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Abatement of Per- and Polyfluoroalkyl Substances with Electrochemical Oxidation

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ABATEMENT OF PER- AND POLYFLUOROALKYL SUBSTANCES WITH
ELECTROCHEMICAL OXIDATION

by

Elise Webb

Presented to

The Environmental Studies Program at the University of Nebraska-Lincoln

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Abstract

Throughout the United States, there is a growing concern for contamination of groundwater with harmful per- and polyfluoroalkyl substances (PFAS). These forever chemicals have no natural degradation pathways and the science community has not had any significant breakthroughs to remediate contaminated sites. Electrochemical oxidation using a boron-doped diamond (BDD) electrode shows excellent potential for becoming an effective therapy for such PFAS contaminated sites. The objective of this research is to provide proof-of-concept that electrochemical oxidation can degrade PFAS, ensure analysis is accurate, and controls of experimental design are optimal. Electrochemical oxidation degraded 10 mg/L perfluorooctanoic acid (PFOA) under a series of controlled conditions. Overall removal rates were measured using ion chromatography and were as high as 60% after 2 hours of an experimental treatment. Unprecedented in similar studies, the technique caused erosion of the BDD anode, and as a result, the efficacy of treatment decreased.

Keywords: per- and polyfluoroalkyl substances (PFAS), bioaccumulation, contamination, electronegativity, (PFOA), perfluorooctanesulfonic acid (PFOS), electrochemically activated persulfate (EAP)

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Introduction

Per- and polyfluoroalkyl substances (PFAS) are synthetic organic chemicals. These substances have been used for more than 60 years to make water, heat, and stain-resistant products such as cosmetics, personal care products, cooking ware, textiles, paint, packaging, pesticides, firefighting foams, food packaging and more.

There are numerous types of PFAS, but for the most part, they all have the same basic structure with a hydrophilic head and a hydrophobic tail. The hydrophilic head of PFAS is either a sulfonate or carbonate functional group. Perfluoroalkyl tail lengths can range from 3 to 14 carbons. The most studied PFAS include the eight carbon perfluoroalkyl sulfonate ($-\text{SO}_3\text{H}$), known as PFOS, and the eight carbon perfluoroalkyl carboxylate ($-\text{COOH}$), referred to as PFOA.¹



Figure. 1 Chemical structures of perfluorooctanoic acid, PFOA and perfluoroalkyl sulfonate, PFOS, which are two of the more commonly detected PFAS.

The overall structure of the organic chemical and each individual bond give the PFAS their unique properties. Fluorine is the most electronegative element. In other words, fluorine has a strong attraction for a shared pair of electrons. Fluorine's electronegativity is a result of the atom's outer electron shell requiring one more valence electron to fill its octet. Additionally, fluorine's small atomic size has a stronger pull on unshared electrons than larger atoms because its positively charged nucleus is closer to those opposite charges. The electronegative property of

fluorine makes it very willing to form bonds with other elements. When bonds between fluorine and other atoms form, the bonds remain very stable; for example, the C-F bond has incredible covalent strength. The C-F bonds found in the hydrophobic tails of PFAS is one of the strongest bonds in organic chemistry.² PFAS are highly stable substances and can credit this stability to the C-F bonds in their structures.

The same chemical stability that makes PFAS products water, heat, and stain-resistant also makes them recalcitrant as they persist in unintended environments. These molecules are often called, “forever chemicals,” as they have no natural degradation processes in the environment. Through production, use, and disposal, PFAS chemicals are released into the environment where they can travel long distances through water and atmosphere.⁴ PFAS are highly water-soluble, which makes contaminated drinking water especially dangerous for human health. PFAS contaminated water has been identified at many types of facilities. Such facilities include industrial sites, military fire training areas, aqueous film-forming foam (AFFF) certified airports, and wastewater treatment plants.⁵ Contamination can also occur in different types of agricultural crops that are used for human consumption.⁹ These contaminated sites were likely a result of contaminated irrigation systems or contaminated soils near the types of facilities previously mentioned. Biotic exposure to PFAS is not limited to drinking water.³ Individuals can be exposed to PFAS many ways; some of these include direct contact, ingestion, inhalation, and exposure from work. A specific type of exposure, which is known by popular media, is contaminated food from packaging or scratched Teflon cooking ware. In brief, there are many sources of PFAS contamination that can cause harm to the environment and human health.



Figure 2. Aqueous film-forming foam (AFFF) is used in firefighting at airports and military bases. AFFF can contaminate groundwater with PFAS.

The increasing number of PFAS-contaminated sites along with the potential harm to local residents are raising concerns in the science community. The United States Environmental Protection Agency has recommended a health advisory limit for PFOA and PFOS of $0.07\mu\text{g/L}$ of PFAS drinking water. This health advisory is exceptionally small in comparison to the other groundwater contaminants.³ Although a health advisory is in place, it is still unclear the specific amount of PFAS or the length of exposure, which can cause harm to humans. One study found that this limit set by the EPA had been exceeded in the drinking water of 6 million U.S. residents.⁵ PFAS are a danger to human and animal health because they have bioaccumulation potential; more specifically, they can bind to proteins once exposed to the body. PFAS can affect many metabolic and endocrine functions. As a result, PFAS exposure causes hepatic toxicity, reproductive and development issues, suppression of the immune system, thyroid issues, and cancer.^{3,6} Unfortunately, PFAS exposure is frequent. In 2011-2012, the U.S. National Health and Nutrition Examination Survey reported detectable amounts of PFAS in the blood of 97% of the

population.⁵ The level of PFAS contamination was alarming to both the popular media and the science community. Consequently, there has been increased attention on identifying PFAS-contaminated sites, finding ways to degrade these chemicals, and subsequently remediating contaminated environments.

The science community is grappling to find ways to degrade the per- and polyfluoroalkyl substances. As previously mentioned, PFAS are incredibly stable compounds, which makes degrading them a difficult task. Wastewater treatment plants have conventional ways to treat water contaminants, but these approaches are generally ineffective in removing PFAS from drinking water. Techniques used to clean up contaminants in water and soil, such as air stripping, sparging, or soil vapor extraction, are also ineffective because PFAS do not readily transform from liquid states to vapors.¹ Bioremediation approaches have also been ineffective because the chemicals are resistant to microorganisms. Scientists have found a few ways to degrade PFAS in the laboratory, but these treatments are generally not possible or cost-effective under field conditions. There have been attempts to degrade PFAS with advanced oxidation process pairing hydrogen peroxide with ferrous iron, ultraviolet light, or ozone, but none of these have been effective specifically in treating PFOS.¹¹ Some of the successful ways to degrade PFAS include photooxidation with UV light, electrochemical oxidation, ultrasonication with oxygen or argon, microwave radiation, persulfate radiation, ionizing radiation, and gamma irradiation.^{7,11}

Although these methods of degradation have been accomplished in laboratories, they have not been successfully applied to the contamination sites. Many of the mentioned methods require extreme physical conditions like high temperature or pressure to have effective removal, and without such conditions, the reactions are too slow or ineffective.¹¹ Another issue is that some remediation treatments are effective in degrading PFOA but not PFOS due to the chemical

difference in the hydrophobic head of the chemical.¹ Additionally, some treatments can break down PFAS but only into smaller, shortened carbon chains, PFAS. Types of remediation may be specific to the length of the carbon chain and are ineffective on different PFAS. Overall, there has not been any substantial breakthrough for remediating PFAS contaminated environments.

