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PFOA Loaded GAC Fall 2021 Report

Introduction

The per- and polyfluoroalkyl substance (PFAS) chemical family contains organic molecules of a vast variety of sizes that are either completely or partially fluorinated along the carbon-carbon chain. The PFAS family can further be broken down into subgroups, two of which are perfluorinated carboxylic acids (PFCAs) and perfluorinated sulfonic acids (PFSAs) (Bentel, et al., 2019). While there is an immense number of configurations in these two subgroups alone, research seems to focus on two main PFASs, perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) (Figure 1) (Huang & Jaffé, 2019; Jing, Peng-yi, & Jian, 2007; Liu, Qu, Wang, Mendoza-Sanchez, & Sharma, 2017; Söregård, Lindh, & Ahrens, 2020; Söregård, Niarchos, Jensen, & Ahrens, 2019; Tenorio, et al., 2020).

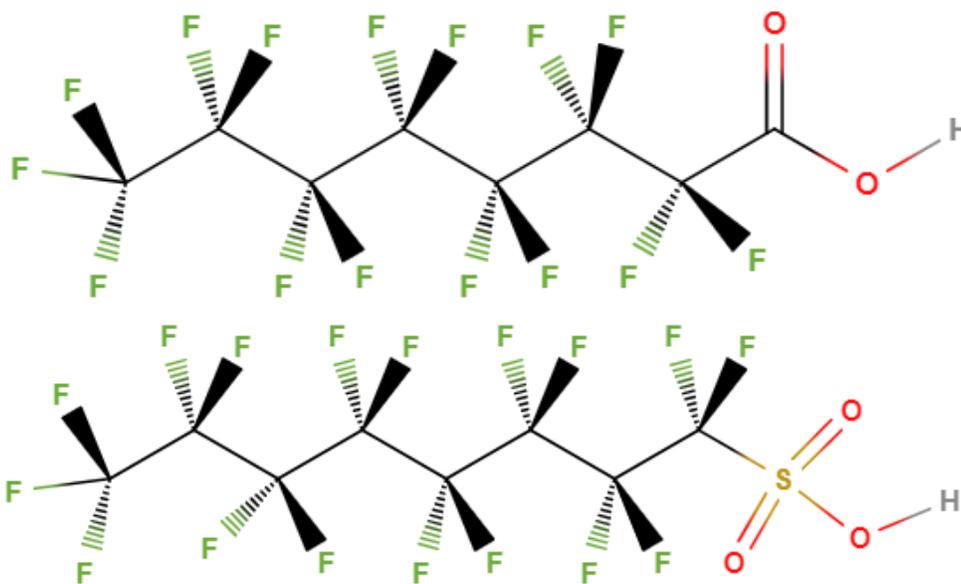


Figure 1: The figure above displays the chemical structures of PFOA and PFOS. From the structures, it can be seen that the core of the molecules are the same and that the only difference between the two are the heads of the chemicals.

PFASs have been used in a variety of industries and products, such as clothing and kitchen utensils. While PFAS utilization has been reduced in light of its environmental

contamination, one of the most notable products is aqueous film-forming foams (AFFFs) that are used by firefighters; this is due to their resistance to degrade when exposed to high temperatures (Bentel, et al., 2019; Liu, Qu, Wang, Mendoza-Sanchez, & Sharma, 2017; Söregård, Lindh, & Ahrens, 2020; Söregård, Östblom, Köhler, & Ahrens, 2020; Tenorio, et al., 2020). Once PFASs have entered the environment, such as through leaching from AFFFs and industrial activities or improper disposal, the chemicals become an environmental and public health concern.

