



Report No. 476

ELECTROCHEMICAL MINERALIZATION OF PERFLUOROOCCTANOIC ACID

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August 2019

UNC-WRRI-476

The research on which this report is based was supported by funds provided by the North Carolina General Assembly and/or the US Geological Survey through the NC Water Resources Research Institute.

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This report fulfills the requirements for a project completion report of the Water Resources Research Institute of The University of North Carolina. The authors are solely responsible for the content and completeness of the report.

WRRI Project No. 18-05-W  
August 2019

# Electrochemical Mineralization of Perfluorooctanoic Acid

1<sup>st</sup> March 2018- 1<sup>st</sup> March 2019

Budget - \$ 10,000

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Keywords-Water treatment, perfluoroalkyl substances, perfluorooctanoic acid, electrochemical mineralization

The proposed project would not involve funds going to a USGS collaborator.

## 1. Introduction

Per- and polyfluoroalkyl substances (PFASs) have been widely used in lubricants, polyurethane production, inks, varnishes, firefighting foams, food packaging, adhesives, electroplating, textiles, and stain resistant coating in clothing and carpets (Hu et al. 2016; ITRC 2018; Lau et al. 2007; Moody et al. 2003; Prevedouros et al. 2006; Quiñones and Snyder 2009). Perfluorooctanoic acid (PFOA) is one of the most widely used and well-studied PFAS species (USEPA, 2016c). Its major application is in the form of its ammonium salt used as a surfactant in the production of Teflon (Emmett et al. 2006). PFOA is also used in the synthesis of fluoroacrylic esters and as aqueous film forming foam in fire extinguishers which had a market of 6.8 million liters in the US during 1985 (Giesy and Kannan 2002; Kudo and Kawashima 2003; Moody and Field 2000). PFOA owe its wide range of applicability to its hydrophobicity, lipophobicity, and the ability to resist high temperatures (ITRC 2018). The hydrophobicity and lipophobicity of PFOA is due to fluorine atoms which lower its surface tension (Lau et al. 2007). The fluorinated tail of PFAS compounds are both hydrophobic and lipophobic while its polar head is hydrophilic (Moody and Field 2000). This is also the reason for reduction in solubility as the chain length increases. Perfluorinated compounds outshine hydrocarbon surfactants also because of their thermal stability owing to the highly polarized carbon-fluorine bonds (Moody and Field 2000).

PFOA has been reported to have a low pKa value of around 2.8, which makes the deprotonated form, the most abundant in natural water sources (Prevedouros et al. 2006; USEPA 2016a). PFOA is reported to have a low vapor pressure of 0.525 mm Hg and a high organic carbon-water partitioning coefficient (Koc) (USEPA 2016a). The partition with soil was found to increase with increase organic carbon content of the soil (Moody et al. 2003). In the atmosphere it usually attaches to particles due to its low vapor pressure (Prevedouros et al. 2006). Hence, PFOA is mainly found as adsorbed to solid substances or dissolved in natural waters. Due to their low vapor pressure, high solubility, and persistence, PFASs tend to accumulate in surface water and groundwater (European Food Safety Authority 2008; ITRC 2018; Prevedouros et al. 2006).

PFASs are produced mainly through electrochemical fluorination and telomerization (Giesy and Kannan 2002; ITRC 2018; Moody and Field 2000). The production of carboxylic PFASs like PFOA started in 1947 using electrochemical fluorination and still majority of its ammonium salts are manufactured this way (Prevedouros et al. 2006). In electrochemical fluorination process, an organic feedstock reacts with anhydrous hydrogen fluoride with the help of electric current to get the desired PFAS compounds. During this process, all hydrogen atoms on the feedstock compounds are replaced by fluorine atoms. The feedstock for PFOA is Heptanecarbonyl fluoride (Lau et al. 2007). In 2002, there were eight fluoropolymer manufacturing sites in North America (Prevedouros et al. 2006). The company 3M, a major PFAS manufacturer in the US, produced 6.5 million tonnes of PFASs in the year 2000, of which majority was used in surfactant and paper industry applications (Giesy and Kannan 2002). 3M discontinued the production of PFOA in May 16, 2000 (Kudo and Kawashima 2003).

PFOA is toxic and carcinogenic for both humans and animals (Selections 2008). Due to its long half-life in humans (2 to 9 years), they get accumulated in serum, kidney, and liver (USEPA 2012). It is estimated that 98% of the Americans have PFOA in their blood (Calafat et al. 2007; USEPA 2016b; a). Studies on rats found that PFOA half-life in male species was much higher than

female rats. This is mainly due to the difference in renal clearance (Kudo and Kawashima 2003). In humans, PFOA mean serum half-life was observed to be 4.4 years (Emmett et al. 2006).

