, Kempisty, & Pabon, 2018; Pabon & Corpart, 2002).

Theory

This research used a bottle study design to determine the efficiency of two forms of GAC in removing PFOS and PFOA from water. Christopher Schmidt conducted a similar bottle study to determine the effectiveness of a variety of GACs. His study focused solely on PFOS and used different brands of GAC (2017). This thesis carried

over the most efficient GAC (Calgon Filtrasorb 600) for comparison to a newly enhanced GAC (Evoqua Aqua Carb 1230CX). PFOS and PFOA were chosen because they are two of the most ubiquitous forms of PFAS. Furthermore, regulatory agencies are most concerned about their presence in the environment as a result of their persistence and toxicological impacts (ATSDR, 2018).

GAC can be derived from a variety of sources. Two of these sources are bituminous coal and coconut shell. These and other materials used for GAC contain high amounts of carbon. Carbon is an efficient adsorbent for many contaminants due to its high porosity and binding capability (Oxbow, 2015). Although previous research has found that GAC derived from bituminous coal is most efficient at PFAS removal, Evoqua has recently created an enhanced version of their coconut shell-based GAC (Evoqua, 2017). The coconut-shell based GAC may have some cost benefits, as well as sustainability implications. The mining of coal, as well as the non-renewable nature of the material causes some concern to the sustainability community even though its effectiveness in PFAS adsorption is, thus far, unmatched. If coconut shell-based GAC, or other forms of biochar, can become competitive with coal-based GAC, it may become a preferred alternative to the status quo. The processes used to determine the efficiency of both forms of GAC will be described in detail in the remainder of this chapter.

Materials and Equipment

Water

The study utilized water from a deionized source. Because this research was focused solely on the removal of PFAS from water, co-contaminants were undesirable due to the competition for adsorption sites that they would have caused. The deionized

water source mitigated these concerns by removing contaminants prior to the spiking of the water with PFAS.

PFAS

The two PFAS compounds that were studied were PFOS and PFOA. These two were selected due to their wide proliferation in industrial goods, legacy firefighting foams, and their bioaccumulative nature in the environment. Additionally, both of these are long-chain PFAS and are suspected to cause multiple carcinogenic and non-carcinogenic toxicological effects in humans (ATSDR, 2018). The PFOS that was used was a technical grade, 40% by weight solution in water manufactured by Sigma Aldrich. The PFOA was a 96% pure crystalline form of the substance and was also manufactured by Sigma Aldrich. The beginning forms of each of these substances can be seen in figure 3-1.



Figure 3-1: Original forms of PFAS solutions. PFOS (left) began as a 40% solution in water while the PFOA (right) was a 96% pure crystal form.

Table 3-1: Concentrations and Forms of Stock PFAS

Analyte	Concentration	Form
PFOA	96% w/w	Crystal
PFOS	40% w/w	Solution in H ₂ O

Preparation of Study Solutions

Both forms of PFAS were prepared in similar manners, with the only difference being the use of a crystalline form of PFOA. In order to ensure a well-mixed solution, a serial dilution procedure was followed. Because of the different concentrations between the starting substances, calculations were made to determine the mass of substance necessary to attain the desired starting concentration. The actual amounts that were measured are shown in Table 3-2. Due to limitations of the equipment used, an error of 5 mg for the PFOS solution and 5 mg for the PFOA crystals was deemed acceptable. To begin with, the equivalent of 200 mg of PFAS was targeted to be placed in 50 ml of water. The resulting solution can be seen in Figure 3-2. This made a solution with a concentration of 4 g/L. In the figure, the white area at the tip of the solution is a layer of foam caused by the surfactant properties of PFAS.

Table 3-2: Targeted and Measured Mass of Analytes in Initial Solutions

Analyte	Target Mass in Initial Solution	Measured Mass in Initial Solution
PFOA Crystals	208.3 mg	209.4 mg
PFOS Solution	500 mg	497.9 mg

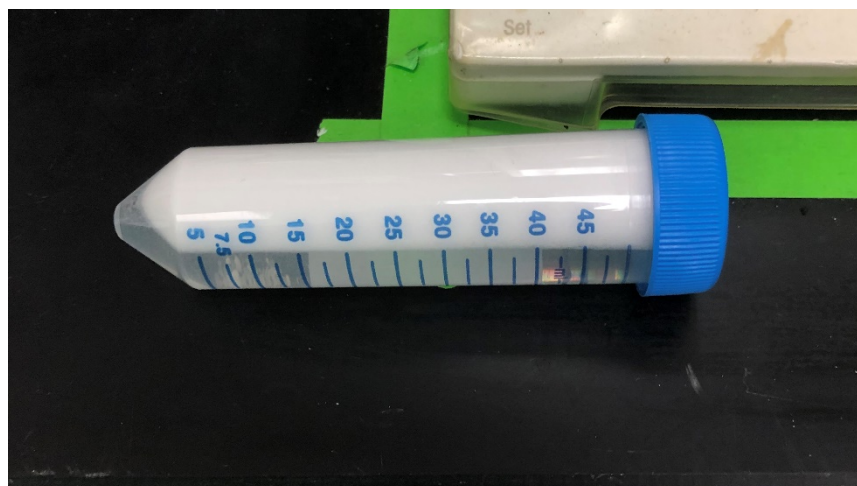


Figure 3-2: The first stage of the serial dilution.

All 50 ml of this solution were then added to 950 ml in a 1 L bottle. This 1 L solution (shown in Figure 3-3) was shaken to mix the constituents, and then allowed to sit and mix at room temperature for 24 hours before the next step in the process. In the figure, it is evident that the concentration is drastically diminished due to the disappearance of much of the foam from the PFAS. During this 24-hour period, the solution was mixed regularly to ensure that the solution was well mixed and did not become stratified. This was especially important for the next step in which part of this solution was drawn off to make the next concentration.

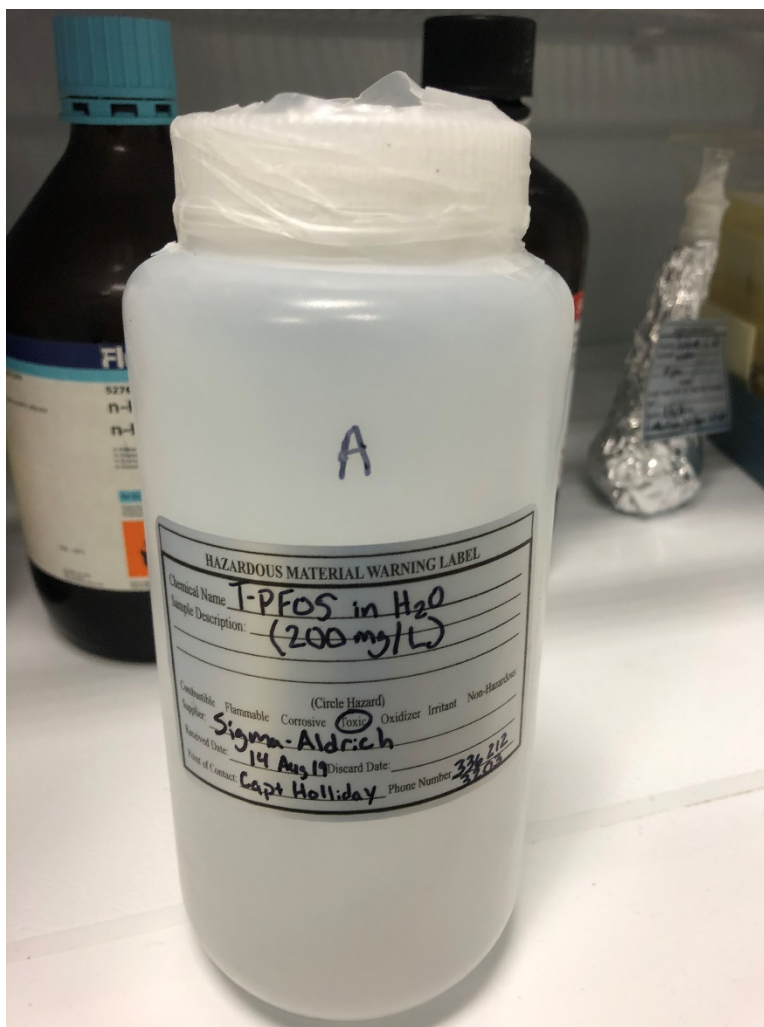


Figure 3-3: The second step of the serial dilution.

After this solution mixed for 24 hours, 200 μ L were drawn and added to 999.8 ml of deionized water (seen in Figure 3-4). This created a solution with a concentration of 40 μ g/L. Due to the low concentration of this solution, it was allowed to sit and mix for five days.

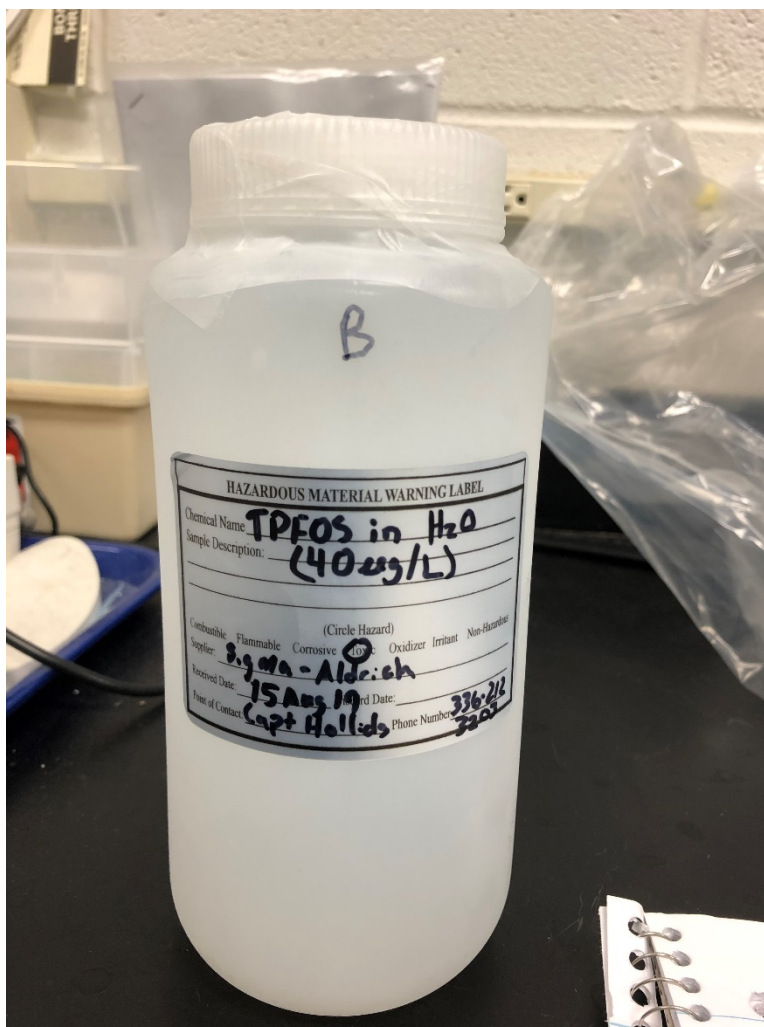


Figure 3-4: The third step of the serial dilution combined.