Approach

Matzek et al. (2018) investigated the degradation of a fluoroquinolone antibiotic called ciprofloxacin using electrochemically activated persulfate (EAP).⁸ Using this study as a guide, we attempted a similar approach. Much like PFAS, ciprofloxacin is a water contaminant that cannot be effectively treated by standard water treatment facilities. EAP techniques are valuable because the carbon backbone of the contaminant is converted to CO₂ (i.e., mineralized). As a result, there are no harmful byproducts from the remedial treatment. The efficacy of many PFAS remediation techniques is dependent on chain length, so an EAP treatment could be useful in eradicating the substances leaving no byproducts behind.¹ The mechanism behind the success of EAP is the formation of reactive chemical radicals. EAP causes hydroxyl radicals to form at the surface of the anode and the solvent, water. Hydroxyl radicals bombard the chemical bonds on the target substance and cause more radicals to form. Persulfate activation occurs on the cathode, which causes the highly reactive sulfate radicals to form. The combination of the sulfate and hydroxyl radicals can be instrumental in degrading a variety of contaminants. This study focused on maximizing the degradation of ciprofloxacin by testing different types of anodes, cathodes, and types of electrolytes. Matzek et al. (2018) found that boron-doped diamond (BDD) was the most effective anode, and a graphite cathode had the highest persulfate activation. Although, some studies found platinum wires or titanium plates to be the most effective cathodes.^{12,13,14} The

combine of the BDD anode and graphite cathode had the most abatement of ciprofloxacin. Overall, this study showed that EAP was successful in degrading the water contaminant.

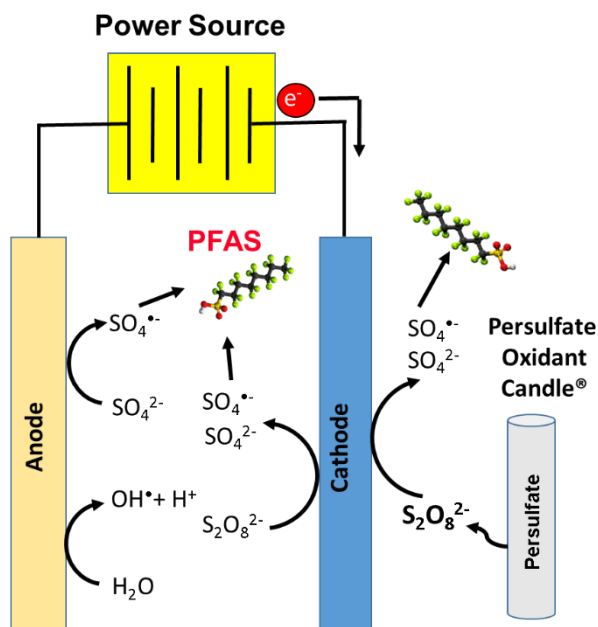


Figure. 3. Schematic of proposed EAP treatment to degrade PFAS. The cathode activates the persulfate to create sulfate radicals. The anode's surface causes sulfate and hydroxyl radicals to form. Both radicals may be able to break the stable fluorine carbon bonds in the PFAS.

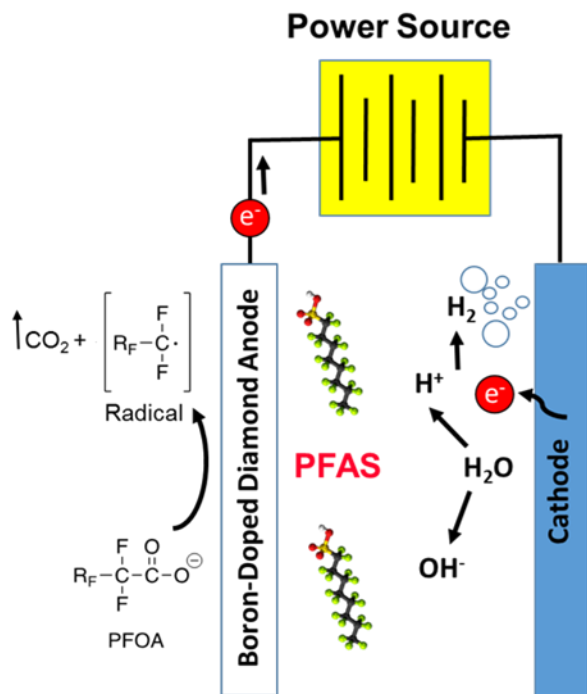


Figure 4. Schematic of electrochemical oxidation of PFOA directly on the BDD electrode. When the PFOA molecule interacts with the surface of the BDD anode, an electron gets removed forming a radical and carbon dioxide.

The success of the EAP technique may not be limited to ciprofloxacin, PFAS may also degrade. It is essential to investigate the abatement of per- and polyfluoroalkyl substances with electrochemically activated persulfate. The research will be conducted using an experimental batch approach where temporal changes in PFAS concentrations and fluoride generation are monitored. Because the chemical structure of PFAS is much different from the antibiotic, the PFAS experiments will test different cathodes, pH, temperatures, and salt solutions to quantify these treatment variables on PFAS degradation. The study also suggested that adding sodium chloride to the solution may cause better degradation results.⁸ The pH of the solution also plays a role in the ratio of hydroxyl and sulfate radicals. Neutral pH has an equal amount of each radical while lowering the pH can increase the number of sulfate radicals.¹⁰ With all the different

variables, it will be essential to have precise methods and repetition to have confidence in any approach.

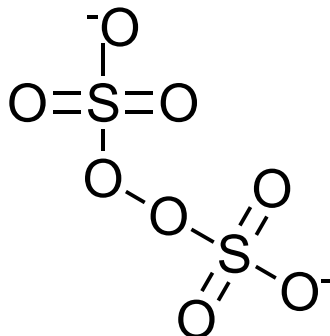


Figure 5. This is the chemical structure of persulfate, where upon activation, sulfate radicals form ($\text{SO}_4^{\cdot-}$). In the proposed experiment, the persulfate will be activated on the surface of the cathode.

One of the most critical aspects of this research is to try to achieve a treatment technology that will easily transition from the laboratory to an *in situ* treatment. Thus, the experimental design will avoid extreme physical conditions that are unachievable under field conditions. The use of the oxidant candle is already looking towards a practical approach for environmental remediation. The persulfate oxidant candle will allow a slower release of persulfate, allowing the treatment to occur in a specific site and not be swept away with groundwater. Persulfate is stable at room temperature and requires activation to undergo the radical formation.¹⁰ The cathode's surface is what is providing the persulfate activation, and the power source can control that activation. In brief, the goal of this study is to generate data that eventually can be used to create an effective treatment for PFAS-contaminated groundwater.

Overall, further research on per- and polyfluoroalkyl substances must take place – specifically, research that tackles the contaminated groundwater before it plays a significant role

in human exposure. PFAS contamination in minimal amounts can have adverse effects on human health. PFAS were used in the production of many consumer goods as they are very heat, water, and stain-resistant. The science community has struggled to degrade PFAS due to the strength of their chemical bonds and mobility through different environments like water, soil, and atmosphere. Conventional methods of environmental remediation of contaminants do not work on PFAS. Electrochemically activated persulfate may be the solution to effectively degrading per- polyfluoroalkyl substances.