Ingestion of contaminated drinking water is one of the most important exposure route to PFOA (Xiao et al. 2015). PFASs from various sources are risking the water quality in NC. As of January 2017, data from the third Unregulated Contaminant Monitoring Rule (UCMR3) (USEPA 2017) placed North Carolina the 3<sup>rd</sup> in the US for the frequency of PFAS detection in drinking water. The sum concentrations of PFOA and PFOS (perfluorooctane sulfonic acid) in some samples were well above the US EPA health advisory level of 70 ng/L (USEPA 2016a; b). In NC, PFASs are detected in both groundwater and surface water. For example, PFASs were detected downstream of a manufacturing plant in Fayetteville in groundwater nearby (Parsons 2016) and in the Cape Fear River (Nakayama et al. 2007), and lead to PFAS detection in 75% of the UCMR3 samples from the downstream city Wilmington. PFAS contamination was also identified in groundwater near six sites of the Seymour Johnson Air Force Base in Goldsboro, NC (Aerostar SES LLC 2016), as well as in stream water/runoff near some civilian airports. Drinking water in Greensboro is derived from surface water possibly impacted by airport runoff and had PFAS detection in 37.5% of the UCMR3 samples. Land application of biosolids from wastewater treatment plant is another PFAS source. Based on contamination observed in other states (Lindstrom et al. 2011) as well as our preliminary data, such contamination may also exist in soil and groundwater in NC.

PFASs are highly recalcitrant to conventional and many advanced treatments practiced in drinking water treatment plants (Liang et al. 2018). Their strong carbon-fluorine bonds prevent natural degradation (Giesy and Kannan 2002). Since conventional treatments cannot remove PFOA, different techniques have been investigated (Li et al. 2010; Schaefer et al. 2015). These explored methods include sonolysis, photochemical oxidation, reduction using elemental zero valent iron, non-thermal atmospheric plasma, and degradation using sulfate radicals. Sonolysis uses sound energy to induce chemical reactions in a solution. Sound waves causes formation and collapse of small bubbles in the solution causing high temperature in areas of bubble formation (Rodriguez-Freire et al. 2015). Whereas photochemical oxidation also known as photocatalytic decomposition is the process by which solar energy is utilized for catalytic oxidation of a compound (Chen et al. 2015). But these methods are found to be energy intensive and uneconomical or ineffective in PFOA degradation, making them difficult to adopt in drinking water treatment plants. This holds true for methods like reduction using elemental zero valent iron, degradation using sulfate radicals (Arvaniti et al. 2015; Lutze et al. 2018). Most of these methods show a steep decline in degradation efficiency even when PFOA concentrations are reduced from 100 mg/L to 10 mg/L.

Among the tested PFAS removal methods, electrochemical mineralization is a promising option, utilizing the electric power to transform PFOA into bicarbonate and fluoride (Lin et al. 2012). During electrolysis of PFAS, various radicals are formed which degrade the PFAS compounds by a stepwise CF<sub>2</sub> elimination (Kutsuna and Hisao 2007). A study on electrochemical oxidation of PFOA showed complete removal of PFOA at 50 mA/cm<sup>2</sup> at a detention time of 8 hours (Schaefer et al. 2017). This process takes place in a time scale of minutes to days. Although a considerable amount of research has been conducted on PFAS electrochemical degradation, the following limitations need to be addressed before such treatment can be applied for PFOA removal:

- i. Low percentage mineralization of PFAS: Most studies show high percentages of PFOA removal but fail to demonstrate complete mineralization (Lin et al. 2012; Yang et al. 2017). This is because during electrolysis, PFOA is degraded to short chain intermediates but their further degradation to inorganic fluoride is challenging.
- ii. Problematic supporting electrolyte: Supporting electrolyte is needed in electrochemical reactions to increase conductivity. Most earlier PFOA studies used sodium perchlorate (NaClO<sub>4</sub>) or sodium chloride (NaCl) as supporting electrolytes (Ma et al. 2015; Trautmann et al. 2015; Zhuo et al. 2014). However, perchlorate is not suitable for water treatment due to its toxicity, whereas chloride can be oxidized to toxic substances like perchlorate, chlorate, and chlorine gas during electrolysis. Thus, environmental benign electrolytes are needed for PFOA electrochemical degradation.
- iii. Incomplete mass balance: Despite the detection of reaction products and intermediates, the complete mass balance of carbon and fluorine before and after electrolysis has not been established by previous studies. This might be due to the gas phase loss of CO<sub>2</sub>, HF, and short-chain PFASs, as well as the possible formation of unknown reaction products (Lin et al. 2012; Trautmann et al. 2015). Without a convincing mass balance, some reaction products and intermediates remain unknown, so it is impossible to declare a reduction in environmental risk after treatment.

**Proposed treatment:** A sequential treatment is proposed to remove PFASs from drinking water derived from contaminated surface water or groundwater in treatment plants, or from groundwater for site remediation purpose (Fig.1). The system includes (1) an ion exchange treatment to exchange ionic PFASs by a non-toxic anion, making the treated water suitable for consumption or discharge, (2) regeneration of the exhausted resin to release the adsorbed PFASs using a concentrated brine containing the exchange anion, and (3) electrochemical treatment of the spent brine to mineralize the released PFASs. Advantages of such sequential treatment over a direct electrochemical treatment are: (1) the volume of water to be electrochemically treated can be reduced by over 100 times, (2) PFASs are concentrated in the spent brine, making the electrochemical treatment more energy efficient, and (3) the brine naturally becomes the supporting electrolyte, so no extra salts are needed. Such treatment is also better than a single-stage ion exchange treatment because ion exchange alone does not destruct PFASs, leaving the management of PFAS contaminated resin another environmental concern.