Finally, a total of 4 L of solution were made by combining this solution with 3 L of water. This final dilution created a solution that had a concentration of 10 μg of PFAS per 1 L of water. The volumes used at each step, as well as the concentrations produced at each step, are shown in Table 3-3.

Table 3-3: Volume of Solution and Water, and Concentration, at Steps in Serial Dilution Process

Amount drawn from previous step	Volume of Water	PFAS Concentration
Initial Mass	50 ml	4 g/L
50 ml	950 ml	200 mg/L
200µL	999.8 ml	40 µg/L
1 L	3 L	10 µg/L

Of note, the PFOA crystals were more difficult to get into solution than the PFOS. Therefore, some of the time intervals used for the PFOA solution dilutions were extended. This is likely due to the fact that the PFOS was already in a solution of water. This characteristic caused the PFOS to mix more readily in a larger solution. In contrast, the crystallized PFOA had less propensity to be quickly dissolved. To reduce the impact of this characteristic of the PFOA, several steps were taken. First, in the early stages of the serial dilution, the tube was continually inspected for visible PFOA crystals. While in the 50 ml tube, these were readily apparent, and the solution remained in the tube until there were no more visible crystals. Second, the 50 ml tube was placed on the automatic tumbler for the time that it contained the solution. This increased the kinetics within the solution and encouraged the PFOA to dissolve. Third, once the solution was placed in the 1 L and 4 L bottles, it was again placed on the automatic tumbler. This was to ensure that the solution was well mixed and reduced stratification of the contaminant. Figure 3-5 shows the setup of the automatic tumbler such that it could hold the 1 L bottle through the dilution process, while Figure 3-6 shows the setup for the 4 L bottle.

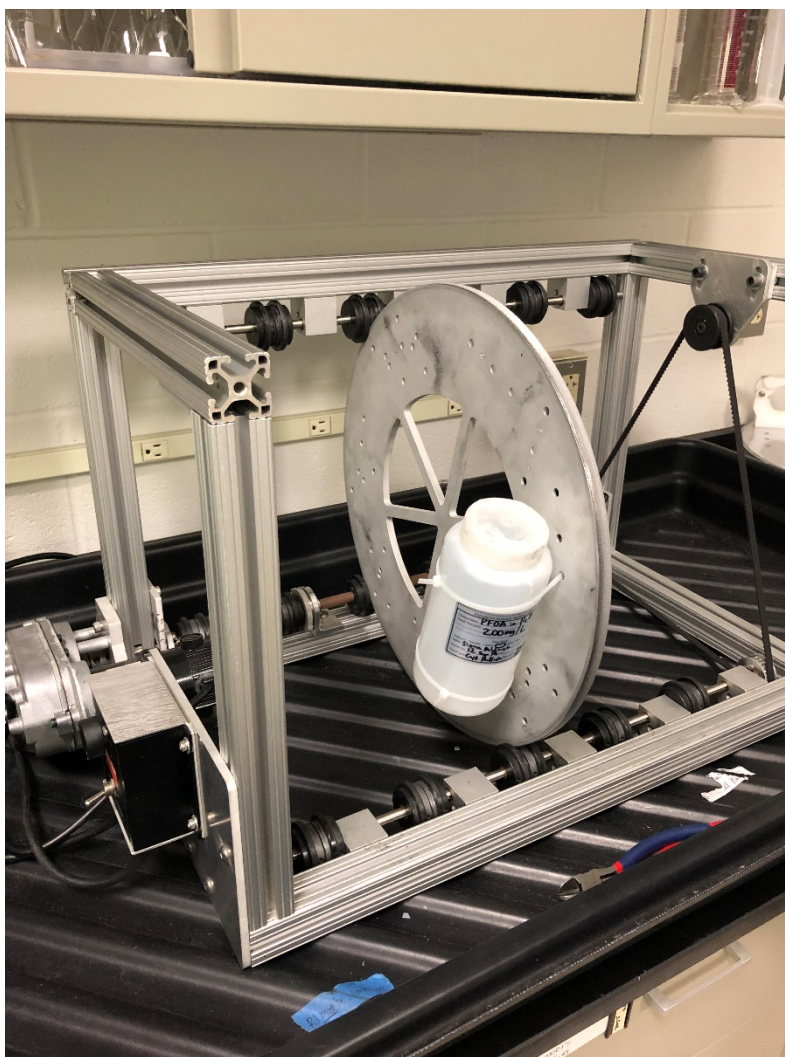


Figure 3-5: Automatic tumbler setup for the 1 L bottle with PFOA.



Figure 3-6: Automatic tumbler setup for the 4 L bottle with PFOA.

Granular Activated Carbon

This research studied the efficiency of two different forms of GAC. One was Calgon Filtrasorb 600 (F600) that was previously used in Schmidt's research. This is a GAC derived from bituminous coal (Schmidt, 2017). The other GAC utilized was Evoqua's Aqua Carb 1230CX GAC, which is made from coconut shell and has enhanced properties to make it more suitable for the removal of PFAS (Evoqua, 2017).

Other equipment

Various pieces of laboratory equipment were utilized throughout the conduct of the study. Containers such as the 1 L and 4 L bottles, as well as the centrifuge tubes, were made of plastics approved by the EPA to hold solutions containing PFAS. The selection of these materials was important because of concern with some types of bottles and materials, such as glass, and the propensity of PFAS to adsorb to them. This means that some of the PFAS would adsorb to the bottle and the analysis would find a lower concentration than what was actually contained in the solution upon separation from the GAC. Additionally, an automatic tumbler was utilized to ensure that the solutions containing PFAS and carbon were well-mixed and homogeneous. Finally, a centrifuge was used to remove the carbon from the solution after the specified time periods, ensuring that the carbon did not remain in contact with the solution in the time frame between the study and analysis at the EPA.

Procedures and Process

Each study began by measuring 2 mg of carbon. Because of the minute amount of carbon being measured, there was concern over some of the carbon being lost to residue on a measuring vessel. In order to reduce the chances of leaving carbon behind on a separate vessel used for measurement, the carbon was measured in the centrifuge tube that it would be in for the study (as opposed to a weigh boat). The tube was placed in a piece of styrofoam and centered on the scale. The scale was then tared with the holder and tube on it, and the carbon was then measured. These tubes were then labeled so that it was identifiable throughout the study and tracked during analysis. The setup for measuring the GAC can be seen in Figure 3-7.

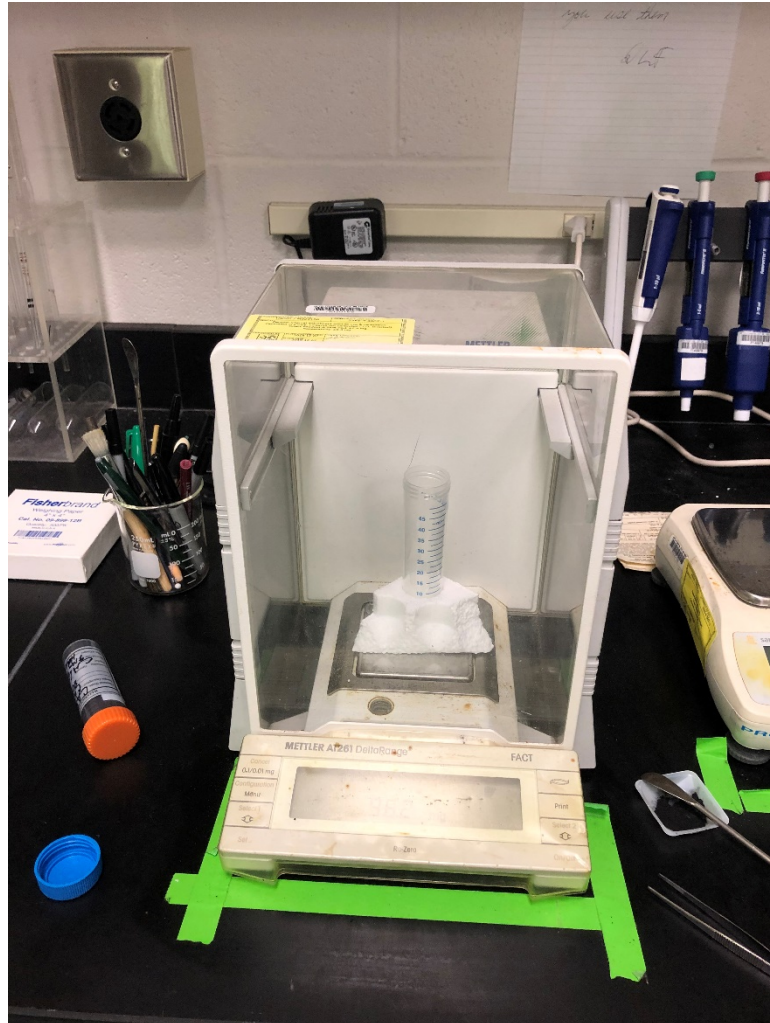


Figure 3-7: Setup of the centrifuge tube and scale used for weighing the carbon used in the study. The white piece under the tube is a piece of styrofoam used to hold the tube during the measurement.

The carbon was measured 24 hours in advance of each study. This was done to increase the fluidity of the studies, making sure that on the day of the study actions were focused on executing the application of solution to the carbon and mixing the substances for the appropriate time. This reduced the amount of activity happening in the lab, and likewise lowered the possibility of time intervals being missed.

At the beginning of each time interval, 50 ml of solution were added to a centrifuge tube containing carbon. The studies used an automatic tumbler set at 2 rotations-per-minute (RPM) to hold the centrifuge tubes that contained the solution in order to ensure the well mixing of the solution and the suspended carbon contained in each tube. This was important to allow the carbon to remain well-mixed throughout the solution and remain in contact with the contaminants present in the solution. The automatic tumbler can be seen in Figure 3-8.