Materials and Methods

Overview

The overall scope of this research is much broader than the completion of this thesis project. The knowledge gained from this research will support the development of a potential *in situ* remediation technology for PFAS-contaminated groundwater using electrochemical oxidation. The specific objectives of this thesis were to provide proof-of-concept that electrochemical oxidation can degrade PFAS and ensure analysis is accurate and controls of experimental design are optimal. A quantitative-experimental approach is most suited to achieve these objectives. Throughout the process of running experiments and collecting data, there was a need to adjust experiments based on new knowledge from literature, experimental results, and upgraded instruments. This adaptability was important in generating credible results and optimizing time and resources. In brief, the overall experimental procedure consisted of solution preparation, trial setup, running the experiment, sample collection, processing of samples, and analyzing data.

Detecting temporal increases in fluoride concentrations during electrochemical treatment provides evidence for the degradation of PFOA. If PFOA is intact, a solution will have no

concentration of fluoride. By contrast, when PFOA degrades, fluoride is removed from the long fluorocarbon chain of the PFOA tail. Therefore, the concentration of fluoride recovered in solution can be representative of PFOA degradation. All experiments will use ion chromatography to measure fluoride in the experimental sample. The ion chromatograph instrument, Dionex DX-120, is located in Dr. Steven Comfort's laboratory in Kiesselbach Crop Research Laboratory.

The following will describe the methods in detail. Due to the nature of adaptability required to meet the objectives, the preliminary procedure will be described first. Next, the instances that caused adjustments and how the procedure then carried on will be explained.

Solution Preparation

Standards Solutions

The Ion Chromatography instrument, Dionex DX-120 (IC), produces plots of voltage (mV) versus time (minutes). Individual analytes are separated by the IC column and individual "peaks" are produced. The peak area can represent the concentration of an analyte in a sample, once a standard calibration curve is established. For research purposes, it is essential to know how much fluoride is in the experimental samples and generated over time. Standard solutions of fluoride were first prepared and injected into the IC to create a calibration curve. These calibration curves plot the peak area versus concentration. An experimental peak area produced from the IC can then be translated directly to concentration. In summary, calibration curves created by known amounts of fluoride can be used to calculate the unknown amount of fluoride in the experimental samples. Therefore, four to five standards are chosen before each data analysis to ensure the amount of fluoride in solution is detected with confidence. Standards were made using ammonium fluoride. The fluoride standard used were: 1, 2, 4, 6, 8, 10, 15, 20, 25, 30,

40, 50, 60, and 75 mg/L. Choosing which standards to use with data analysis is based on the potential maximum amount of fluoride that could be produced by each experiment. For example, if the experimental solution concentration was 10 mg/L PFOA, then around 6 mg/L of fluoride could be generated in complete removal; see calculation below.

$$\frac{10 \text{ mg PFOA}}{1 \text{ L}} \times \frac{1 \text{ g PFOA}}{1000 \text{ mg PFOA}} \times \frac{1 \text{ mol PFOA}}{414.07 \text{ g PFOA}} \times \frac{15 \text{ mol F}^-}{1 \text{ mol PFOA}} \times \frac{19 \text{ grams F}^-}{1 \text{ mol F}^-}$$

$$= 0.00688 \text{ grams/L F}^-$$

In that instance, fluoride standards between 1 and 10 mg/L were used to produce the most accurate calibration curve. The protocol for making the standards is as follows: the correct amount of ammonium fluoride is weighed to produce a stock of fluoride at a concentration of 1000 mg/L, the stock solution is diluted to the desired concentration using a 100 mL volumetric flask and deionized water, the flask is covered, inverted several times, and the solution is store in sealed vials. All fluoride standards are run through the IC and peak areas were used to generate a calibration curve through linear regression.

Experimental Solutions

To test whether the experimental treatment could degrade PFOA-contaminated water, it was necessary to create known concentrations of PFOA solutions. The PFOA solutions were prepared using 95% pure crystallized perfluorooctanoic acid (PFOA) and diluted to make 100 mg and 10 mg of PFOA per liter with deionized water. Initially, 100 mg/L PFOA was used because it is easier to detect fluoride with the IC when fluoride removal was minimal and slow.

Once the experimental design was consistently producing results, the solution was changed to 10 mg/L PFOA, as lower concentrations are more typical of environmental conditions.

The protocol used to make standard stock solutions were as follows; weight out the correct amount of crystallized perfluorooctanoic acid to make 100 mg/L (100 mg), quantitatively transfer to a 1000 mL volumetric flask, add deionized water to the appropriate fill line, cover the flask with parafilm, invert several times, and finally store in a sealed container. To make the 10 mg/L PFOA solution, 100 mL of the 100 mg/L PFOA solutions is transferred to a 1000mL volumetric flask, fill with deionized water to the appropriate fill line cover the flask with parafilm, invert several times, and store in a sealed container. It is important to always invert a couple of times before use, after storing for long periods of time. Inverting the PFOA solution before use is important to make sure all crystallized perfluorooctanoic acid is dissolved in solution.

Experimental Procedure

With standard PFOA stock solutions prepared, the electrochemical oxidation experiment began. Electrochemistry describes the chemical processes behind the flow of electrons or electricity. This experimental design takes advantage of the oxidation/reduction reactions that occur at the anode and cathode. Direct-current power supplies are used to produce the currents. The original power supply was the Extech Instruments DC Power Supply Model 382200. Although, after the first couple of months of experiments, the power supply was traded for a more powerful system, Extech Instrument Switching DC Power Supply Model 382275. There are many variables to consider when choosing the experimental design. Initially, the research consists of many experiments with one change to a potential control of future experiments. It is important to optimize the control experiment before testing whether persulfate improved the

treatment. A baseline experimental procedure was developed based on the first successful experiment (i.e., significant F generated). From there, one treatment variable of the experiment design was changed to see if there was improved fluoride removal. The baseline experiment procedure was as follows:

1. Obtain 200 mL of 100 mg PFOA/L solution in a 400-mL graduated cylinder.
2. Add 1.4204 g of sodium sulfate to the solution, so the overall salt concentration is 50 mM.
3. Agitate the solution with a magnetic stir bar running at 350 rpm until all of the salt is dissolved.
4. Run a direct current through the solution using a power supply, Extech Instruments 382200 DC Power Supply, with a BDD anode and platinum wire cathode. With the current set to 0.11 A and the electrical potential set to 12.1 V.
5. Turn on the power supply and run for 2 hours. Take two 1.5 mL samples at time 0 h, 0.5 h, 1 h, 1.5 h, and 2.0 h using a micropipette. The power supply and stir bar are turned off during sampling.
6. Run fluoride standards of 1, 25, 50, and 70 mg/L through the IC. IC graphs with peak areas and retention times will be automatically processed and printed.
7. Run samples through the IC, and data will also be automatically printed.