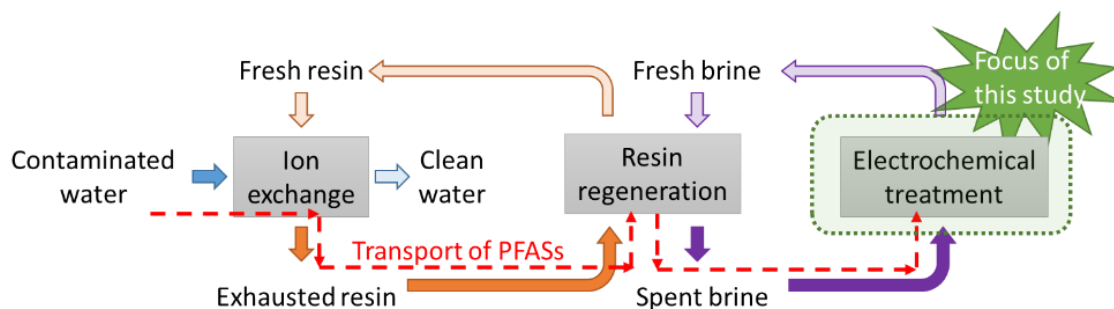


Fig.1. Proposed flow diagram of PFAS removal from contaminated water

Due to the limited time of this project, only the electrochemical treatment part is studied. Specific **objectives** of the project include:

**Objective 1:** Identify suitable anode materials for electrochemical degradation of PFOA.

We **hypothesized** that various anodes will have different oxidation potentials and characteristics that can influence PFOA degradation. By studying the PFOA degradation using these anodes at different current densities, the best suited anode for PFOA degradation can be found.

**Objective 2:** Assess PFOA mineralization and mass balance

We tried to close the PFOA mass balance by analyzing samples for PFOA, short chain PFAS compounds and fluoride. We **hypothesized** that when a complete mass balance of PFOA electrochemical degradation is available, a more thorough assessment on if such treatment can achieve mineralization and risk reduction will be possible.

## 2. Materials and Methods

**Chemical Reagents:** PFOA potassium salt was purchased from Matrix Scientific. Sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) was purchased from Acros Organics. Liquid chromatography–mass spectrometry (LC-MS) grade methanol was purchased from Fisher Scientific. PFAS standards with a mixture of 21 PFAS compounds (PFAC-MXC) and mass-labeled PFAS as internal standards (MPFAC-C-ES) were purchased from Wellington Laboratories. Anhydrous sodium fluoride was obtained from VWR.

**Electrodes:** Ebonex Plus electrodes (Fig.2.a) were purchased from Vector Corrosion Technologies. Reduced graphene oxide membrane (Fig.2.b) was obtained Goographene, and Ti/ $\text{RuO}_2$  plates (Fig.2.c) from American Elements.

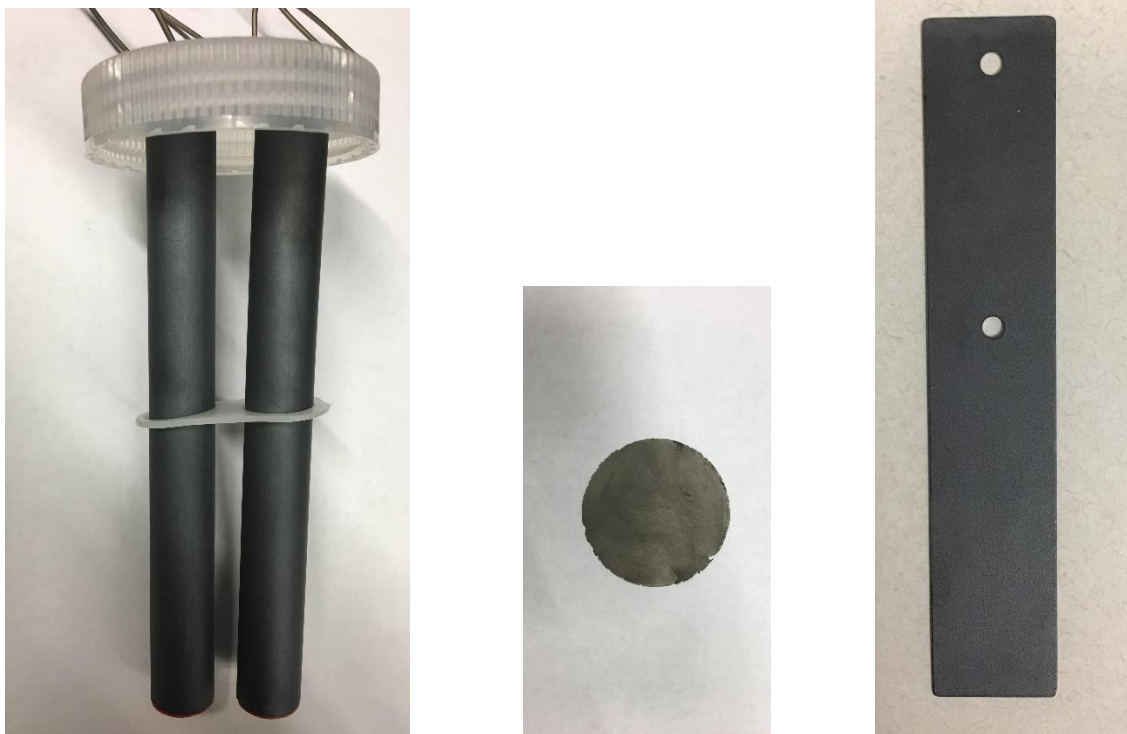


Fig.2. (a) Ebonex Plus electrodes (b) Reduced graphene oxide membrane (c) Ti/RuO<sub>2</sub> sheet