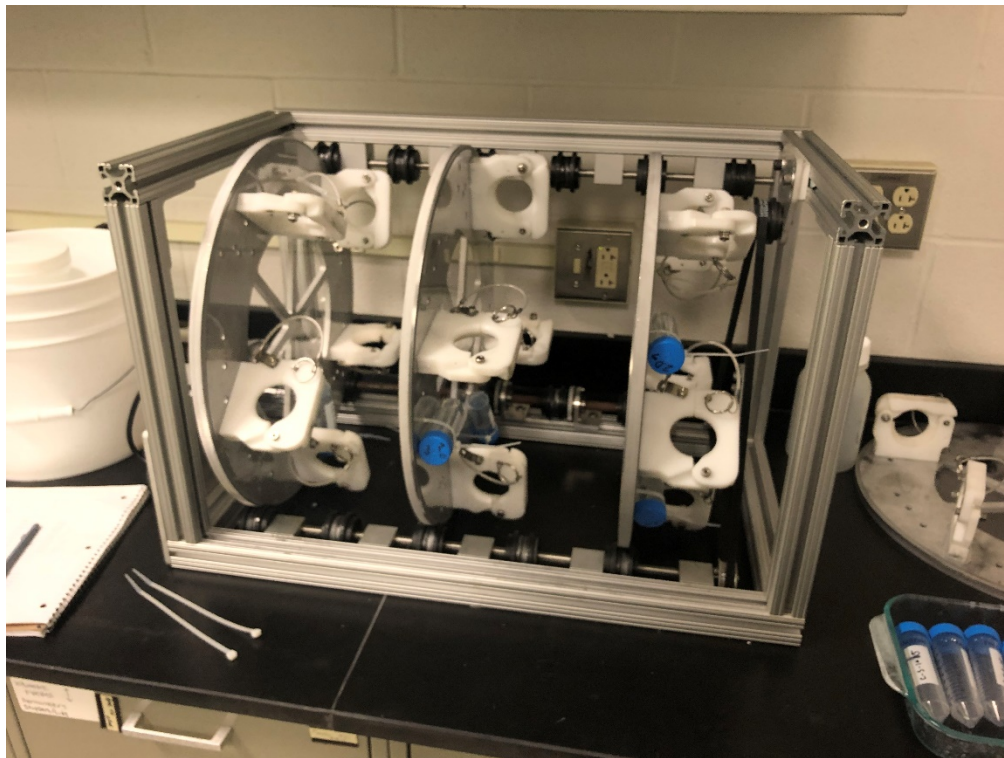


Figure 3-8: Automatic tumbler used to continuously rotate samples.

Each wheel on the tumbler had multiple 50 ml centrifuge tubes attached to it using zip ties, allowing for concurrent tests to be run at various time intervals. This method allowed for an appropriate speed to be applied, and easy access to the bottles that needed to be removed from the tumbler. For each carbon and PFAS combination, 8

samples, with triplicates at each time interval, were run and analyzed at the EPA. The time intervals for carbon-PFAS contact are shown in Table 3-4.

Table 3-4: Sample Time Intervals

Sample Number	Time Interval
1	0 minutes
2	15 minutes
3	30 minutes
4	60 minutes
5	120 minutes
6	240 minutes
7	24 hours
8	Blank

At the end of the appropriate time interval, the tubes were placed in a centrifuge to separate the carbon from the solution. The centrifuge was set to the parameters displayed in Table 3-5.

Table 3-5: Centrifuge Settings

Parameter	Setting
Temperature	6°Celcius
RPM	4000
Time	10 Minutues

Analysis of the concentration of PFAS contained in each sample was conducted at the EPA's laboratory in Cincinnati, Ohio. This was done using a direct injection method with ultra-high performance liquid chromatography (UHPLC)-tandem mass spectrometry (MS/MS) (EPA, Analysis). Once results were returned, the concentration of PFAS in each sample was normalized to the initial concentration, or C_0 . Average concentration at each time period was determined, along with standard deviation to allow for analysis of the variation in concentrations, and the determination of the most efficient GAC. In order to determine statistical significance of any differences in the data, F-Tests and T-Tests were then conducted. This will be discussed further in Chapter Four.

Conclusion

This methodology allowed for the comparison between the PFOS and PFOA adsorption capabilities of two GACs. It also allowed for a comparison of the rates at which PFOS and PFOA are removed from water. This is important due to the proliferation of these chemicals in the environment and their toxicological effects on humans and other species. As the DOD, industry, and regulatory agencies continue to wrestle with the most efficient and cost-effective ways to contend with this problem, it is important that they understand the benefits presented by different technologies, to include varying forms of GAC. Chapter 4 will discuss the results that were obtained by the procedures followed in this chapter. Detailed analysis of the meaning of these results will be discussed in detail.

IV. Results and Analysis

Chapter Overview

This chapter presents the results gathered from the conduct of the bottle studies described in the previous chapters. This data will be presented as it pertains to the two research objectives and the associated hypotheses, showing that there is support for each of the hypotheses discussed. The results of the adsorption of PFOS, PFOA, and the combined solutions by both forms of GAC will be discussed and supported by appropriate charts and illustrations.

PFOS Adsorption Results

The first experiment to be conducted was the PFOS removal comparing both carbons. Results were gathered from the EPA in ng/ml. The results at each time interval were then averaged and the standard deviation was calculated. There was some concern in the recovery percentage during the analysis of the results. This resulted in some unexpected values for initial concentration. In order to normalize the data such that it could be compared, the averages for each time interval were used to relate the average concentration at that time interval with the average concentration at the initial time. This is the C/C_0 ratio. The equation for this is shown in Equation 1. This mitigates the issue with the recovery percentages because it is simply a ratio of the analyzed concentration at each time interval compared to the analyzed initial concentration. As long as the recovery percentage remained the same throughout each individual analysis, which it was assumed that it did, these ratios could be used to effectively compare the results between each of the substances and carbons.

$$\frac{C}{C_0} = \frac{\text{Concentration at Time } t}{\text{Initial Concentration } (t = 0)}$$

Equation 1

Table 4-1 provides the concentration of PFOS over time for Evoqua AC1230CX, while Table 4-2 provides the data for Calgon F600. Both tables also provide the averages, standard deviations and C/C₀ data. Figure 4-1 takes the data from both of these tables and charts the C/C₀ data together so that one can easily visualize the trend of PFOS removal from both carbons.

From these tables, it appears that the Evoqua AC1230CX begins removing PFOS more quickly than Calgon F600. Through the 120-minute mark, the coconut-based carbon had a lower C/C₀ ratio, indicating that it was removing more of the PFOS. However, at the 240-minute time interval this trend began to change. At this point, the C/C₀ ratios for Evoqua and Calgon were 0.0515 and 0.0340 respectively. This continued through the 24-hour period with the ratios for Evoqua and Calgon being 0.0013 and 0.0006 respectively.

Table 4-1: Results for PFOS Removal by Evoqua AC1230CX

Concentration of PFOS Over Time (ng/ml) With Evoqua AC1230CX								
Triplicate	Blank	0 Minutes	15 Minutes	30 Minutes	60 Minutes	120 Minutes	240 Minutes	24 Hours
1	0	6.23	0.03	0.29	0.07	0.02	0.79	0.01
2	0	4.99	0.38	0.02	0.02	0.23	0	0.01
3	0	4.51	0.36	0.01	0.04	0.02	0.02	0
Avg	0	5.2433	0.2567	0.1067	0.0433	0.0900	0.2700	0.0067
Std Dev	0	0.8875	0.1966	0.1589	0.0252	0.1212	0.4504	0.0058
Time	Evoqua C/C0							
0	1.0000							
15	0.0490							
30	0.0203							
60	0.0083							
120	0.0172							
240	0.0515							
1440	0.0013							

Table 4-2: Results for PFOS Removal by Calgon F600

Concentration of PFOS Over Time (ng/ml) With Calgon F600																								
Triplicate	Blank	0 Minutes	15 Minutes	30 Minutes	60 Minutes	120 Minutes	240 Minutes	24 Hours																
1	0.03	4.77	1.16	0.04	0.53	0.03	0.14	0.01																
2	0.05	5.44	0.64	0.2	0	0.21	0.05	0																
3	0	5.36	0.8	0.51	0.02	0.05	0.34	0																
Avg	0.0267	5.1900	0.8667	0.2500	0.1833	0.0967	0.1767	0.0033																
Std Dev	0.0252	0.3659	0.2663	0.2390	0.3004	0.0987	0.1484	0.0058																
<table><tr><th>Time</th><th>Calgon C/C0</th></tr><tr><td>0</td><td>1.0000</td></tr><tr><td>15</td><td>0.1670</td></tr><tr><td>30</td><td>0.0482</td></tr><tr><td>60</td><td>0.0353</td></tr><tr><td>120</td><td>0.0186</td></tr><tr><td>240</td><td>0.0340</td></tr><tr><td>1440</td><td>0.0006</td></tr></table>									Time	Calgon C/C0	0	1.0000	15	0.1670	30	0.0482	60	0.0353	120	0.0186	240	0.0340	1440	0.0006
									Time	Calgon C/C0														
									0	1.0000														
									15	0.1670														
									30	0.0482														
									60	0.0353														
									120	0.0186														
									240	0.0340														
									1440	0.0006														