PFASs have the ability to disturb natural phenomena and bioaccumulate once inside of an organism (Ahmed, et al., 2020; Söregård, Lindh, & Ahrens, 2020). It has been reported that PFAS contamination has had adverse effects on human health. PFAS contamination has been linked to cancer, thyroid complications, infertility and premature menopause amongst women, and premature puberty amongst children (Ahmed, et al., 2020; Liu, Qu, Wang, Mendoza-Sanchez, & Sharma, 2017; Tenorio, et al., 2020). To exemplify the issue, several sources have reported that PFAS is detectable in water sources throughout the world. In an effort to combat the negative effects of PFAS contamination in the U.S., the U.S. Environmental Protection Agency has issued a Provisional Health Advisory level of 70 ng/L for PFOA and PFOS. (Bao, et al., 2018; Bentel, et al., 2019; Liu, Qu, Wang, Mendoza-Sanchez, & Sharma, 2017; Tenorio, et al., 2020). Individual states have also taken an initiative to reduce PFAS concentrations in water sources. For example, the North Carolina Department of Health and Human Services issued a nonregulatory benchmark for PFOA concentrations of 140 ng/L (Pica, et al., 2019). While the action taken place by governing bodies is important, treatment of PFASs is a major issue that needs to be addressed.

Based on a paper written by Söregård et al. (2020), PFASs have been shown to have a tendency to adsorb to activated carbon based sorbents; however, it should be noted that the adsorbance strength decreases with chain length. Nonetheless, this is an important finding because the process can be scaled up to see its effectiveness in a wastewater treatment plant. However, the issue is then transferred from the treatment of water contaminated with PFAS to the disposal of contaminated filter material.

Söregård, Lindth, and Ahrens (2020) reported that they were able to desorb PFAS from materials at 450°C . However, in the same paper, they report degradation temperatures for PFAS

ranging from 725°C, for partial destruction, to 1100°C, for complete destruction. However, reaching temperatures high enough to decompose the PFAS is not a cost effective solution (Sörengård, Lindh, & Ahrens, 2020). There is a need to determine a method for treating materials that may be contaminated with PFAS, which leads to the basis of this study.

The aim of this study is to determine how exposure to UV radiation impacts PFOA adsorbed to granulated activated carbon (GAC). While there have been mixed results for UV radiation degradation of PFASs, they have not focused on filter material contaminated with PFASs. In this study, in an effort to bring insight into this gap in literature, GAC was contaminated with a known amount of PFOA and exposed to a UV-lamp for a set period of time.

Procedure

Acrylic Box

An 11 in x 5 in x 6 in acrylic box was provided. At the center of the long sides of the box, 2.5 in above the bottom, a marking was made. With frequent industrial lubricant applications, a hole was drilled, centered on the marking. It is important to note that careful control over the speed of the drill is necessary to ensure that the acrylic does not crack and that a small drill was used at first and slowly changed out for a larger size until the desired hole size was achieved. Once both long sides had a desired sized hole, the acrylic box was properly cleaned (Figure 2).



Figure 2: Displayed in the figure above is the acrylic box after the holes have been drilled in both of the long sides.

GAC PFOA Experiment

50 g of GAC was washed and allowed to dry in an oven overnight at 105°C. 1.00 g of PFOA was completely dissolved in 100 mL of water. The GAC was taken out of the oven, allowed to cool, and weighed. 5 mL of PFOA solution was pipetted out of the flask and set aside in a glass vial. The remaining PFOA solution was poured into the container holding the dry GAC. The GAC PFOA solution was placed on an orbital stirrer and allowed to mix at 180 rpm for 24 hours. 5 mL of the top liquid layer was pipetted out of the container, labeled, and set aside; this was done three times. The remaining PFOA loaded GAC was then vacuum dried. Once dry, 5 g of PFOA loaded GAC was taken, labeled, and placed to the side.

A 5 in x 11 in sheet of aluminum foil was cut and used to completely cover the bottom of the acrylic box. The PFOA loaded GAC was evenly spread over the aluminum foil. The UV-lamp and its protective glass cover were inserted into the holes on the long sides of the acrylic box (Figure 3). The acrylic box was covered with aluminum foil and the UV-lamp was turned on.



Figure 3: Displayed in the figure above is the PFOA loaded GAC distributed over the aluminum foil used to cover the bottom of the acrylic box and the UV-lamp and its protective sleeve fed through the holes.