**Water matrix:** To better understand the underlying mechanisms, PFOA electrochemical mineralization was studied in laboratory prepared synthetic water samples. Such samples mimicked the composition of spent brine after ion exchange resin regeneration as shown in Fig.1 and have concentrated PFOA and sodium sulfate. Typical concentrations of PFOA in contaminated groundwater are at low ug/L levels (Schaefer et al. 2015). Assuming the ion exchange and resin regeneration process can concentrate PFOA for 100 folds, PFOA concentration in the spent brine will be at a few mg/L. Thus, an initial concentration of 1 mg/L of PFOA was used in this study. Sodium sulfate concentration in the synthetic samples was at 1.42g/L (0.01 M) as used in the resin regeneration practice.

**Reactors:** PFOA electrochemical mineralization was studied in bench-scale electrolyzers (900 mL) (Trautmann et al. 2015). A schematic diagram and an image of the actual reactor setup are displayed in Figure.3. Three PS-305DM DC power supplies were used to power three reactors as replicates. Reactions were conducted in batch mode using Ebonex Plus, reduced graphene oxide, and Ti/RuO<sub>2</sub> as anodes. In the Ebonex Plus study, Ebonex Plus electrodes served as both cathode and anode. Whereas Ti served as the cathode for reduced graphene oxide and Ti/RuO<sub>2</sub> study. Aqueous samples of 10 mL were taken every hour to monitor the disappearance of PFOA and the production of PFAS intermediates and fluoride. The reactors were designed to capture gaseous products. This was done by employing a continuous vacuum pull from the reactor to an absorption solution. The absorption solution was a mixture of methanol and water (1:1 v/v) with a total volume of 10 mL. A PEEK tubing was employed to connect the reactor to the vacuum flask to prevent any PFAS adsorption or leaching. Throughout this study, Na<sub>2</sub>SO<sub>4</sub> served as the supporting

electrolyte. The electrolysis conditions were: a distance of 5 mm between the electrodes, a stirring speed of 500 rpm, and a total electrolysis time of 8 hours (Lin et al. 2012; Ma et al. 2015; Niu et al. 2013; Schaefer et al. 2017; Yang et al. 2017; Zhuo et al. 2014).

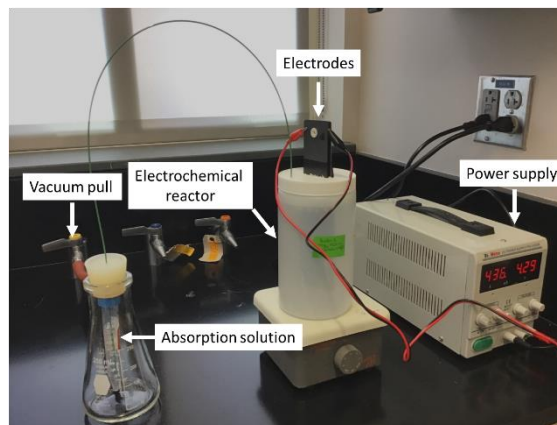
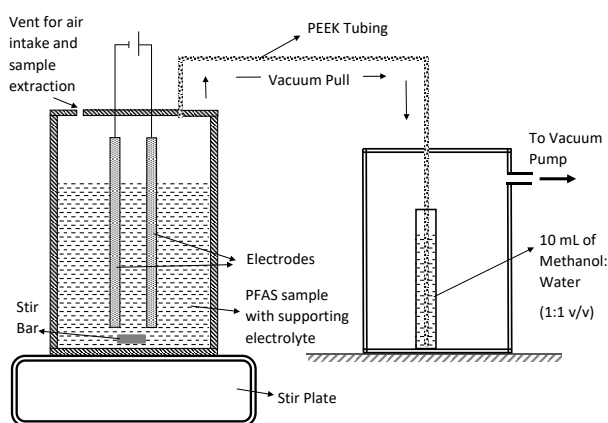


Fig.3. Electrochemical reactor setup

**Task 1:** Electrochemical degradation of PFOA using three different anodes.

**Approach:** In this task, three different anodes were compared for their effectiveness in mineralizing PFOA. The three anodes compared were Ebonex Plus, reduced graphene oxide membrane and Ti/RuO<sub>2</sub>.

Electrochemical mineralization using 18 mm  $\phi$  Ebonex Plus electrodes was carried out at a current density of 0.14 mA/cm<sup>2</sup>. This current density was chosen based on the current rating given by the manufacturer and the length of the electrode which was immersed in the PFOA sample. The 18 mm  $\phi$  Ebonex Plus electrode has a current rating of 7.9 mA per 100 mm. Since the immersed electrode length was 120 mm, this translates to a maximum allowable current of 9.5 mA.

Study using reduced graphene oxide membrane was done at 10 mA/cm<sup>2</sup>. The membrane has a diameter of 38 mm and a surface area of 19.8 cm<sup>2</sup> submerged in the solution. So, 198 mA of current was passed through the membrane to achieve the desired current density.