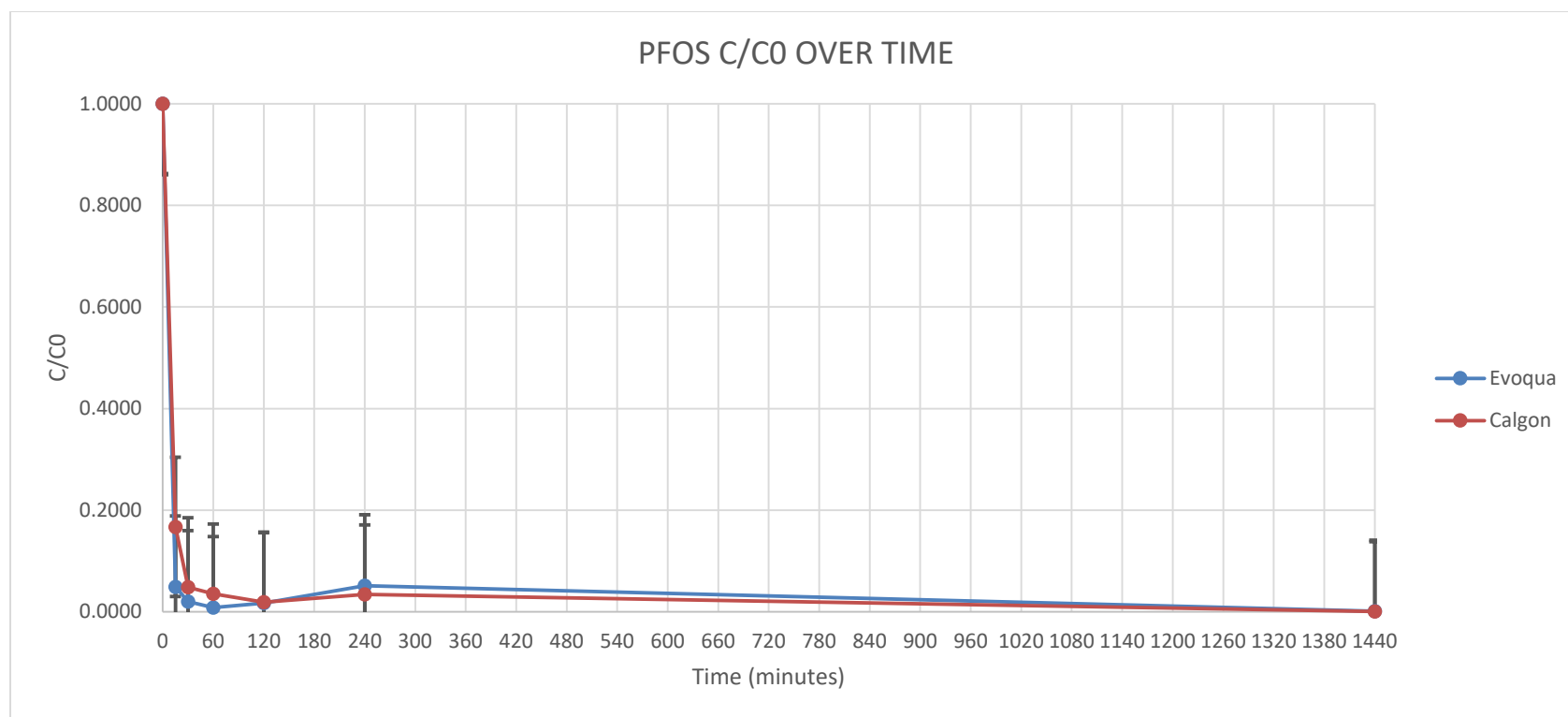


Figure 4-1: C/C_0 at selected time intervals for PFOS removal by Evoqua AC1230CX and Calgon F600 GAC.

To determine whether these differences were significant, a Student's T-Test was calculated between the two GACs' C/C_0 at each time interval. It was assumed that data for each time interval, if the sample size were to be large enough, would be normal. Differences in surface area and solution concentration would be distributed in a way that would meet this assumption. With a larger sample size, this theory could be tested with tests such as the Shapiro-Wilk test. The hypotheses for the tests were as follows:

$$H_0: \mu_c - \mu_e = 0$$

$$H_a: \mu_c - \mu_e \neq 0$$

Where:

μ_c = Average C/C_0 for Calgon at the specified time interval

μ_e = Average C/C_0 for Evoqua at the specified time interval

An alpha level of 0.05 was chosen for the level of significance ($\alpha = .05$). The equation for the t-score is shown in Equation 2 (McClave, Benson, & Sincich, 2014).

$$t = \frac{(\bar{x}_1 - \bar{x}_2) - D_0}{\sqrt{s_p^2 \left(\frac{1}{n_1} + \frac{1}{n_2} \right)}}$$

Equation 2

Where:

$\bar{x}_1$ = Average C/C_0 for Evoqua PFOS adsorption

$\bar{x}_2$ = Average C/C_0 for Calgon PFOS adsorption

D_0 = Hypothesized difference between the averages (in this case, 0)

s_p^2 = Pooled variance

n_1 = Number of observations for Evoqua

n_2 = Number of observations for Calgon

For the purposes of this research, the Microsoft Excel Data Analysis Tool was used to calculate the t-statistics and the p-values. Additionally, F-Tests were run to

determine any significant difference in variance. Where this was the case, the T-Test in Excel that accounts for this with fewer degrees of freedom was selected. The results of the F-Tests and T-Tests for PFOS C/C_0 at each time interval are recorded in Table 4-3.

Table 4-3: F-Test and Student's T-Test P-Values for PFOS C/C_0

Time Interval (Minutes)	F-Test P Value	T-Test P-Value
15	0.59	0.06
30	0.49	0.38
60	0.01	0.49
120	0.70	0.99
240	0.25	0.84
1440	0.87	0.62

Based on the calculated data, there is not a statistically significant difference between the PFOS adsorption ability of the Evoqua AC1230CX and Calgon F600 GACs. Therefore, the null hypothesis was not able to be rejected, and the data supports the hypothesis of the study that there would not be a significant difference between the enhanced coconut GAC and the previously more efficient Calgon F600 coal- based GAC.

PFOA Adsorption Results

The second experiment focused on the GACs' abilities to adsorb PFOA and remove it from the water. The samples were run with the same procedure as the PFOS, and results gathered in ng/ml. Similar to the PFOS results, the concentrations at each time interval were averaged and concentrations were compared to the initial concentration.

Table 4-4 shows the raw data gathered for PFOA removal by Evoqua AC1230CX, while Table 4-5 shows the same data for Calgon F600. This data includes the averages, standard deviations, and C/C_0 data for each GAC. Figure 4-2 shows the C/C_0 data in chart form so that it can be easily visualized.

Similar to the PFOS results, the Evoqua initially appears to remove the PFOA at a more rapid rate. This trend continued until the 120-minute time interval where the average C/C_0 ratio for Evoqua and Calgon were 0.0210 and 0.0107 respectively. This also continued through the rest of the 24-hour period.

Table 4-4: Results for PFOA Removal by Evoqua AC1230CX

Concentration of PFOA Over Time (ng/ml) With Evoqua AC1230CX								
Triplicate	Blank	0 Minutes	15 Minutes	30 Minutes	60 Minutes	120 Minutes	240 Minutes	24 Hours
1	0.02	8.29	1.99	0.44	0.54	0.17	0.17	0.31
2	0.02	9.58	1.93	0.33	0.25	0.17	0.16	0.28
3	0.04	8.30	1.37	0.48	0.22	0.21	0.16	0.36
Avg	0.0267	8.7233	1.7633	0.4167	0.3367	0.1833	0.1633	0.3167
Std Dev	0.0115	0.7419	0.3420	0.0777	0.1767	0.0231	0.0058	0.0404
Time	Evoqua C/C0							
0	1.0000							
15	0.2021							
30	0.0478							
60	0.0386							
120	0.0210							
240	0.0187							
1440	0.0363							

Table 4-5: Results for PFOA Removal by Calgon F600

Concentration of PFOA Over Time (ng/ml) With Calgon F600								
Triplicate	Blank	0 Minutes	15 Minutes	30 Minutes	60 Minutes	120 Minutes	240 Minutes	24 Hours
1	0.00	4.53	0.99	0.40	0.30	0.47	0.06	0.04
2	0.02	3.58	0.83	0.83	1.26	0.25	0.05	0.02
3	0.02	4.08	0.90	1.19	0.59	0.18	0.02	0.05
Avg	0.0133	4.0633	0.9067	0.8067	0.7167	0.3000	0.0433	0.0367
Std Dev	0.0115	0.4752	0.0802	0.3955	0.4924	0.1513	0.0208	0.0153
Time	Calgon C/C0							
0	1.0000							
15	0.2231							
30	0.1985							
60	0.1764							
120	0.0738							
240	0.0107							
1440	0.0090							

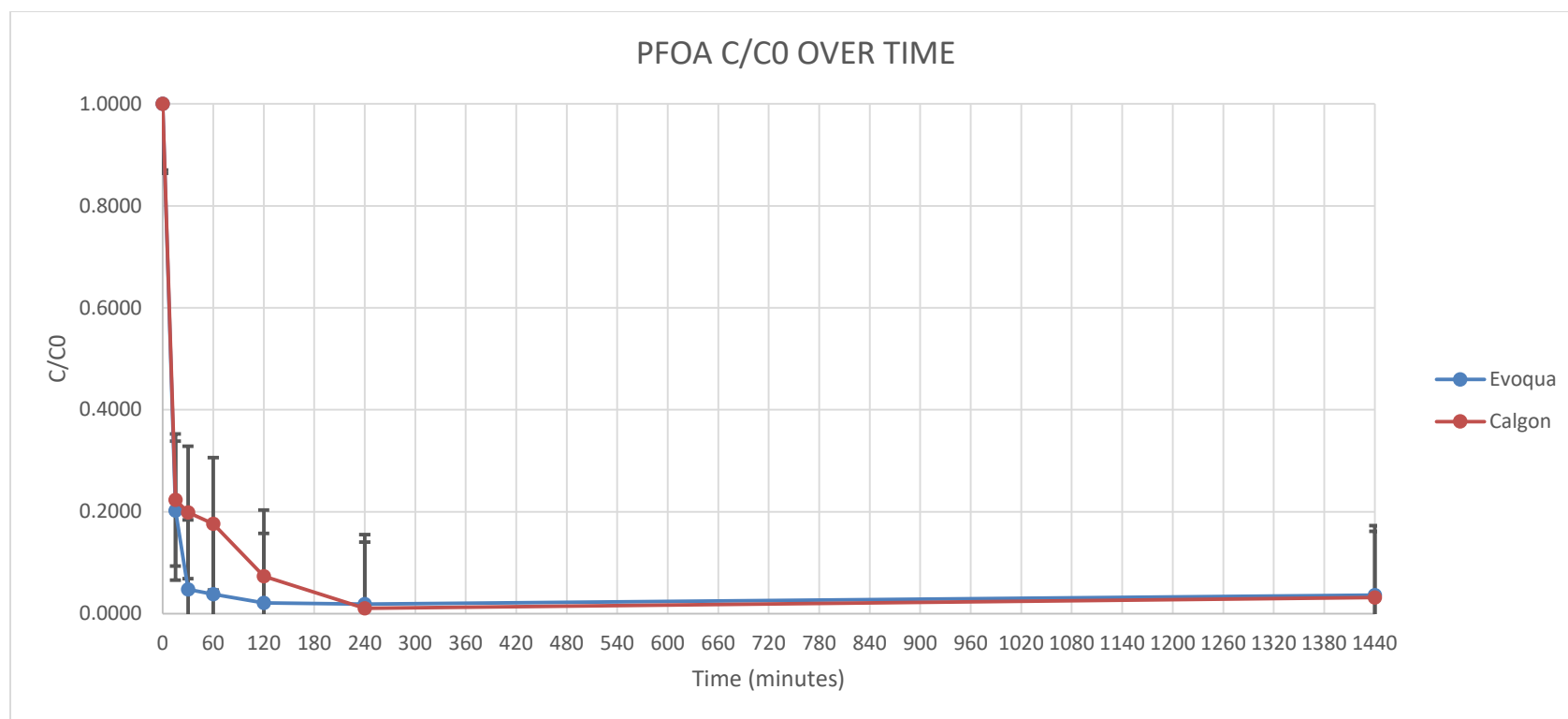


Figure 4-2: C/C_0 at selected time intervals for PFOA removal by Evoqua AC1230CX and Calgon F600 GAC.