After an hour, the UV-lamp was turned off and fed out of the holes, the foil covering the box was taken off, and 5 g of PFOA loaded GAC was collected. It is important to note that the 5 g of PFOA loaded GAC was not taken from specific area of the GAC layer. Rather, the sample was intended to be representative of the entire PFOA loaded GAC layer, thus GAC was taken from all areas of the box. The acrylic box was covered, and the UV-lamp was fed back through the holes and turned on. Using the same sample gathering procedure, four more samples were

obtained, one an hour after the second sample and the other three an hour apart, starting upon arrival at the laboratory the next day.

Each PFOA loaded GAC sample was collected into a bottle with 200 mL of water. The solution was placed on an orbital stirrer and allowed to mix at 180 rpm for 48 hours.

Solid Phase Extraction

The following procedure was provided by Cory Klemashevich and Smriti Shankar located at Texas A&M College Station.

22 g of ammonium hydroxide was dissolved in 250 mL of methanol to create a 0.1% ammonium hydroxide solution. 0.48 g of ammonium acetate was dissolved in 250 mL of water to create a 25 mM solution. 2 glass tubes were gathered for each sample; one was labeled “Sample Name – W” for waste and the other was labeled “Sample Name – E” for the eluent. The glass tubes were placed inside of the vacuum manifold, with the waste tubes in the foreground and the eluent tubes in the background (Figure 4). 10 solid phase extraction cartridges were each labeled for their respective sample and arranged on the top of the vacuum manifold so that they were over the glass tubes intended for waste.

Under low-medium vacuum pressure, the solid phase extraction cartridges were washed 3 times with 1 mL of 0.1% ammonium hydroxide. During the process, it is important to ensure that the cartridge always has liquid in it so that it does not have an opportunity to dry. Under the same low-medium vacuum pressure, the cartridges were then washed 3 times with 100% methanol. Immediately after the methanol has left the cartridge, the pressure was drastically reduced to create a very low-pressure environment and 1 mL of sample was added to each cartridge. The very low pressure should only allow a small amount of drops of liquid to drip into the waste glass tube under it. Once the liquid has left the cartridge, 1 mL of 25 mM ammonium acetate was used to wash each cartridge. The cartridges were then allowed to dry for 3 to 5 minutes, under low vacuum.



Figure 4: Displayed in the figure above is the top and side views of the vacuum manifold.

Once dry, the cartridge locations were switched to where they were over the glass tubes intended for the eluent for the respective sample. Under very low vacuum, 1 mL of 0.1% ammonium hydroxide was added and the cartridge was allowed to dry. Once all the cartridges were dry, the vacuum manifold was opened, and all of the elution tubes were quickly covered with parafilm so that little to none of the methanol in the eluent glass tubes would evaporate. The liquid samples, including the sample from the original PFOA solution and the top layer of GAC PFOA solution, were then transferred into HPLC glass vials and analyzed using a LCQQQ.

Results and Discussion

Throughout the course of the semester, there were four experiments conducted. However, there are no results for any of the experiments. For the first two experiments, there was a large inconsistency with the sample gathering process; there was a wide range of sample masses

(Table 1). Because of this, when the samples were taken to Texas A&M College Station for analysis, those that were gathered from the first two experiments did not undergo the solid phase extraction process; this is specifically due to samples PFOA GAC 1-4, PFOA GAC 1-5, PFOA GAC 1-7, PFOA GAC 1-8, PFOA GAC 2-1, PFOA GAC 2-3, PFOA GAC 2-4, and PFOA GAC 2-5. Upon arrival at the laboratory at Texas A&M – San Antonio, there was a conversation about the importance of consistent sampling held with those involved. To avoid this in the future, a conversation, before any individual is to be assigned to this project, must be held about the incredible importance of consistent sampling.

Table 1: The following table displays the samples and their masses for the first two experiments that were conducted.