From the baseline condition, one treatment variable was adjusted or added to see if it increased or decreased defluorination of PFOA. The BDD anode is not switched out due to its success in many other electrochemical experiments. The area of the BDD anode is 1 cm². Different cathodes were tested, including platinum wire, carbon, and stainless steel. The pH and salt concentration are adjusted, and different types of salts are tested. Lowering pH and adding

electrolytes to the experiment solution can assist the current across the electrodes. Heat, 50 °C, will be added to the overall experiment. Heat can act as a catalyst to increase reaction rates that degrade the PFOA. Also, there were adjustments to current and electric potential. These different experiments were documented and filed with their results (Figure 6). From there, calibration curves were created using Excel from standards' peaks, and the amount of fluoride in the unknown solutions was calculated. These experiments allow for a systematic comparison of the treatments.

| | |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Operator/Chemist: | Date: |
| Anode (Check one) <input type="checkbox"/> BDD <input type="checkbox"/> Stainless Steel <input type="checkbox"/> Platinum wire <input type="checkbox"/> Carbon | Cathode (Check one) <input type="checkbox"/> BDD <input type="checkbox"/> Stainless Steel <input type="checkbox"/> Platinum wire <input type="checkbox"/> Carbon |
| Solution Being Treated <input type="checkbox"/> 200 mL of 100 mg/L PFOA <input type="checkbox"/> Other (list) | Initial pH <input type="checkbox"/> Unadjusted <input type="checkbox"/> Adjusted to _____ |
| Salt Concentration | Volts/Amp (average over 2 h) <input type="text"/> Volts <input type="text"/> Amps |
| Stirrer RPMs | |
| Sampling Times (list): | Start Time _____ End Time _____ |
| Baseline Conditions: 200 mL of 100 mg/L PFOA treated with BDD anode and Platinum wire cathode for 2 hours, no pH adjustment and 50 mM Na ₂ SO ₄ | |
| Experimental Treatment Being Tested (i.e., persulfate is being added to baseline conditions). Please list: | |
| Comments/Observations: | |

Please attach relative Chromatographs

Figure 6. Initial documentation used to record experimental conditions.

As previously mentioned, there were a couple of instances where new insight caused a need for the experiments to be slightly adjusted. Updated equipment caused the operations to be

improved. For example, a new BDD anode was purchased that increased the surface area of chemical oxidation. The surface area of this anode is 46.57cm^2 . With increased surface area BDD anode and matching steel cathode (46.57cm^2), there was a need for more power to optimize current and the voltage across the electrodes. As previously mentioned, this updated device was the Extech Instrument Switching DC Power Supply. Testing lower concentrations of PFOA solution started with the upgrade in technology. The experiments moved from using 100 mg PFOA/L to 10 mg PFOA/L to produce more realistic data.

One major issue occurred when the most successful experiment from the previous procedure was run for 6 hours instead of 2 hours. After analysis, the experiment was found to have over 200% removal. The fluoride peaks from the IC had to be measuring more than just fluoride to produce over 100% removal. Steps were taken to ensure there was a high level of confidence with analysis. Eluent is a fluid used in ion chromatography to carry a sample through the column, the eluent concentration is 30 mM NaOH in deionized water. Adjustments to eluent and flow rate, eluent rate through the column, did not produce cleaner peaks. Although once cleaned, the IC added a new guard column, and adjusted the salt concentration from 50 mM Na_2SO_4 to 1 mM Na_2SO_4 , the peaks were significantly cleaner and undistinguishable from the standard peaks. Using 50 mM of salt during these types of experiments is not uncommon. One study used 1.4 g/L NaClO_4 for only 40 mL of a PFAS experimental solution.¹² The idea behind decreasing salt concentration was because the IC peak for NaSO_4 was relatively close to the IC peak for fluoride. It seemed 50 mM Na_2SO_4 concentrations were contributing to peak area for fluoride. Decreasing salt concentration resulted in sharper peaks for both fluoride and Na_2SO_4 .

After fixing the analysis and updating equipment, it was essential to adjust and repeat some of the previous experiments. A new baseline experiment was as follows: 400 mL of 10

mg/L PFOA treated with BDD plate anode and Steel plate cathode for 2 hours, no pH adjustment, 1 mM Na₂SO₄, and current set to 0.4 A. The following is the updated procedure:

1. Obtain 400 mL of 10 mg PFOA/L solution in a 600-mL graduated cylinder.
2. Add 0.5684 g of sodium sulfate to the solution, so the overall salt concentration is 1 mM.
3. Agitate the solution with a magnetic stir bar running at 350 rpm until all salt is dissolved.
4. Take the initial weight of the solution.
5. Take the initial pH of the solution.
6. Run a direct current through the solution using a power supply, Extech Instrument Switching DC Power Supply Model 382275, with the 46.47 cm² BDD anode and the 46.47 cm² steel cathode, set 10 mm apart, with the current set to 0.4 A. (record the corresponding voltage)
7. Turn on the power supply and run for 2 hours. Take one 1.5 mL samples at time 0 h, 0.25 h, 0.5 h, 0.75 h, 1 h, 1.25 h, 1.5 h, 1.75 h, and 2.0 h using a micropipette. The power supply and stir bar are turned off during sampling.
8. Run fluoride standards of 1 mg/L, 25 mg/L, 50 mg/L, and 70 mg/L through the IC. IC graphs with peak areas and retention times will be automatically processed and printed.
9. Run samples through the IC, and data will also be automatically printed.
10. Record both the final pH and weight of the solution.
11. File all results using the experimental recording sheet. (Figure 7)

| | |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------|
| Operator/Chemist: | Date: |
| Anode (Check one) <input type="checkbox"/> BDD <input type="checkbox"/> Other (list) | Cathode (Check one) <input type="checkbox"/> Stainless Steel <input type="checkbox"/> Other (list) |
| Solution Being Treated <input type="checkbox"/> 400 mL of 10 mg/L PFOA <input type="checkbox"/> Other (list) Weight Initial _____ Weight Final _____ | pH of Solution <input type="checkbox"/> Initial <input type="checkbox"/> Adjusted (if applicable) <input type="checkbox"/> Final |
| Salt Concentration | Volts/Amp (average over 2 h) _____ Volts _____ Amps (Baseline 0.4 to produce 10-15mV/cm ²) |
| Agitation <input type="checkbox"/> Stirrer RPMs _____ <input type="checkbox"/> Bubbling System | |
| Sampling Times (list): | Start Time _____ End Time _____ |
| Baseline Conditions: 400 mL of 10 mg/L PFOA treated with BDD plate anode and Steel plate cathode for 2 hours, no pH adjustment, 1 mM Na ₂ SO ₄ , and current set to 0.4 A. | |
| Experimental Treatment Being Tested (i.e., persulfate is being added to baseline conditions). Please list: (Only add one new variable) | |
| Comments/Observations: | |

Please attach relative Chromatographs

Figure 7. This is the updated experiment filing sheet.

Following the changes to the baseline and procedure, it was necessary to retest some of the experimental conditions to ensure the baseline was optimal. A series of 2-hour experiments were conducted. One experimental variable was changed to see if defluorination increased. Then the most successful treatment was run for 6 hours. Experimental variables that were changed to see if the fluoride removal improved were:

- Lowering the initial pH of the solution to assist the current by adding 0.4 mL of H₂SO₂.
In this case, both the initial, adjusted, and final pH is measured.
- Using less current, 0.2A instead of 0.4A.

- Trying a different salt to assist the current. Using 1 mM of aluminum sulfate instead of 1 mM sodium sulfate.
- Trying to use sodium chloride as the salt instead of sodium sulfate.
- Decreasing the distance between the electrode plates from 10 mm to 6 mm.
- Adding 0.1 g of persulfate at the beginning of the experiment.

After running all the experiments and making a systematic comparison of treatments, the baseline conditions experiment was run for 6 hours instead of 2 hours. Samples were taken every 30 min instead of every 15 min.