As was done with the PFOS results, a Student's T-Test was conducted to determine whether there was a statistically significant difference between the PFOA removal rates for the two GACs. The hypotheses for these tests were:

$$H_0: \mu_c - \mu_e = 0$$

$$H_a: \mu_c - \mu_e \neq 0$$

Where:

μ_c = Average C/C_0 for Calgon at the specified time interval

μ_e = Average C/C_0 for Evoqua at the specified time interval

Again, the alpha level was set to 0.05 and F-Tests were conducted to ensure the data met the assumption of equal variance. If the datasets were not equally variable, the modified T-Test with fewer degrees of freedom was utilized. The results of the F-Tests and T-Tests at each selected time are provided in Table 4-6.

Table 4-6: F-Test and Student's T-Test P-Values for PFOA C/C_0

Time Interval (Minutes)	F-Test P Value	T-Test P-Value
15	0.07	0.39
30	0.03	0.06
60	0.05	0.16
120	0.03	0.04
240	0.26	0.06
1440	0.36	0.00

In this case, there is one time interval, 24 hours, at which there was a significant difference between the C/C_0 for Evoqua and Calgon. This is one of the intervals where the Calgon F600 C/C_0 was lower than the Evoqua equivalent. While this is counter to the hypothesis that there would be no significant difference, the overall trend of no statistical significance in the difference supports the hypothesis for PFOA as it did with PFOS.

Removal Comparison between PFOS and PFOA

The final analysis was done to determine whether PFOS or PFOA were removed more quickly. To do this, the researcher began by comparing the average C/C_0 values for each carbon's adsorption of PFOS and PFOA to identify any trends in the data. The average C/C_0 values are provided in Tables 4-7 and 4-8 and graphically in Figures 4-3 and 4-4.

Table 4-7: Evoqua PFOS and PFOA C/C_0

Time	Evoqua PFOS C/C_0	Evoqua PFOA C/C_0
0	1.0000	1.0000
15	0.0490	0.2021
30	0.0203	0.0478
60	0.0083	0.0386
120	0.0172	0.0210
240	0.0515	0.0187
1440	0.0013	0.0363

Table 4-8: Calgon PFOS and PFOA C/C_0

Time	Calgon PFOS C/C_0	Calgon PFOA C/C_0
0	1.0000	1.0000
15	0.1670	0.2231
30	0.0482	0.1985
60	0.0353	0.1764
120	0.0186	0.0738
240	0.0340	0.0107
1440	0.0006	0.0090

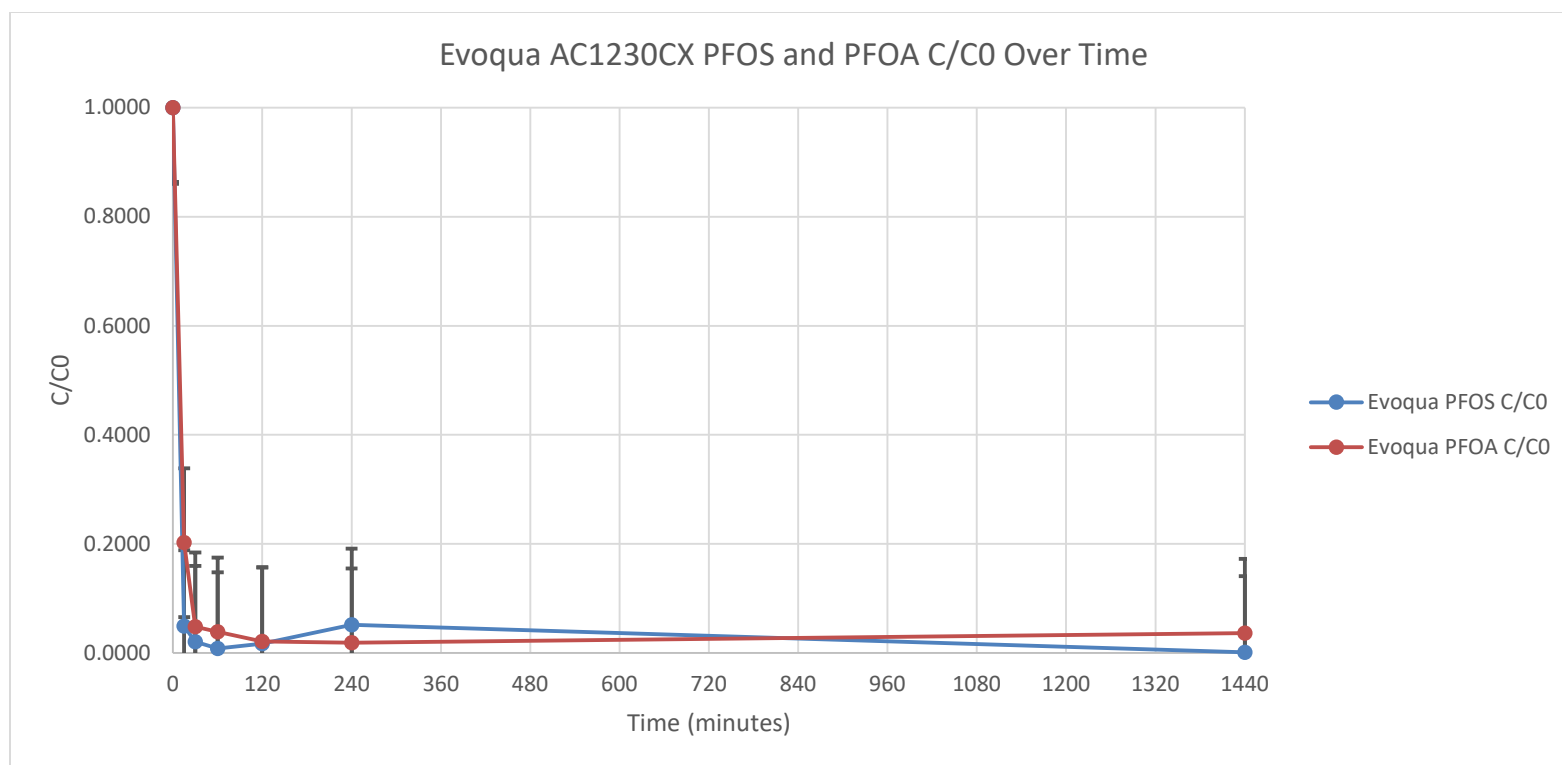


Figure 4-3: PFOS and PFOA C/C_0 over time using Evoqua AC1230CX

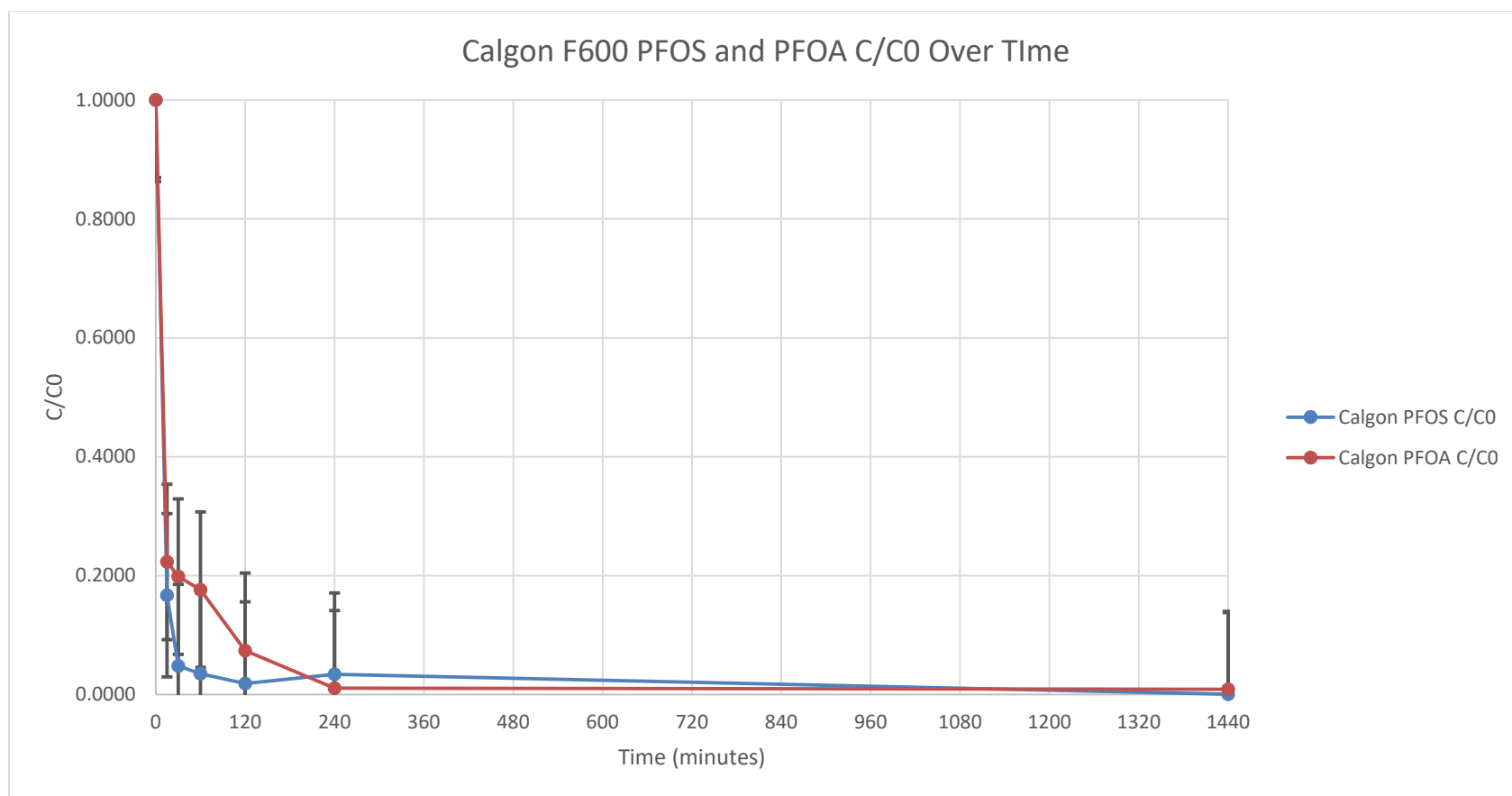


Figure 4-4: PFOS and PFOA C/C_0 over time using Calgon F600

These tables show an overall trend of PFOS being removed more quickly by both GACs. The only exception among the averages was observed at the 240-minute time interval. This trend supported the hypothesis that PFOS would be removed more quickly due to its sulfonic functional group that creates a stronger bond with the surface of the adsorbent.