Experiment 1		Experiment 2	
Sample Name	Sample Mass	Sample Name	Sample Mass
PFOA GAC S 1-1	5.055 g	PFOA GAC S 2-1	4.970 g
PFOA GAC S 1-2	5.121 g	PFOA GAC S 2-2	4.973 g
PFOA GAC S 1-3	5.126 g	PFOA GAC S 2-3	4.996 g
PFOA GAC S 1-4	4.929 g	PFOA GAC S 2-4	5.012 g
		PFOA GAC S 2-5	4.996 g
		PFOA GAC S 2-6	5.083 g
PFOA GAC 1-1	4.931 g	PFOA GAC 2-1	4.579 g
PFOA GAC 1-2	4.972 g	PFOA GAC 2-2	5.217 g
PFOA GAC 1-3	4.902 g	PFOA GAC 2-3	4.235 g
PFOA GAC 1-4	1.471 g	PFOA GAC 2-4	4.513 g
PFOA GAC 1-5	3.067 g	PFOA GAC 2-5	3.492 g
PFOA GAC 1-6	4.719 g		
PFOA GAC 1-7	4.442 g		
PFOA GAC 1-8	1.664 g		

While at Texas A&M College Station, the samples for experiment 3 had undergone the solid phase extraction and were analyzed at a later date. Unfortunately, when the results came back from the laboratory located at Texas A&M College Station, none of the samples, including those gathered from the original PFOA solution used for the experiment, contained a detectable

amount of PFOA. Upon further investigation and a discussion with the other researchers from the group, it was discovered that GAC was used, instead of PFOA, to create the solution. Thus, experiment 3 was not viable.

The fourth and final experiment that was conducted was completed too close to the end of the semester for the results to be included in this report. Additionally, a few more materials are needed before the solid phase extraction can be conducted.

Future Work

There are five experiments that can be conducted to continue this project. The first being a continuation of the experiment that has been outlined in this report. As of now, there is no viable data that has been gathered from the experiments that have been conducted due to improper setup and care. Ensuring that solutions are made and samples are gathered correctly are of the utmost importance in any laboratory setting. It is important for all those conducting the experiments to understand the entire procedure and be able to perform the necessary tasks at hand.

The second experiment for this project is to exchange the GAC for another solid media. For example, one of the materials that would be interesting to experiment with is sand. Currently, in the laboratory, there are two different types of sand: Accusand 20/30 and Accusand 30/40. Understanding how sand impacts the degradation of PFOA when the chemical is adsorbed to it would have very impactful insight on future wastewater treatment methods. For example, if it is shown that PFOA has better degradation rates when it is adsorbed to sand, wastewater treatment plants may benefit from implementing a sand filter as opposed to one that utilizes GAC.

The third experiment would be to drill a second set of holes located in a higher position on the box. This path would provide useful insight into how photon intensity impacts PFOA degradation rates. Having the UV-lamp higher would result in a lower photon intensity. While it may be intuitive that the PFOA would have a slower degradation rate, that cannot be stated without proper testing.

The fourth experiment would be to change the initial concentration of PFOA that the GAC is loaded with. Allowing for testing of different PFOA concentrations would give insight into the upper and lower bounds of the effectiveness of the procedure and test its viability in

wastewater treatment uses. For example, if a PFOA concentration is low enough, it may be the case that the procedure is ineffective.

The fifth experiment for this project would be to use a different radiation source. It may be worth using a larger wavelength to understand how it interacts with the PFOA adsorbed to the GAC. A larger wavelength would also require less energy, which may lead to lower cost of operations. Alternatively, a shorter light wavelength is also an option. In an experiment conducted by Jing, Peng-yi, and Jian (2007), it was shown that light that came from a 185 nm vacuum UV-lamp, PFOA displayed a faster degradation rate than when exposed to light from a 254 nm VU-lamp. During the course of the fall 2021 semester, discussions took place to explore this option. However, due to time constraints, the stronger UV-lamp was not able to be obtained, thus the experiment was not conducted.

Conclusion

While the final experiment to be conducted seems promising, there were many mishaps during the course of the semester that made it extremely difficult to gather meaningful results. This is because of a lack of communication and insufficient laboratory training from those conducting the experiments. To avoid this in the future, student researchers who are new to the research laboratory setting to gradually take on responsibilities rather than transfer directly from observation to unsupervised practice. By having the those involved have a constant stream of communication, they can collaboratively practice conducting the experiments repeatedly. This would allow for improved comfort and skill with project protocol and prevent mishaps.

Nonetheless, if done correctly, the experiments for this project should yield valuable results and insight into treatment of PFOA loaded GAC. With as much of a concern PFAS contamination is around the world, this project has the potential to bring peace of mind to various populations.

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