Results

Standard calibration curves were created each day for the IC to ensure confidence in analytical results. The R^2 (a statistical measure of how close the data are to the fitted regression line) values for the fluoride standards were between 0.9991 and 0.9995. The baseline treatment was overall the most successful, with a fluoride removal of 60.4% after 2 hours (Figure 8). Lowering the current of the solution (from 0.4 to 0.2 A) resulted in the total fluoride removal to be 45.0% after 2 hours (Figure 8). When the initial pH was lowered the removal after treatment was 37.5% (Figure 8). After changing the salt to aluminum sulfate and sodium chloride, the resulting overall fluoride removals were 34.9% and 33.4% accordingly (Figure 8). A defluorination rate of 37.4% resulted after decreasing the distance between electrodes (Figure 8), and 38.5% was the removal after adding 0.1 g of persulfate to the treatment (Figure 8). The baseline conditions were selected for the 6-hour treatment due to its success in the 2-hour experiment (Figure 8). After 6 hours, the overall fluoride removal rate was 53.1% after the baseline condition treatment (Figure 9). At the 2-hour mark of this experiment, the removal was 37.5%, which is 22.7% less removal than the first baseline experiment after 2 hours (Figure 10).

Figure 11 shows the state of the boron-doped diamond electrode after all the experiments conducted between 3/11/20 until 3/27/20. Finally, Table 8, in the Appendix, shows a 2-hour baseline condition experiment ran on 3/30/20 with a new BDD plate. This experiment had a removal rate of 61.0% (Appendix, Table 8).

Figure 8. Fluoride removal rates of all experiments during 2 hours of treatments.

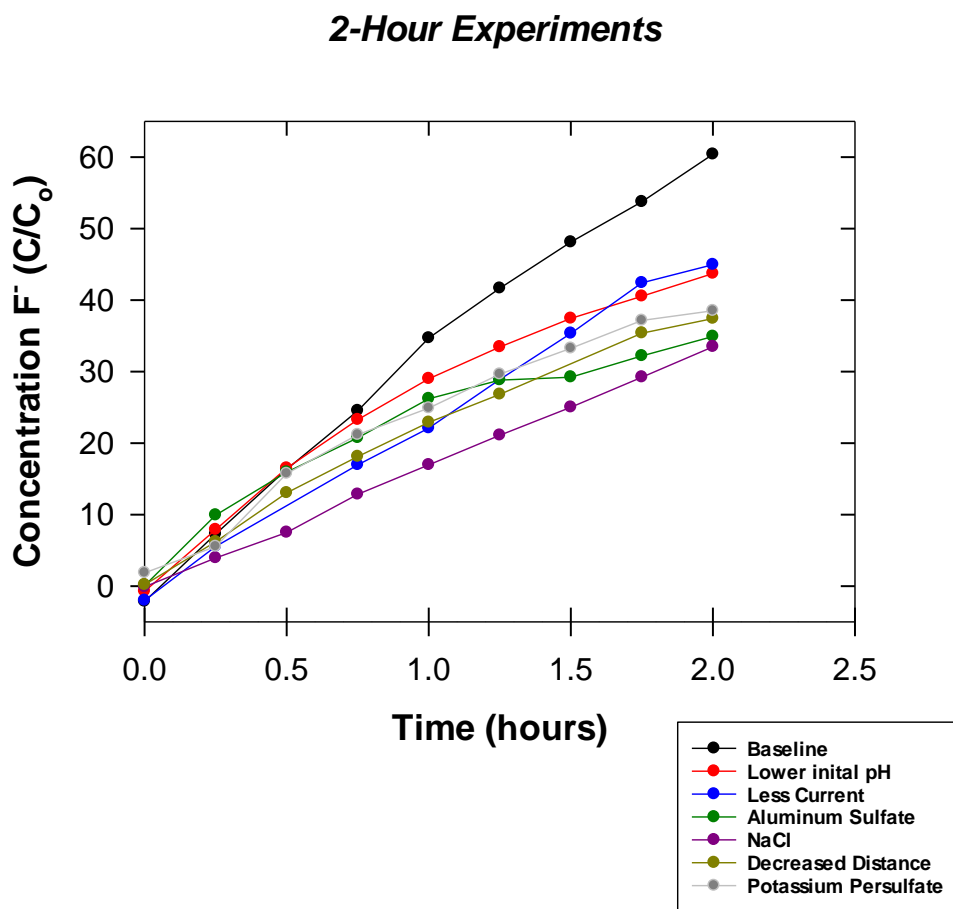


Fig. 8 Fluoride generated under various electrochemical oxidation treatments. The F⁻ removal rate was the baseline at 60.4%. Changing the salt from the baseline condition from sodium sulfate to sodium chloride resulted in the lowest removal rate in 2 hours of 33.5%.

Figure 9. Fluoride removal rate of baseline condition during 6 hours of treatment.

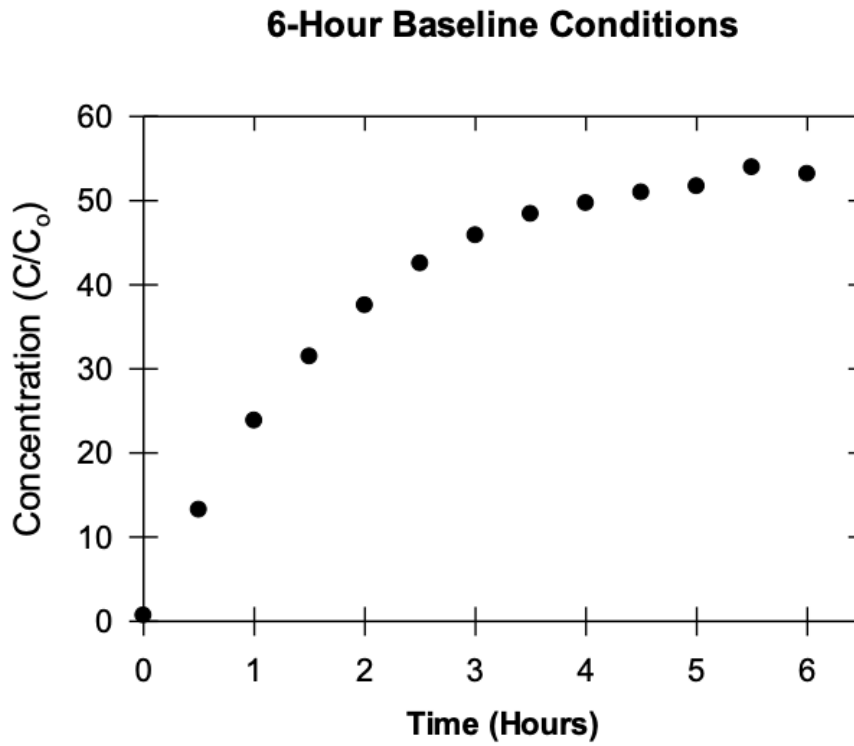


Fig. 9 The overall removal rate of fluoride during baseline conditions treatment after 6 hours was 53.1%.

Figure 10. Comparison of fluoride removal rate of baseline conditions during 2 hours of treatment.