Next, the researcher conducted the F-Test and T-Test for each dataset to determine the significance of these results. An alpha level of 0.05 ($\alpha=0.05$) was once again utilized. However, in contrast with the previous T-Test, a one-tailed test was used. This was due to previous literature indicating that PFOS is typically removed quicker than PFOA. Therefore, the alternative hypothesis was that the average C/C_0 for PFOS would be lower than that of PFOA. The hypotheses were:

$$H_0: \mu_s - \mu_a = 0$$

$$H_a: \mu_s - \mu_a < 0$$

Where:

μ_s = Average C/C_0 for PFOS at the specified time interval

μ_a = Average C/C_0 for PFOA at the specified time interval

The resulting p-values at each time interval are shown in Tables 4-9 and 4-10.

Table 4-9: F-Test and T-Test Results for Evoqua PFOS and PFOA Removal

Time Interval (Minutes)	F-Test P Value	T-Test P-Value
15	0.88	0.01
30	0.39	0.06
60	0.05	0.04
120	0.05	0.41
240	0.00	0.30
1440	0.04	0.00

Table 4-10: F-Test and T-Test Results for Calgon PFOS and PFOA Removal

Time Interval (Minutes)	F-Test P Value	T-Test P-Value
15	0.02	0.15
30	0.30	0.04
60	0.31	0.09
120	0.52	0.03
240	0.07	0.11
1440	0.23	0.01

From these values, the significance of the difference is primarily evident in three instances for Evoqua (15 minutes, 60 minutes, and 24 hours) and three time intervals for Calgon (30 minutes, 120 minutes, and 24 hours). At each of these times, PFOS was removed more efficiently than PFOA, again supporting the hypothesis that the carbons would remove it at a more rapid rate.

Due to issues with the analytical equipment, analysis on the PFOS and PFOA combined solution was not able to be completed. While this would have shown how the competition for adsorption sites affects the adsorption of each individual solution, the results from the individual solutions help understand how the chemicals interact with the carbons. With the overall trend showing the adsorption affinity of PFOS being stronger, it is likely that it would have outcompeted the PFOA for adsorption sites in a combined solution as well.

Limitations

There were two main sources of limitations and potential sources of error throughout the study: equipment and materials. The first of these, equipment, was due to the minute amount of materials that were measured during the study. Most of the masses were in the low milligrams range (such as the 2 milligrams of carbon used in each centrifuge tube), while some of the volumes were measured in microliters, particularly for the mixing of the solutions. While appropriate pipettes and scales were used, these

instruments introduce their own error which may be magnified when using such small amounts. Additionally, impurities within the materials themselves introduced some error into the study. In particular, one concern is the use of technical grade PFOS, which has a range of purity between 35% and 45% (Sigma-Aldrich, 2018). As was discussed in the methodology, the researcher used the average of these two numbers and measured the mass of PFOS mixed in solution based on an assumption of 40%. The results show a lower initial concentration of PFOS than expected, indicating that this chemical may not have been as pure as the researcher assumed. This could be mitigated in the future by utilizing a purer alternative to the technical grade PFOS.

Summary

This chapter discussed the results of the study in detail. It went through each step of the results and analysis phase of the experiment, showing data that overall supported the hypotheses made during the research objectives discussion in Chapter One. In Chapter Five, the conclusions made from these results will be discussed, along with recommendations for future research into PFAS remediation.

V. Conclusions and Recommendations

Chapter Overview

This chapter provides the significance of the results that were observed and discussed in Chapter Four. The research objectives and hypotheses will be briefly reintroduced, and the answers to those questions discussed. The significance of this research will also be discussed as it relates to the furtherance of the field of study into PFAS remediation efforts.

Finally, recommendations for how this study can lead to future research will be discussed. Although this data will be useful and further the ability for researchers to broaden treatment options, more work on the topic remains due to the limitations discussed previously. Optimization of the methodology will be important in enhancing the relevance of similar data.

Research Objectives and Hypotheses Discussion

The first objective that was discussed was determining whether there was a difference in the efficiency of PFAS removal between the two different carbons. The hypothesis for this objective was that there would not be a significant difference between

the two. This objective was of interest due to previous literature that has shown that bituminous coal is more efficient, and other claims that Evoqua's new AC1230CX enhanced coconut carbon is capable of competing with coal based GAC (Schmidt, 2017; Evoqua, 2017). Additionally, there may be some benefit in terms of cost and sustainability. Overall, the data supported the hypothesis with two exceptions. One of the exceptions was in favor of Evoqua, while the other was in favor of Calgon. Therefore, the hypothesis that there would be no significant difference, and that Evoqua AC1230CX would compete with the previously more efficient F600, was accepted.

The second research objective was to determine which form of PFAS would be removed more quickly: PFOS or PFOA. The first hypothesis related to this objective was that PFOS would be removed at a more rapid rate due to its functional group and tendency to be attracted to GAC more readily while in individual solutions. The data shows three significant differences between the C/C_0 of PFOS and PFOA for each GAC. Each point that was significant was in favor of PFOS being removed more rapidly, which was in line with the overall trend of that data. Therefore, this hypothesis was accepted. The second hypothesis also related to the two compounds, but when they were in solution together. As discussed in the results section, this part of the study was delayed due to analytical equipment. However, the data for the individual solutions indicates that a more rapid adsorption of PFOS would have been observed. Further research should be conducted on this matter in order to fully understand the amount of effect that this difference would have on the adsorption of both compounds as co-contaminants.

Significance of Research

The DOD continues to explore new methods of remediating drinking water that is contaminated with PFOS and PFOA, as well as other types of PFAS. These contamination issues are the result of decades of legacy AFFF use which used long-chain forms of PFAS that do not readily degrade in the environment or in the human body. These chemicals may go on to cause significant non-cancerous disease in organs such as the thyroid, reproductive, and liver organs, as well as cancer.

While significant research has been done on numerous treatment methods, this research expanded the body of knowledge by exploring a new possibility for effective GAC. Previously, bituminous coal based GAC has been the premier form of GAC due to its efficiency and effectiveness. However, bituminous coal presents a sustainability and cost issue. Evoqua's claim that its enhanced coconut based GAC AC1230CX is as effective at removing contaminants as bituminous coal presented an opportunity to compare these two side-by-side.

With the results presented and the conclusions made, this research provides justification to further explore the possibility of utilizing more sustainable products for remediation in the future. The study showed that biochar GACs, when enhanced by the manufacturer, are capable of competing with coal-based carbons when used to remediate PFAS contaminated water. Additionally, due to the potential cost savings, more exploration into the benefits is warranted.

Recommendations for Future Research

While this research was able to show that the coconut-based GAC was able to compete with the bituminous coal-based GAC, more research needs to be done that is

more representative of a full-scale system. The next step beyond bottle studies of this type is likely work with a Rapid Small-Scale Column Test (RSSCT). This would enable the results of the two carbons to be further evaluated when the GAC is compacted together and has water steadily running through it.

Furthermore, future research should focus on determining the optimal ratio of carbon to PFAS and determine the behavior of adsorption at higher and lower amounts. This research focused solely on one level for each constituent and the results at those concentrations. This particular ratio contributed to a rapid rate of removal. In order to attain more granularity, the ratio of PFAS to carbon should be increased to slow down the removal rate.

Finally, water that is not deionized and contains other constituents should be utilized in the future. This would enable the researcher to understand the effect of other organic matter and contaminants on the carbons. Some work has been done previously on this matter with other carbons, but these effects may be more or less from one carbon to the next.

Summary

This research studied the propensity of two different types of GAC to adsorb and remove PFOS and PFOA from a deionized water source. The results were compared using statistical analysis. While biochar GACs have historically shown less capability in remediation efforts of PFAS, the AC1230CX enhanced coconut-based GAC by Evoqua competed in these bottle studies with Calgon's F600 bituminous coal-based GAC. This shows that there may be reason in the future to consider more sustainable, cost-effective

sources of GAC as municipalities and industries pursue effective PFAS remediation techniques.