Tests using Ti/RuO<sub>2</sub> anode was conducted at 5, 20, 30 and 40 mA/cm<sup>2</sup>. The Ti/RuO<sub>2</sub> anode had a submerged surface area of 97 cm<sup>2</sup>. Hence current inputs of 484, 1935, 2903, and 3871mA were applied to achieve current densities of 5, 20, 30 and 40 mA/cm<sup>2</sup> respectively. Another study was also conducted at 20 mA/cm<sup>2</sup> to find the effect of pH adjustment of the initial sample to 7.

**Task 2:** Determination of intermediates and mass balance

**Approach:** To achieve complete mass balance, solutions after treatment were analyzed for PFOA, intermediates (perfluorocarboxylic acids of shorter chain length), and fluoride.

**Analytical methods:** The concentration of PFOA and PFAS intermediates were measured using liquid chromatography–tandem mass spectrometry (LC-MS/MS) using a direct injection method. The instrument used was an Agilent 1100 LC and a 6410 triple quadrupole MS with a Poroshell 120 EC-C18 column (4.6 mm x 50 mm x 4 μm). Fluoride was measured using a Dionex ICS-3000 ion chromatography (IC) from Thermo Fisher Scientific and a Dionex IonPac AS22 analytical column. An AR15 pH meter from Accumet Research was used to measure pH of all the samples.

### 3. Results & Discussion

#### 3.1 Ebonex Plus electrodes

Ebonex Plus is a commercial product with titanium- ceramic composite and is a type of Magneli phase titanium oxide. A study using Magneli phase titanium oxide electrodes achieved 96% PFOA removal within 3 hours of electrochemical oxidation (Liang et al. 2018). These electrodes served as both cathode and anode (Fig.4). The applied current density was much lower than previous studies due to the low current rating of Ebonex Plus electrodes.

If the 1 mg/L PFOA were completely mineralized, 0.69 mg/L fluoride would have produced. However, IC analysis of samples taken each hour showed that fluoride content in all samples were below the limit of quantification of 1 ug/L. Even if only 1% PFOA were mineralized, fluoride peaks should have been detectable.

From the pH results, it can be observed that the pH dropped from 5.5 for the initial sample to around 4 for the final 24-hour sample (Table.1). Whether this is due to the release of hydrogen ions during degradation of PFOA or other side reactions was not confirmed.

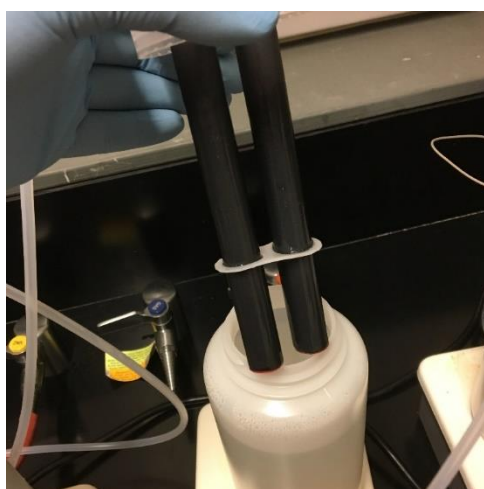


Fig.4. Ebonex Plus electrodes as anode and cathode

Table.1. Change in pH over time

Sample	pH
Hour-0	5.5
Hour- 24 Reactor 1	3.7
Hour- 24 Reactor 2	4
Hour- 24 Reactor 3	3.7

So, when considering the pH and fluoride analysis results, it can be concluded that the applied current density was too low to cause complete conversion of PFOA to fluoride and bicarbonates. Since the electrode material cannot withstand a higher current density, this material was concluded not capable of supporting PFOA degradation.

### 3.2 Reduced Graphene Oxide anode

In this study, reduced graphene oxide served as the anode whereas titanium served as the cathode. The study was planned at a current density of  $10 \text{ mA/cm}^2$ . But the reduced graphene oxide membrane was too delicate and tore off after a few minutes immersed in the sample even when the solution was not mixed using a stir plate (Fig.5). A better skeletal support using a non-conductive mesh needs to be provided for the reduced graphene oxide membrane before further investigations can be done.

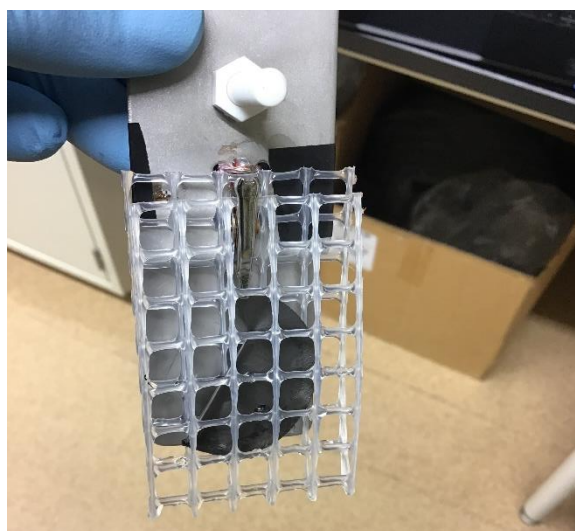


Fig.5. Torn reduced graphene oxide membrane

### 3.3 Ti/RuO<sub>2</sub> anode

#### 3.3.1 Effect of Current Density on PFOA removal

The study was conducted to determine the effect of applied current density on PFOA removal efficiency using Ti/RuO<sub>2</sub> anode. The study included a control (no current) and tested current densities of 5, 20, 30 and  $40 \text{ mA/cm}^2$ .