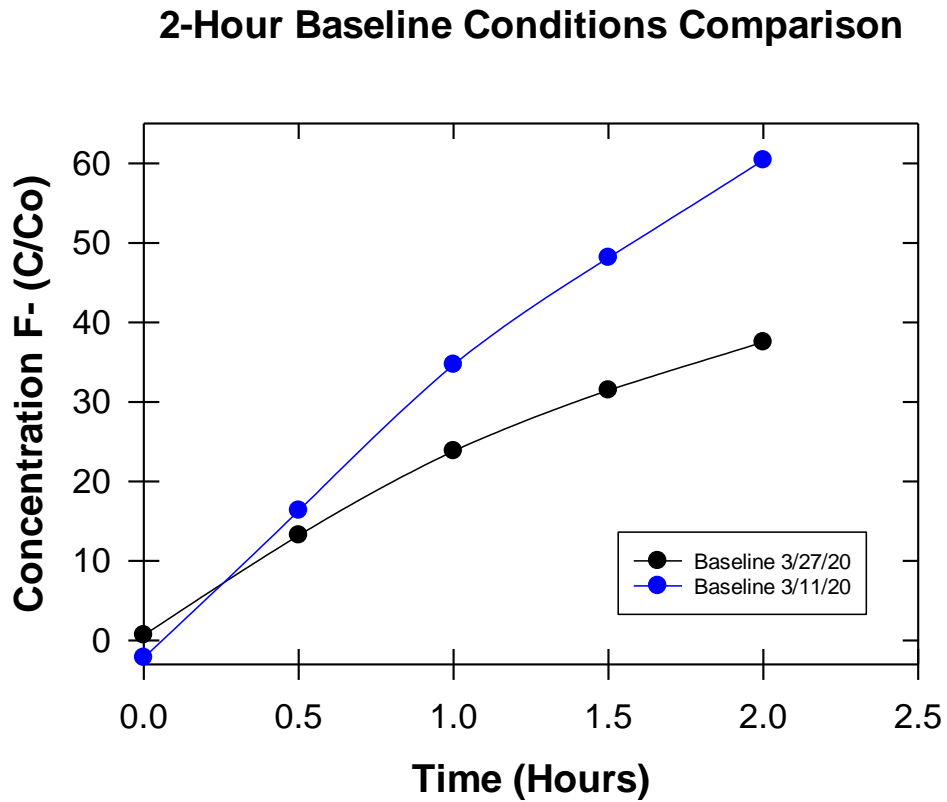


Fig. 10 The exact same experiment was conducted on 3/11/20 and 3/27/20. The removal rate for the first experiment was 60.4% while the removal for the second experiment was 37.5% after 2 hours of experiments.

Figure 10. Boron Doped Diamond electrodes

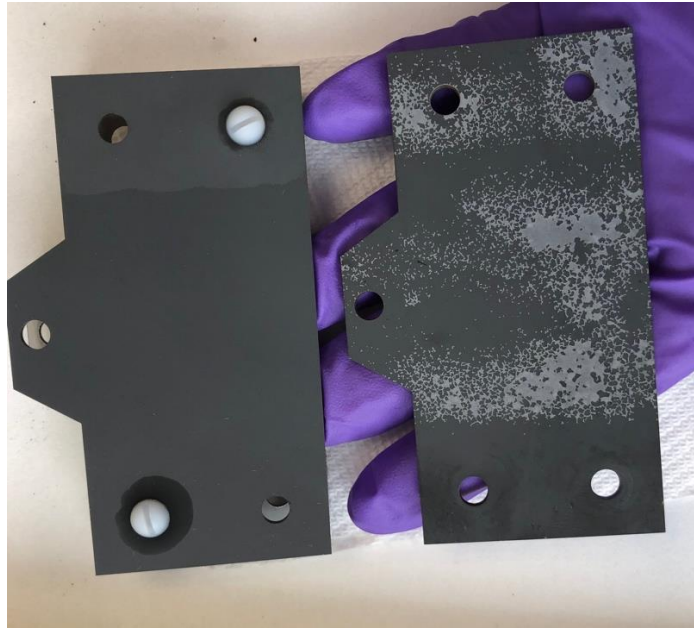


Fig. 11 The electrode on the right is the boron doped diamond electrode that was used throughout the all the experiments. The electrode on the left is a brand new BDD electrode.

Discussion

Before the 6-hour experiment, it seemed the baseline conditions were overwhelmingly more successful in degrading PFOA than any other treatment. For that reason, the baseline conditions were run for 6 hours. It was disappointing to see the removal rates were significantly lower for the same treatment. After 2 hours, the second baseline experiment removed 35.7% less fluoride than the original (Figure 10). Even after 6 hours, the overall removal rate was 53.1%, which is less than the removal rate in only 2 hours of the first baseline treatment. It was necessary to take a step back to try to predict what was causing this decrease in efficacy. The surface of the BDD anode plate looked as if it was degrading (Figure 11). The wear on the plate may be salt deposits on the surface. Although, if gently rubbed, black flakes come off the surface

of the BDD anode plate. The visible wear on the BDD plate seemed to be a possible reason for the decreased efficacy of the second baseline condition and a factor in the lower results of the other experiments. It was essential to run the baseline once more but with a brand-new plate. After this 2-hour experiment, there was a removal rate of 61.0% (Appendix, Table 9). Since this is a similar rate to the initial baseline experiment, there is more evidence that the decreased efficacy is due to the BDD plate interference. It will be essential to test whether this interference is due to plate erosion or salt deposits in the future. Switching the polarity of the plates (making the anode the cathode) might remove some of the salt deposits, therefore increasing the performance of the plate again. Although, if the plate is eroding during treatment, it is vital to find a way to perform these experiments, so the plates have a longer lifetime, especially when the ultimate goal is a field experiment.

Furthermore, it will also be essential to rerun some of the 2-hour experiments to see if they increase removal rates. However, it is not necessary to repeat a few of the treatments. For example, it seems the best salt to assist the current in the electrochemical oxidation reactions is sodium sulfate. Despite being the last experiment tested on the effected BDD plate, more likely to be affected by wear, the second baseline conditions experiment has a higher removal rate than aluminum sulfate and sodium chloride. Other studies have found that chloride ions may slow the reactions down, and it is evident in our experiments with the lowest removal rate.¹⁵ There is interest in seeing the removal rates with the addition of persulfate without plate erosion due to its success in other studies⁸.

Summary & Conclusions

The first objective of this thesis is to prove that electrochemical oxidation could in fact degrade PFAS. This objective was met when removal rates were as high as 61%. Although, there needs to be some adjustments to decrease electrode erosion, it is evident that electrochemical oxidation can be a PFAS removal therapy. The second objective of this thesis is to ensure the confidence of analyses. The R^2 values for the calibration curves were very close to one. The experimental IC peaks were indistinguishable from those of the known standards. However, it is possible to further this confidence in future experiments, the same experiments can be performed but with small amounts of ^{14}C -PFOA. The radioactive carbon is on the carboxylic head of the PFOA. A liquid scintillation counter measures the degradation of PFOA by measuring the amount of radioactivity in a sample. When the carboxylic head of the PFOA breaks off, it is transformed into CO_2 gas and leaves the solution. If the treatment is successful, the overall radioactivity of the sample will decrease, evidence of PFOA breaking down. Collecting data that quantifies both loss of ^{14}C -PFOA and generation of fluoride will increase the credence of the technology.

The final objective of the thesis is to optimize the controls of the experiment. This objective continues to be working beyond the completion of this thesis. Throughout this experience, there were many instances where it was necessary to stop and assess the way experiments were being conducted and analyzed. Degrading these “forever chemicals,” PFAS is no easy task, and for many years, scientists have struggled to do so. It is easy to become discouraged from unexpected results, but it all has been a continuous process of learning. It is beneficial to occur problems in the laboratory setting. That way, it is less likely to face problems after many resources have been invested in a field treatment. That being said, the next step would

be identifying what is causing BDD plate wear. A field treatment will have to function for long periods to be practical and cost-effective. Whether research is successful or not, as long as learning continues, research can come a step closer to degrading per- and polyfluoroalkyl substances and keeping both the environment and people safe from these harmful chemicals.