Appendix A: Chains of Custody



Chain of Custody Record (COC)

U.S. EPA, ORD, NRMRL, LMMD

Shipping Method: MANUAL
 Airbill No.: _____

Page: 1 of 1
 Shipping Container: 1 of 1

Project: PFAS Adsorption Comparison

Location: AFIT

Project Manager: Matthew Holliday

Site or Field Phone: _____

Lab Name: Center Hill NRMRL, LMMD, ECEB NRMRL \ LMMD

Address: 5895 Center Hill Ave 26 W. MARTIN LUTHER KING DRIVE

Contact: Todd Lutzon JIM VOIT

Phone: 513-569-7210 513-487-2867

Sample ID	Description	Date/Time Collected	Volume/ Mass	Requested Analysis	Special Instructions
1 C-S-1-B	DI Water ✓	9-Sep-19	15 mL		
2 C-S-1-0	PFOS ✓	9-Sep-19	15 mL		
3 C-S-1-15	PFOS ✓	9-Sep-19	15 mL		
4 C-S-1-30	PFOS ✓	9-Sep-19	15 mL		
5 C-S-1-60	PFOS ✓	9-Sep-19	15 mL		
6 C-S-1-120	PFOS ✓	9-Sep-19	15 mL		
7 C-S-1-240	PFOS ✓	9-Sep-19	15 mL		
8 C-S-1-24H	PFOS ✓	9-Sep-19	15 mL		
9 C-S-2-B	DI Water ✓	9-Sep-19	15 mL		
10 C-S-2-0	PFOS ✓	9-Sep-19	15 mL		
11 C-S-2-15	PFOS ✓	9-Sep-19	15 mL		
12 C-S-2-30	PFOS ✓	9-Sep-19	15 mL		
13 C-S-2-60	PFOS ✓	9-Sep-19	15 mL		
14 C-S-2-120	PFOS ✓	9-Sep-19	15 mL		
15 C-S-2-240	PFOS ✓	9-Sep-19	15 mL		
16 C-S-2-24H	PFOS ✓	9-Sep-19	15 mL		
17 C-S-3-B	DI Water ✓	9-Sep-19	15 mL		
18 C-S-3-0	PFOS ✓	9-Sep-19	15 mL		
19 C-S-3-15	PFOS ✓	9-Sep-19	15 mL		
20 C-S-3-30	PFOS ✓	9-Sep-19	15 mL		
21 C-S-3-60	PFOS ✓	9-Sep-19	15 mL		
22 C-S-3-120	PFOS ✓	9-Sep-19	15 mL		
23 C-S-3-240	PFOS ✓	9-Sep-19	15 mL		
24 C-S-3-24H	PFOS ✓	9-Sep-19	15 mL		
25 E-S-1-B	DI Water ✓	9-Sep-19	15 mL		
26 E-S-1-0	PFOS ✓	9-Sep-19	15 mL		
27 E-S-1-15	PFOS ✓	9-Sep-19	15 mL		
28 E-S-1-30	PFOS ✓	9-Sep-19	15 mL		
29 E-S-1-60	PFOS ✓	9-Sep-19	15 mL		
30 E-S-1-120	PFOS ✓	9-Sep-19	15 mL		
31 E-S-1-240	PFOS ✓	9-Sep-19	15 mL		
32 E-S-1-24H	PFOS ✓	9-Sep-19	15 mL		
33 E-S-2-B	DI Water ✓	9-Sep-19	15 mL		
34 E-S-2-0	PFOS ✓	9-Sep-19	15 mL		
35 E-S-2-15	PFOS ✓	9-Sep-19	15 mL		
36 E-S-2-30	PFOS ✓	9-Sep-19	15 mL		
37 E-S-2-60	PFOS ✓	9-Sep-19	15 mL		
38 E-S-2-120	PFOS ✓	9-Sep-19	15 mL		
39 E-S-2-240	PFOS ✓	9-Sep-19	15 mL		
40 E-S-2-24H	PFOS ✓	9-Sep-19	15 mL		
41 E-S-3-B	DI Water ✓	9-Sep-19	15 mL		
42 E-S-3-0	PFOS ✓	9-Sep-19	15 mL		
43 E-S-3-15	PFOS ✓	9-Sep-19	15 mL		
44 E-S-3-30	PFOS ✓	9-Sep-19	15 mL		
45 E-S-3-60	PFOS ✓	9-Sep-19	15 mL		
46 E-S-3-120	PFOS ✓	9-Sep-19	15 mL		
47 E-S-3-240	PFOS ✓	9-Sep-19	15 mL		
48 E-S-3-24H	PFOS ✓	9-Sep-19	15 mL		

Total No. of sample containers: 48 Datetime: 10 Sept 2019

Signature: Matthew Holliday

Printed Name: Matthew Holliday

Company Affiliation: AFIT

Total No. of sample containers: 48 Datetime: 10 Sept 2019

Signature: Matthew Holliday

Printed Name: Matthew Holliday

Company Affiliation: AFIT

Sample Analysis Request and Chain of Custody (COC) Record

Lab Name AWBERC		Project Identification PFAS Adsorption Comparison		Container Type	Preservation	Number of Containers	Notes	Requested Parameters									
Address 26 W. MLK Dr Cinti 45268		Location AFIT						PFCA Analysis									
Contact Person Jim Voit		Project Manager Matthew Holliday															
Shipping Method Manual ☐		Total Number of Shipping Containers 48															
Sampled By		☐															
#	Sample Identification	Date Collected	Time Collected														
1	C-A-1-B	10/09/19	1200	50 mL tube	N/A	1		X									
2	C-A-1-0	10/09/19	1200	50 mL tube	N/A	1		X									
3	C-A-1-15	10/09/19	1200	50 mL tube	N/A	1		X									
4	C-A-1-30	10/09/19	1200	50 mL tube	N/A	1		X									
5	C-A-1-60	10/09/19	1200	50 mL tube	N/A	1		X									
6	C-A-1-120	10/09/19	1200	50 mL tube	N/A	1		X									
7	C-A-1-240	10/09/19	1200	50 mL tube	N/A	1		X									
8	C-A-1-24H	10/09/19	1200	50 mL tube	N/A	1		X									
9	C-A-2-B	10/09/19	1200	50 mL tube	N/A	1		X									
10	C-A-2-0	10/09/19	1200	50 mL tube	N/A	1		X									
11	C-A-2-15	10/09/19	1200	50 mL tube	N/A	1		X									
12	C-A-2-30	10/09/19	1200	50 mL tube	N/A	1		X									
13	C-A-2-60	10/09/19	1200	50 mL tube	N/A	1		X									

Relinquished by:	Date	Time	Received by:	Date	Time	Notes / Comments: received from Matthew Holliday 11:30am 10/16/2019
Received in Lab by:	Date	Time				

**Sample Analysis Request
and
Chain of Custody (COC) Record**

Lab Name AWBERC		Project Identification PFAS Adsorption Comparison		Container Type	Preservation	Number of Containers	Notes	Requested Parameters						
Address 26 W. MLK Dr Cinti 45268		Location AFIT						PFCA Analysis						
Contact Person Jim Volt		Project Manager Matthew Holliday												
Shipping Method Manual ☐		Total Number of Shipping Containers 48 ☐												
Sampled By														
#	Sample Identification	Date Collected	Time Collected											
14	C-A-2-120	10/09/19	1200	50 mL tube	N/A	1		X						
15	C-A-2-240	10/09/19	1200	50 mL tube	N/A	1		X						
16	C-A-2-24H	10/09/19	1200	50 mL tube	N/A	1		X						
17	C-A-3-B	10/09/19	1200	50 mL tube	N/A	1		X						
18	C-A-3-0	10/09/19	1200	50 mL tube	N/A	1		X						
19	C-A-3-15	10/09/19	1200	50 mL tube	N/A	1		X						
20	C-A-3-30	10/09/19	1200	50 mL tube	N/A	1		X						
21	C-A-3-60	10/09/19	1200	50 mL tube	N/A	1		X						
22	C-A-3-120	10/09/19	1200	50 mL tube	N/A	1		X						
23	C-A-3-240	10/09/19	1200	50 mL tube	N/A	1		X						
24	C-A-3-24H	10/09/19	1200	50 mL tube	N/A	1		X						
25	E-A-1-B	10/10/19	1200	50 mL tube	N/A	1		X						
26	E-A-1-0	10/10/19	1200	50 mL tube	N/A	1		X						

Relinquished by:	Date	Time	Received by:	Date	Time	Notes / Comments: received from Matthew Holliday 11:30am 10/16/2019
Received in Lab by:	Date	Time				



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Sample Analysis Request
and
Chain of Custody (COC) RecordPage 3 of 4

Lab Name AWBERC		Project Identification PFAS Adsorption Comparison		Container Type	Preservation	Number of Containers	Notes	Requested Parameters									
Address 26 W. MLK Dr Cinti 45268		Location AFIT						PFOA Analysis									
Contact Person Jim Volt		Project Manager Matthew Holliday															
Shipping Method Manual ☐																	
Sampled By		Total Number of Shipping Containers 48															
#	Sample Identification	Date Collected	Time Collected														
27	E-A-1-15	10/10/19	1200	50 mL tube	N/A	1		X									
28	E-A-1-30	10/10/19	1200	50 mL tube	N/A	1		X									
29	E-A-1-60	10/10/19	1200	50 mL tube	N/A	1		X									
30	E-A-1-120	10/10/19	1200	50 mL tube	N/A	1		X									
31	E-A-1-240	10/10/19	1200	50 mL tube	N/A	1		X									
32	E-A-1-24H	10/10/19	1200	50 mL tube	N/A	1		X									
33	E-A-2-8	10/10/19	1200	50 mL tube	N/A	1		X									
34	E-A-2-0	10/10/19	1200	50 mL tube	N/A	1		X									
35	E-A-2-15	10/10/19	1200	50 mL tube	N/A	1		X									
36	E-A-2-30	10/10/19	1200	50 mL tube	N/A	1		X									
37	E-A-2-60	10/10/19	1200	50 mL tube	N/A	1		X									
38	E-A-2-120	10/10/19	1200	50 mL tube	N/A	1		X									
39	E-A-2-240	10/10/19	1200	50 mL tube	N/A	1		X									

Relinquished by:	Date	Time	Received by:	Date	Time	Notes / Comments: received from Matthew Holliday 11:30am 10/16/2019
Received in Lab by:	Date	Time				



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Sample Analysis Request
and
Chain of Custody (COC) RecordPage 4 of 4

Lab Name AWBERC		Project Identification PFAS Adsorption Comparison		Container Type	Preservation	Number of Containers	Notes	Requested Parameters									
Address 26 W. MLK Dr Cinti 45268		Location AFIT						PFOA Analysis									
Contact Person Jim Volt		Project Manager Matthew Holliday															
Shipping Method Manual ☐																	
Sampled By		Total Number of Shipping Containers 48															
#	Sample Identification	Date Collected	Time Collected														
40	E-A-2-24H	10/10/19	1200	50 mL tube	N/A	1		X									
41	E-A-3-8	10/10/19	1200	50 mL tube	N/A	1		X									
42	E-A-3-0	10/10/19	1200	50 mL tube	N/A	1		X									
43	E-A-3-15	10/10/19	1200	50 mL tube	N/A	1		X									
44	E-A-3-30	10/10/19	1200	50 mL tube	N/A	1		X									
45	E-A-3-60	10/10/19	1200	50 mL tube	N/A	1		X									
46	E-A-3-120	10/10/19	1200	50 mL tube	N/A	1		X									
47	E-A-3-240	10/10/19	1200	50 mL tube	N/A	1		X									
48	E-A-3-24H	10/10/19	1200	50 mL tube	N/A	1		X									