The DC supply maintained a constant current by regulating voltage. Figure.6 shows the variation of applied voltage over the reaction time period of 8 hours. From the results, it can be seen that, as the electrochemical reaction progressed there is drop in voltage which is more evident in the initial hours. The voltage drop indicates a reduction in resistance of the liquid sample as time progressed. This might be due to the increase in ionic concentrations due to breaking of bonds.

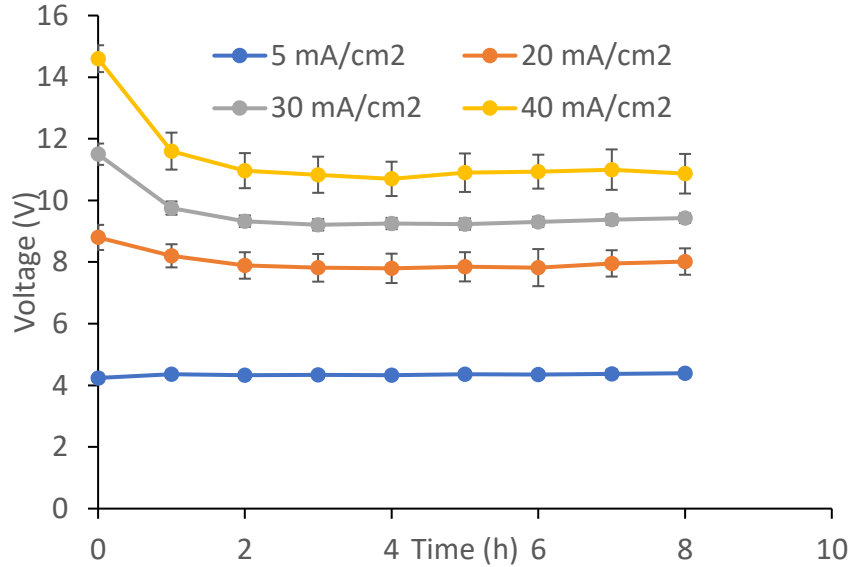


Fig.6. Variation of voltage over time

The results of PFOA reduction in the reaction vessel and PFOA mass balance are shown in Fig.7 and Fig.8 respectively. The control experiment showed no significant change in PFOA concentration, indicating minimal adsorption or any other losses (Fig.7). Under no current condition, PFOA was observed in the absorption solution even though it was just 0.001% of the initial PFOA mass in the reactor, suggesting the possibility that a small amount of PFOA might have migrated to the absorption solution in the aerosol form (Fig.8).

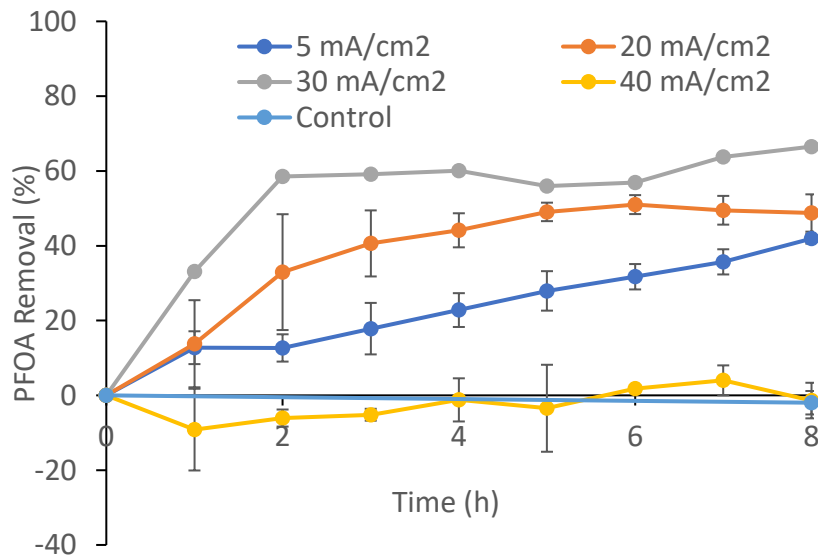


Fig.7. PFOA removal from the active sample volume over time

The results of 5, 20 and 30 mA/cm<sup>2</sup> experiments appeared to show a trend of increasing PFOA removal with increasing current density; at 30 mA/cm<sup>2</sup> condition, more than 60% PFOA was removed from the reactor in 2 hours (Fig.7). However, no short chain PFAS compounds as intermediates or fluoride as the final mineralization product was detected in samples collected from the reactors every hour. Meanwhile, significant amount of PFOA was found in the absorption solution at 5 and 20 mA/cm<sup>2</sup>, accounting for ~20% of the initial PFOA mass in the reactor. Almost no PFOA was detected in the absorption solution at 30 mA/cm<sup>2</sup>, due to a possible failure in the vacuum system or the reactor sealing during the experiment.