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Appendix

Table 1

Removal rate of fluoride under baseline conditions in 2 hours.

| Time (h) | Peak Area | Measured concentration (mg/L) | Measured concentration (g/L) | Maximum concentration (g/L) | Percent removal (%) |
|-----------------|------------------|--------------------------------------|-------------------------------------|------------------------------------|----------------------------|
| 0.0 | 754 | -0.14863 | -1.49E-04 | 6.88E-03 | -2.159 |
| 0.25 | 130463 | 0.499915 | 5.00E-04 | 6.88E-03 | 7.263 |
| 0.5 | 255367 | 1.124435 | 1.12E-03 | 6.88E-03 | 16.337 |
| 0.75 | 368024 | 1.68772 | 1.69E-03 | 6.88E-03 | 24.520 |
| 1.0 | 508221 | 2.388705 | 2.39E-03 | 6.88E-03 | 34.705 |
| 1.25 | 604131 | 2.868255 | 2.87E-03 | 6.88E-03 | 41.672 |
| 1.5 | 693127 | 3.313235 | 3.31E-03 | 6.88E-03 | 48.137 |
| 1.75 | 770717 | 3.701185 | 3.70E-03 | 6.88E-03 | 53.774 |
| 2.0 | 861990 | 4.15755 | 4.16E-03 | 6.88E-03 | 60.404 |

Note. This experiment was conducted 3/11/20 with an average current of 0.4 A and average voltage of 28 V. Fluoride standards were 1 mg/L, 3 mg/L, 5 mg/L, and 10 mg/L. The calibration curve was $C \text{ (mg/L)} = 5\text{E-}06 * (\text{Peak Area}) - 0.1524$ with $R^2 = 0.9993$.

Table 2
Removal rate of fluoride under less current in 2 hours.

| Time (h) | Peak Area | Measured concentration (mg/L) | Measured concentration (g/L) | Maximum concentration (g/L) | Percent removal (%) |
|-----------------|------------------|--------------------------------------|-------------------------------------|------------------------------------|----------------------------|
| 0.0 | 2115 | -0.13871 | -1.39E-04 | 6.88E-03 | -2.015 |
| 0.25 | 88756 | 0.381136 | 3.81E-04 | 6.88E-03 | 5.537 |
| 0.75 | 219704 | 1.166824 | 1.17E-03 | 6.88E-03 | 16.953 |
| 1.0 | 278674 | 1.520644 | 1.52E-03 | 6.88E-03 | 22.093 |
| 1.25 | 356874 | 1.989844 | 1.99E-03 | 6.88E-03 | 28.910 |
| 1.5 | 430737 | 2.433022 | 2.43E-03 | 6.88E-03 | 35.349 |
| 1.75 | 512008 | 2.920648 | 2.92E-03 | 6.88E-03 | 42.433 |
| 2.0 | 541091 | 3.095146 | 3.10E-03 | 6.88E-03 | 44.969 |

Note. This experiment was conducted 3/12/20 with an average current of 0.2 A and average voltage of 16.2 V. Fluoride standards were 1 mg/L, 3 mg/L, 5 mg/L, and 10 mg/L. The calibration curve was $C \text{ (mg/L)} = 6\text{E-}06 * (\text{Peak Area}) - 0.1514$ with $R^2 = 0.9995$.

Table 3*Removal rate of fluoride with lowering of initial pH in 2 hours.*

| Time (h) | Peak Area | Measured concentration (mg/L) | Measured concentration (g/L) | Maximum concentration (g/L) | Percent removal (%) |
|-----------------|------------------|--------------------------------------|-------------------------------------|------------------------------------|----------------------------|
| 0.0 | 564 | -0.050716 | -5.07E-05 | 6.88E-03 | -0.737 |
| 0.25 | 99441 | 0.542546 | 5.43E-04 | 6.88E-03 | 7.883 |
| 0.5 | 198074 | 1.134344 | 1.13E-03 | 6.88E-03 | 16.481 |
| 0.75 | 275951 | 1.601606 | 1.60E-03 | 6.88E-03 | 23.269 |
| 1.0 | 341771 | 1.996526 | 2.00E-03 | 6.88E-03 | 29.007 |
| 1.25 | 392713 | 2.302178 | 2.30E-03 | 6.88E-03 | 33.448 |
| 1.5 | 438710 | 2.57816 | 2.58E-03 | 6.88E-03 | 37.457 |
| 1.75 | 474221 | 2.791226 | 2.79E-03 | 6.88E-03 | 40.553 |
| 2.0 | 510737 | 3.010322 | 3.01E-03 | 6.88E-03 | 43.736 |

Note. This experiment was conducted 3/16/20 with an average current of 0.4 A and average voltage of 10.4 V. The pH was lowered to 2.46 by adding 0.4 mL of H₂SO₄ (10%). Fluoride standards were 1 mg/L, 3 mg/L, 5 mg/L, and 10 mg/L. The calibration curve was $C \text{ (mg/L)} = 6E-06 * (\text{Peak Area}) - 0.0541$ with $R^2 = 0.9993$.

Table 4***Removal rate of fluoride with aluminum sulfate salt in 2 hours.***

| Time (h) | Peak Area | Measured concentration (mg/L) | Measured concentration (g/L) | Maximum concentration (g/L) | Percent removal (%) |
|-----------------|------------------|--------------------------------------|-------------------------------------|------------------------------------|----------------------------|
| 0.0 | 15990 | 0.00294 | 2.94E-06 | 6.88E-03 | 0.043 |
| 0.25 | 129188 | 0.682128 | 6.82E-04 | 6.88E-03 | 9.911 |
| 0.5 | 198167 | 1.096002 | 1.10E-03 | 6.88E-03 | 15.924 |
| 0.75 | 253422 | 1.427532 | 1.43E-03 | 6.88E-03 | 20.740 |
| 1.0 | 316058 | 1.803348 | 1.80E-03 | 6.88E-03 | 26.200 |
| 1.25 | 346200 | 1.9842 | 1.98E-03 | 6.88E-03 | 28.828 |
| 1.5 | 350777 | 2.011662 | 2.01E-03 | 6.88E-03 | 29.227 |
| 1.75 | 384949 | 2.216694 | 2.22E-03 | 6.88E-03 | 32.206 |
| 2.0 | 416137 | 2.403822 | 2.40E-03 | 6.88E-03 | 34.925 |

Note. This experiment was conducted 3/17/20 with an average current of 0.4 A and average voltage of 21.7 V. The aluminum sulfate concentration was 1 mM. Fluoride standards were 1 mg/L, 3 mg/L, 5 mg/L, and 10 mg/L. The calibration curve was $C \text{ (mg/L)} = 6E-06 * (\text{Peak Area}) - 0.093$ with $R^2 = 0.9991$.