Relinquished by:	Date	Time	Received by:	Date	Time	Notes / Comments: received from Matthew Holliday 11:30am 10/16/2019
Received in Lab by:	Date	Time				

JAMES VOIT
Digitally signed by JAMES VOIT
DN: cn=JAMES VOIT, o=USEPA, ou=ORD, email=j.volt@epa.gov, c=US



USEPA, ORD, NRMRL

Sample Analysis Request
and
Chain of Custody (COC) Record

Page 1 of 4

Lab Name AWBERC		Project Identification PFAS Adsorption Comparison		Container Type	Preservation	Number of Containers	Notes	Requested Parameters									
Address 26 W. MLK Dr Cinti 45268		Location AFIT						PFAS Analysis									
Contact Person Jim Voit		Project Manager Matthew Holliday															
Shipping Method Manual ☐																	
Sampled By		Total Number of Shipping Containers 48 ☐															
#	Sample Identification	Date Collected	Time Collected														
1	C-M-1-B	10/25/2019	1200	50 mL tube	N/A	1		X									
2	C-M-1-0	10/25/2019	1200	50 mL tube	N/A	1		X									
3	C-M-1-15	10/25/2019	1200	50 mL tube	N/A	1		X									
4	C-M-1-30	10/25/2019	1200	50 mL tube	N/A	1		X									
5	C-M-1-60	10/25/2019	1200	50 mL tube	N/A	1		X									
6	C-M-1-120	10/25/2019	1200	50 mL tube	N/A	1		X									
7	C-M-1-240	10/25/2019	1200	50 mL tube	N/A	1		X									
8	C-M-1-24H	10/25/2019	1200	50 mL tube	N/A	1		X									
9	C-M-2-B	10/25/2019	1200	50 mL tube	N/A	1		X									
10	C-M-2-0	10/25/2019	1200	50 mL tube	N/A	1		X									
11	C-M-2-15	10/25/2019	1200	50 mL tube	N/A	1		X									
12	C-M-2-30	10/25/2019	1200	50 mL tube	N/A	1		X									
13	C-M-2-60	10/25/2019	1200	50 mL tube	N/A	1		X									

Relinquished by:	Date	Time	Received by:	Date	Time	Notes / Comments: received from Matthew Holliday 10/31/2019 12:10 pm
Received in Lab by:	Date	Time				



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Sample Analysis Request
and
Chain of Custody (COC) Record

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Lab Name AWBERC		Project Identification PFAS Adsorption Comparison		Container Type	Preservation	Number of Containers	Notes	Requested Parameters									
Address 26 W. MLK Dr Cinti 45268		Location AFIT						PFAS Analysis									
Contact Person Jim Voit		Project Manager Matthew Holliday															
Shipping Method Manual ☐																	
Sampled By		Total Number of Shipping Containers 48 ☐															
#	Sample Identification	Date Collected	Time Collected														
14	C-M-2-120	10/25/2019	1200	50 mL tube	N/A	1		X									
15	C-M-2-240	10/25/2019	1200	50 mL tube	N/A	1		X									
16	C-M-2-24H	10/25/2019	1200	50 mL tube	N/A	1		X									
17	C-M-3-B	10/25/2019	1200	50 mL tube	N/A	1		X									
18	C-M-3-0	10/25/2019	1200	50 mL tube	N/A	1		X									
19	C-M-3-15	10/25/2019	1200	50 mL tube	N/A	1		X									
20	C-M-3-30	10/25/2019	1200	50 mL tube	N/A	1		X									
21	C-M-3-60	10/25/2019	1200	50 mL tube	N/A	1		X									
22	C-M-3-120	10/25/2019	1200	50 mL tube	N/A	1		X									
23	C-M-3-240	10/25/2019	1200	50 mL tube	N/A	1		X									
24	C-M-3-24H	10/25/2019	1200	50 mL tube	N/A	1		X									
25	E-M-1-B	10/30/19	1200	50 mL tube	N/A	1		X									
26	E-M-1-0	10/30/19	1200	50 mL tube	N/A	1		X									

Relinquished by:	Date	Time	Received by:	Date	Time	Notes / Comments: received from Matthew Holliday 10/31/2019 12:10 pm
Received in Lab by:	Date	Time				



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Sample Analysis Request and Chain of Custody (COC) Record

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Lab Name AWBERC		Project Identification PFA8 Adsorption Comparison		Container Type	Preservation	Number of Containers	Notes	Requested Parameters									
Address 28 W. MLK Dr Cinti 46288		Location AFIT						PFAS Analysis									
Contact Person Jim Voit		Project Manager Matthew Holliday															
Shipping Method Manual ☐																	
Sampled By		Total Number of Shipping Containers 48															
#	Sample Identification	Date Collected	Time Collected														
27	E-M-1-15	10/30/2019	1200	50 mL tube	N/A	1		X									
28	E-M-1-30	10/30/2019	1200	50 mL tube	N/A	1		X									
29	E-M-1-60	10/30/2019	1200	50 mL tube	N/A	1		X									
30	E-M-1-120	10/30/2019	1200	50 mL tube	N/A	1		X									
31	E-M-1-240	10/30/2019	1200	50 mL tube	N/A	1		X									
32	E-M-1-24H	10/30/2019	1200	50 mL tube	N/A	1		X									
33	E-M-2-8	10/30/2019	1200	50 mL tube	N/A	1		X									
34	E-M-2-0	10/30/2019	1200	50 mL tube	N/A	1		X									
35	E-M-2-15	10/30/2019	1200	50 mL tube	N/A	1		X									
36	E-M-2-30	10/30/2019	1200	50 mL tube	N/A	1		X									
37	E-M-2-60	10/30/2019	1200	50 mL tube	N/A	1		X									
38	E-M-2-120	10/30/2019	1200	50 mL tube	N/A	1		X									
39	E-M-2-240	10/30/2019	1200	50 mL tube	N/A	1		X									
Relinquished by:	Date	Time	Received by:	Date	Time	Notes / Comments: received from Matthew Holliday 10/31/2019 12:10 pm											
Received in Lab by:	Date	Time															



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Sample Analysis Request and Chain of Custody (COC) Record

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Lab Name AWBERC		Project Identification PFA8 Adsorption Comparison		Container Type	Preservation	Number of Containers	Notes	Requested Parameters									
Address 28 W. MLK Dr Cinti 46288		Location AFIT						PFAS Analysis									
Contact Person Jim Voit		Project Manager Matthew Holliday															
Shipping Method Manual ☐																	
Sampled By		Total Number of Shipping Containers 48															
#	Sample Identification	Date Collected	Time Collected														
40	E-M-2-24H	10/30/2019	1200	50 mL tube	N/A	1		X									
41	E-M-3-8	10/30/2019	1200	50 mL tube	N/A	1		X									
42	E-M-3-0	10/30/2019	1200	50 mL tube	N/A	1		X									
43	E-M-3-15	10/30/2019	1200	50 mL tube	N/A	1		X									
44	E-M-3-30	10/30/2019	1200	50 mL tube	N/A	1		X									
45	E-M-3-60	10/30/2019	1200	50 mL tube	N/A	1		X									
46	E-M-3-120	10/30/2019	1200	50 mL tube	N/A	1		X									
47	E-M-3-240	10/30/2019	1200	50 mL tube	N/A	1		X									
48	E-M-3-24H	10/30/2019	1200	50 mL tube	N/A	1		X									
Relinquished by:	Date	Time	Received by:	Date	Time	Notes / Comments: received from Matthew Holliday 10/31/2019 12:10 pm											
Received in Lab by:	Date	Time															

JAMES VOIT

Digitally signed by JAMES VOIT
Date: 2019.11.01 08:37:51
+0400

Appendix B: Certificates of Analysis

SIGMA-ALDRICH®

sigma-aldrich.com

3050 Spruce Street, Saint Louis, MO 63103, USA

Website: www.sigmaaldrich.com

Email USA: techserv@sial.com

Outside USA: eurtechserv@sial.com

Certificate of Analysis

Product Name:
Perfluorooctanoic acid – 96%

Product Number: 171468
Batch Number: MKBX5537V
Brand: ALDRICH
CAS Number: 335-87-1
MDL Number: MFCD00004174
Formula: C₈HF₁₅O₂
Formula Weight: 414.07 g/mol
Quality Release Date: 03 FEB 2016



Test	Specification	Result
Appearance (Color)	White to Off-White	White
Appearance (Form)	Conforms to Requirements	Crystals
Powder, Crystals, Crystalline Powder and/or Flakes		
Infrared Spectrum	Conforms to Structure	Conforms
Purity (Titration by NaOH)	95.5 - 104.5 %	102.7 %
GC (area %)	> 95.5 %	95.8 %
Water (by Karl Fischer)	≤ 4.5 %	0.2 %

Michael Grady, Manager
Quality Control
Milwaukee, WI US

Sigma-Aldrich warrants, that at the time of the quality release or subsequent retest date this product conformed to the information contained in this publication. The current Specification sheet may be available at Sigma-Aldrich.com. For further inquiries, please contact Technical Service. Purchaser must determine the suitability of the product for its particular use. See reverse side of invoice or packing slip for additional terms and conditions of sale.

Certificate of Analysis

Product Name : Heptadecafluorooctanesulfonic acid solution ~40% in H₂O (T)
Product Number : 77283-50ML
Batch Number : 0000087479
Source Batch : 0000024002
CAS Number : 1763-23-1
Molecular Formula : C₈HF₁₇O₂S
Formula Weight : 500.13
Quality Release Date : 29 May 2018

Test	Specification	Result
Appearance (Color)	Colorless to Dark Yellow and Very Faint	Colorless
Appearance (Form)	Liquid	Liquid
Titration with NaOH	35.0 - 45.0 %	41.4 %
¹⁹ F NMR Spectrum	Conforms to Structure	Conforms
Water (by Karl Fischer)	55 - 65 %	58 %

Champaka. G.

Champaka Gurudevanu, Manager

Analytical

Bangalore

IN

Sigma-Aldrich warrants, that at the time of the quality release or subsequent retest date this product conformed to the information contained in this publication. The current Specification sheet may be available at Sigma-Aldrich.com. For further inquiries, please contact Technical Service. Purchase must determine the suitability of the product for its particular use. See reverse side of website or packing slip for additional terms and conditions of sale

Version Number: 01 Doc: 1040056

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