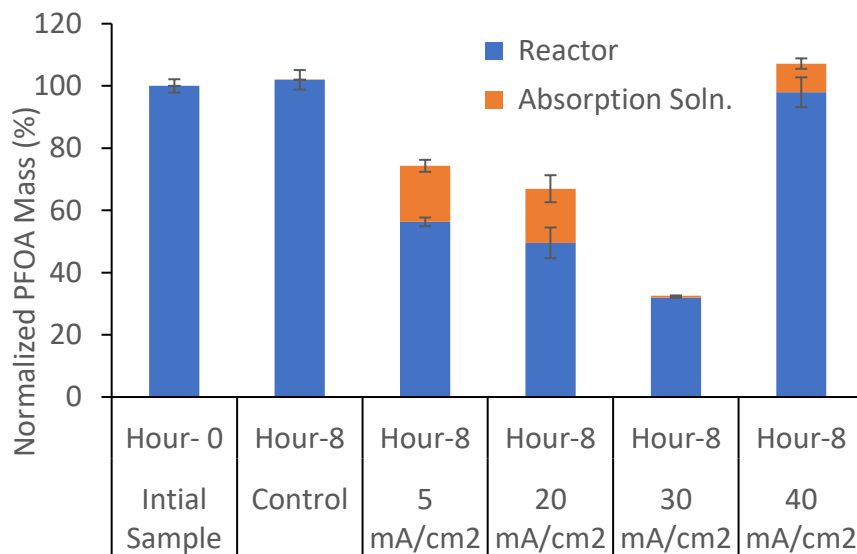


Fig.8. Normalized PFOA mass balance comparison over different current densities

PFOA being a soluble compound with a pKa of 2.8 will be completely dissociated at a pH of 5.5 (initial sample pH) and is not expected to go to the gas phase (USEPA 2016a). Hence the plausible explanation for the presence of PFOA in the absorption solutions is that, during the electrochemical reaction, aerosol is generated due to water electrolysis/gas production and associated heat generation. PFOA has a high tendency to partition at the air-water interface (Costanza et al. 2019), hence it is concentrated on the aerosol surface. Some of the aerosol transported to and was captured by the absorption solutions, some got condensed on the reactor lids, and some might escape to the atmosphere either due to the inefficiency of the absorption solution for full PFOA capture or through the small gaps between the electrodes and the lids.

To verify our speculation on PFAS losses in the aerosol form, the tests under 40 mA/cm<sup>2</sup> were conducted slightly differently, by manually shaking the reactors before taking all the hourly samples to allow the condensate on the lids to be reintroduced to the active reaction volume. No significant change in PFOA concentration was observed under this condition, implying that no PFOA degradation happened. This is further supported by the PFOA mass balance data (Fig.8). From these results, it can be inferred that the PFOA removal that was observed for 5, 20 and 30 mA/cm<sup>2</sup> were also just losses in aerosols.

Interestingly, many previous papers have reported high PFOA removal while failing to report a fluorine mass balance or achieve complete fluorine mass balance. A study done on the electrochemical oxidation of PFOA using PbO<sub>2</sub> electrodes showed more than 90% PFOA removal but a lower defluorination ratio (Zhuo et al. 2017). And no data on fluorine mass balance was provided. Similarly, a study done using novel PbO<sub>2</sub> electrodes showed around 75% PFOS degradation but a defluorination ratio of just 12% and no mass balance was reported (Zhuo et al. 2016). Another study showed high defluorination, but couldn't close the fluorine mass balance and fell short by 15% even though they looked for short chain PFAS intermediates (Yang et al. 2017). Similar results were observed by various other studies (Lin et al. 2012; Xiao et al. 2011; Yu et al. 2015; Zhao et al. 2013; Zhuo et al. 2011, 2014). The missing fluorine in these above cases might be due to aerosol phase losses as observed by the current study.

It should be noted that a few studies have displayed high PFOA degradation as well as a fluorine mass balance with high recovery. For instance, a study done on PFOA degradation using a stable Zirconium doped PbO<sub>2</sub> electrode showed a PFOA degradation of around 90%, defluorination of 50% and a fluorine recovery of more than 90% (Xu et al. 2016). Similar results were observed by another study which employed Yb doped Ti/SnO<sub>2</sub>-Sb/PbO<sub>2</sub> anodes to degrade PFOA (Ma et al. 2015). But that missing 10% could also be aerosol phase PFOA loss.

In light of the current results, there is a possibility that a considerable portion of the high PFOA and PFOS electrochemical removal reported by previous studies might actually be caused by aerosol phase losses, including a study which used the same Ti/RuO<sub>2</sub> anode as used in this study and reported 90% PFOA removal and 58% defluorination (Schaefer et al. 2015). There were certain differences from the current study, such as separate anode and cathode chambers, and recirculation of the PFAS sample through the reactor. Interestingly, they didn't observe short chain PFAS compounds and provided no fluorine mass balance. Hence there is high probability that the PFOA removal Schaefer et al observed was partially due to aerosol phased PFOA loss.