Table 5*Removal rate of fluoride with sodium chloride salt in 2 hours.*

| Time (h) | Peak Area | Measured concentration (mg/L) | Measured concentration (g/L) | Maximum concentration (g/L) | Percent removal (%) |
|-----------------|------------------|--------------------------------------|-------------------------------------|------------------------------------|----------------------------|
| 0.0 | 6050 | -0.00705 | -7.05E-06 | 6.88E-03 | -0.102 |
| 0.25 | 61518 | 0.27029 | 2.70E-04 | 6.88E-03 | 3.927 |
| 0.5 | 110685 | 0.516125 | 5.16E-04 | 6.88E-03 | 7.499 |
| 0.75 | 184011 | 0.882755 | 8.83E-04 | 6.88E-03 | 12.825 |
| 1.0 | 240891 | 1.167155 | 1.17E-03 | 6.88E-03 | 16.957 |
| 1.25 | 297837 | 1.451885 | 1.45E-03 | 6.88E-03 | 21.094 |
| 1.5 | 351754 | 1.72147 | 1.72E-03 | 6.88E-03 | 25.011 |
| 1.75 | 409978 | 2.01259 | 2.01E-03 | 6.88E-03 | 29.241 |
| 2.0 | 468348 | 2.30444 | 2.30E-03 | 6.88E-03 | 33.481 |

Note. This experiment was conducted 3/18/20 with an average current of 0.4 A and average voltage of 16 V. The sodium chloride concentration was 5 mM. Fluoride standards were 1 mg/L, 3 mg/L, 5 mg/L, and 10 mg/L. The calibration curve was $C \text{ (mg/L)} = 5E-06 * (\text{Peak Area}) - 0.0373$ with $R^2 = 0.9995$.

Table 6
Removal rate of fluoride with decreased electrode distance in 2 hours.

| Time (h) | Peak Area | Measured concentration (mg/L) | Measured concentration (g/L) | Maximum concentration (g/L) | Percent removal (%) |
|-----------------|------------------|--------------------------------------|-------------------------------------|------------------------------------|----------------------------|
| 0.0 | 11068 | 0.01284 | 1.28E-05 | 6.88E-03 | 0.187 |
| 0.25 | 93608 | 0.42554 | 4.26E-04 | 6.88E-03 | 6.183 |
| 0.5 | 187828 | 0.89664 | 8.97E-04 | 6.88E-03 | 13.027 |
| 0.75 | 257704 | 1.24602 | 1.25E-03 | 6.88E-03 | 18.103 |
| 1.0 | 323607 | 1.575535 | 1.58E-03 | 6.88E-03 | 22.891 |
| 1.25 | 377943 | 1.847215 | 1.85E-03 | 6.88E-03 | 26.838 |
| 1.75 | 495610 | 2.43555 | 2.44E-03 | 6.88E-03 | 35.386 |
| 2.0 | 523760 | 2.5763 | 2.58E-03 | 6.88E-03 | 37.430 |

Note. This experiment was conducted 3/19/20 with an average current of 0.4 A and average voltage of 22 V. Distance between electrodes decreased from 10 mm to 6 mm. Fluoride standards were 1 mg/L, 3 mg/L, 5 mg/L, and 10 mg/L. The calibration curve was $C \text{ (mg/L)} = 5E-06 * (\text{Peak Area}) - 0.0425$ with $R^2 = 0.9991$.

Table 7***Removal rate of fluoride with addition of potassium persulfate in 2 hours.***

| Time (h) | Peak Area | Measured concentration (mg/L) | Measured concentration (g/L) | Maximum concentration (g/L) | Percent removal (%) |
|-----------------|------------------|--------------------------------------|-------------------------------------|------------------------------------|----------------------------|
| 0.0 | 13442 | 0.12751 | 1.28E-04 | 6.88E-03 | 1.853 |
| 0.25 | 63999 | 0.380295 | 3.80E-04 | 6.88E-03 | 5.525 |
| 0.5 | 204540 | 1.083 | 1.08E-03 | 6.88E-03 | 15.735 |
| 0.75 | 279320 | 1.4569 | 1.46E-03 | 6.88E-03 | 21.167 |
| 1.0 | 330589 | 1.713245 | 1.71E-03 | 6.88E-03 | 24.891 |
| 1.25 | 396013 | 2.040365 | 2.04E-03 | 6.88E-03 | 29.644 |
| 1.5 | 445843 | 2.289515 | 2.29E-03 | 6.88E-03 | 33.264 |
| 1.75 | 499546 | 2.55803 | 2.56E-03 | 6.88E-03 | 37.165 |
| 2.0 | 518229 | 2.651445 | 2.65E-03 | 6.88E-03 | 38.522 |

Note. This experiment was conducted 3/26/20 with an average current of 0.4 A and average voltage of 17 V. 0.1 g of potassium persulfate was added to the solution. Fluoride standards were 1 mg/L, 3 mg/L, 5 mg/L, and 10 mg/L. The calibration curve was $C \text{ (mg/L)} = 5E-06 * (\text{Peak Area}) - 0.0603$ with $R^2 = 0.9992$.

Table 8*Removal rate of fluoride under baseline conditions in 6 hours.*

| Time (h) | Peak Area | Measured concentration (mg/L) | Measured concentration (g/L) | Maximum concentration (g/L) | Percent removal (%) |
|-----------------|------------------|--------------------------------------|-------------------------------------|------------------------------------|----------------------------|
| 0.0 | 5583 | 0.045615 | 4.56E-05 | 6.88E-03 | 0.663 |
| 0.5 | 178479 | 0.910095 | 9.10E-04 | 6.88E-03 | 13.223 |
| 1.0 | 324357 | 1.639485 | 1.64E-03 | 6.88E-03 | 23.820 |
| 1.5 | 429670 | 2.16605 | 2.17E-03 | 6.88E-03 | 31.470 |
| 2.0 | 513052 | 2.58296 | 2.58E-03 | 6.88E-03 | 37.527 |
| 2.5 | 581771 | 2.926555 | 2.93E-03 | 6.88E-03 | 42.519 |
| 3.0 | 627818 | 3.15679 | 3.16E-03 | 6.88E-03 | 45.864 |
| 3.5 | 662662 | 3.33101 | 3.33E-03 | 6.88E-03 | 48.395 |
| 4.0 | 680454 | 3.41997 | 3.42E-03 | 6.88E-03 | 49.688 |
| 4.5 | 697846 | 3.50693 | 3.51E-03 | 6.88E-03 | 50.951 |
| 5.0 | 708071 | 3.558055 | 3.56E-03 | 6.88E-03 | 51.694 |
| 5.5 | 738985 | 3.712625 | 3.71E-03 | 6.88E-03 | 53.940 |
| 6.0 | 728032 | 3.65786 | 3.66E-03 | 6.88E-03 | 53.144 |

Note. This experiment was conducted 3/27/20 with an average current of 0.4 A and average voltage of 28 V. Fluoride standards were 1 mg/L, 3 mg/L, 5 mg/L, and 10 mg/L. The calibration curve was $C \text{ (mg/L)} = 5E-06 * (\text{Peak Area}) + 0.0177$ with $R^2 = 0.9993$.

Table 9*Removal rate of fluoride during baseline treatment with new BDD plate.*

| Time (h) | Peak Area | Measured concentration (mg/L) | Measured concentration (g/L) | Maximum concentration (g/L) | Percent removal (%) |
|-----------------|------------------|--------------------------------------|-------------------------------------|------------------------------------|----------------------------|
| 0.0 | 9493 | 0.109965 | 1.10E-04 | 6.88E-03 | 1.598 |
| 1.0 | 519499 | 2.659995 | 2.66E-03 | 6.88E-03 | 38.646 |
| 2.0 | 826884 | 4.19692 | 4.20E-03 | 6.88E-03 | 60.976 |

Note. This experiment was conducted 3/30/20 with an average current of 0.4 A and average voltage of 28 V. Fluoride standards were 1 mg/L, 3 mg/L, 5 mg/L, and 10 mg/L. The calibration curve was $C \text{ (mg/L)} = 5\text{E-}06 * (\text{Peak Area}) + 0.0625$ with $R^2 = 0.9997$.