### 3.3.2 Effect of pH Adjustment on Electrochemical degradation of PFOA

In other experiments under this project, the test solution had a natural initial pH of ~5.5 after PFOA addition, and these solutions were tested as is for PFOA electrochemical removal. In this experiment, pH of the initial sample was adjusted to 7 to assess the effect of initial pH on PFOA electrochemical removal at an applied current density of 20 mA/cm<sup>2</sup>. From the results of PFOA removal from the reaction vessel, it can be seen that both cases (with and without pH adjustment) show a very similar trend (Fig.9). However, it is evident that PFOA mass captured in the absorption solutions reduced for the samples whose initial pH was adjusted to 7 (Fig.10). This might be due to a weaker vacuum pull owing to the difficulty in keeping a consistent vacuum pull across experiments, thus a greater portion of aerosol phase PFOA escaped into the atmosphere. No short chain PFAS intermediates or fluoride was detected. Hence it can be concluded that a pH adjustment to 7 didn't have any significant effect on PFOA degradation.

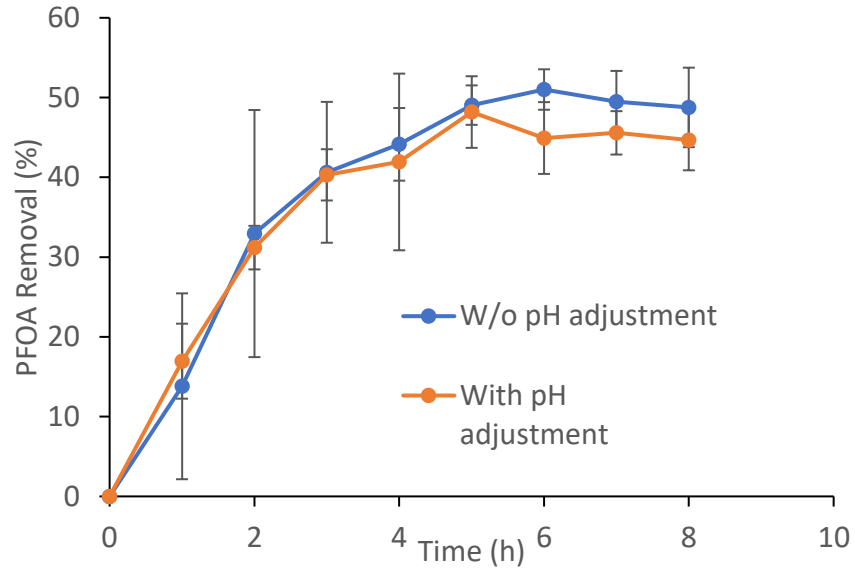


Fig.9. Effect of pH adjustment on PFOA removal from the active reaction volume

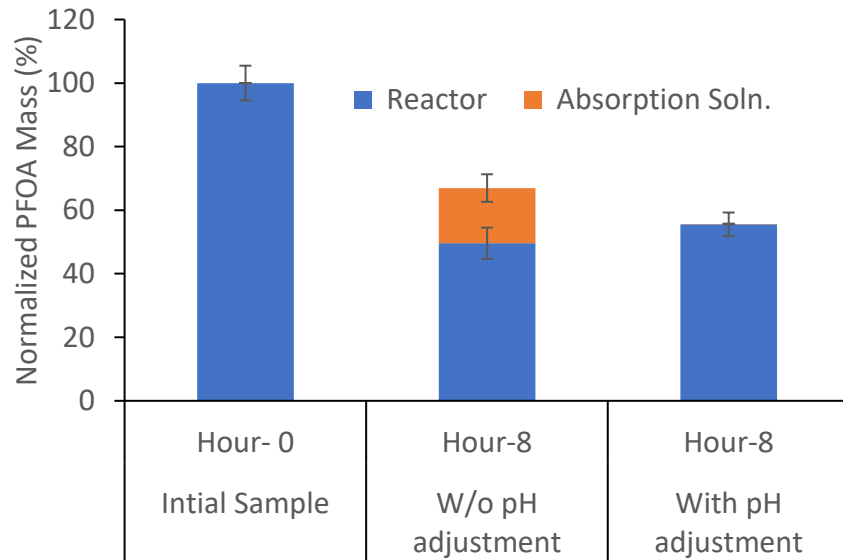


Fig.10. Effect of pH adjustment on normalized PFOA mass balance

#### **4. Conclusions, implications & Future research plans**

Magneli phase titanium oxide anodes have been reported successful for PFOA degradation, but the type of Magneli phase titanium oxide we tested, Ebonex Plus electrodes, is not effective at PFOA mineralization due to their low current allowance. Other forms of Magneli phase titanium oxides with higher current rating needs to be explored. Reduced graphene oxide membrane is delicate and requires a proper skeletal support using a nonconductive mesh before further investigations can be done. Ti/RuO<sub>2</sub> anode is concluded to be an ineffective anode for PFOA mineralization.

The results from this study point out that aerosol based PFOA losses during electrochemical studies can be a significant. Capturing such losses will be an essential part in achieving complete fluorine mass balance. There is also a chance that previous studies done on electrochemical oxidation of PFAS compounds were not able to complete the fluorine mass balance due to these aerosol losses.

Although one-year project does not provide a successful treatment approach for PFAS electrochemical mineralization, it opened up research opportunities in multiple directions, and leading to findings on important pitfalls from other previous studies. To extend the conclusions from this project to better evaluate the feasibility of PFAS electrochemical mineralization, a few other studies are planned for future studies after the termination of this project:

- Modify the reactor design to minimize aerosol PFAS losses.
- Explore the electrochemical oxidation potential of boron doped diamond and other commercially available electrodes.
- Study performance of the best anode on real samples of spent brine obtained from regeneration of ion exchange resins.

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