SIMULTANEOUS DEGRADATION OF PFAS AND AMMONIA IN LANDFILL LEACHATE

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Abstract

The presence of Per- and Poly fluoroalkyl substances (PFAS) in landfill leachate has become a significant challenge. In this study, Aclarity's electrochemical oxidation (EOx) system was tested at different power settings to determine the conditions at which PFAS and ammonia are simultaneously degraded at satisfactory rates in synthetic wastewater and landfill leachate. PFAS and ammonia test results revealed that both degrade more quickly in this system as applied power to the system increases. However, for solutions with lower background organics, a low power with a lower pH proved to be just as effective in the degradation of the MA6 PFAS. Further landfill leachate tests with known composition should be conducted to better understand the effects of precursors and other organics on the electrochemical oxidation of PFAS and ammonia. Optimizing flow within the reactor is an additional way to boost PFAS degradation.

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Executive Summary

Introduction and Background

Perfluoroalkyl and Polyfluoroalkyl substances (PFAS), also dubbed forever chemicals, are a group of over 15,000 synthetic chemicals with strong carbon-fluorine bonds. PFAS are used in many everyday products and processes such as nonstick pans, dental floss, chip manufacturing, etc. These compounds do not break down naturally in the environment or in the human body. Their presence in human blood is linked to thyroid disease, liver and kidney cancer, fertility issues, and more. PFAS leach off products into wastewaters, landfill leachates, and groundwater, ending up in our drinking water. Landfill leachate is a common source of PFAS and ammonia, another toxic contaminant that poses risk to humans and aquatic life. Massachusetts has its own regulations focused on six main PFAS known as the MA6. A limit of 20 ng/L or less of combined total concentration of the MA6 in drinking water is enforced to improve public health. There are increasing regulatory efforts and treatment technologies to remedy this issue.

Conventional treatment methods for PFAS removal, such as granular activated carbon (GAC), ion exchange resin (IEX), nanofiltration (NF), and foam fractionation do not eliminate PFAS. These methods transfer PFAS from aqueous phases to concentrated mediums or streams, which can end up in landfills, encapsulated, deep well injected, or shipped to other countries, taking up space and risking contamination to the public. In other cases, the PFAS captured with these technologies is incinerated. Electrochemical oxidation (EOx), employing an electrode, is an emerging treatment method that can break PFAS down into its elemental components. Aclarity's EOx system destroys PFAS and other contaminants with energy usage comparable to current treatment options. The electrode oxidizes constituents in the water with two methods: direct and indirect oxidation. PFAS is degraded through direct oxidation by contacting the surface of the anode where it undergoes direct electron transfer. Oxidant radicals, such as O_2, OH, or H_2, created by the system degrade ammonia through indirect oxidation. The goal of this study was to determine the optimal power setting at which both PFAS and ammonia are simultaneously degraded at satisfactory rates in Aclarity's EOx system.

Methods

Aclarity's EOx system consisted of a reactor, a 3 gallon tank, a pump, a line of PVC pipe, a globe valve, a pressure gauge, two hose fittings, a stand, a chilling coil connected to a chiller, a power supply box for the reactor, and another power supply for an ultrasonic flow meter on the pipe. A synthetic wastewater solution was created by dosing reagent grade (RG) water with the MA6 PFAS, ammonia, and various salts. This synthetic wastewater and a sample of landfill leachate from a Massachusetts landfill were tested at three power settings: low, medium and high power. A fourth synthetic wastewater test was run at low/medium power while lowering the pH to 5 with HCl. The testing parameters including time and flow rate were chosen arbitrarily for this study and do not reflect the conditions under which Aclarity runs their tests.

PFAS samples were taken at time 0 and 3 hours. Ammonia samples were taken every hour. Benchtop analysis of ammonia was conducted in-house for the synthetic wastewater using HACH Method 8155. PFAS and ammonia samples collected from the landfill leachate tests were sent for external lab analysis using EPA method 1633 and Method 350.1, respectively.

After each test, the system was shut off and disconnected from the power supply. The system was thoroughly drained and any remaining test solution was labeled and placed into hazardous waste containers. The reactor itself was disassembled, the electrode was submerged in a 6% HCl solution to clean off contaminants and scale, and the electrode was rinsed in a bath of RG water to clean off remaining acid. The reactor and the whole system was reassembled and three gallons of RG water was recirculated through the system for a final rinse. This final rinse water was disposed of appropriately.

Results and Discussion

Conductivity, amperage, flow, and pH were recorded for each test every hour. The power and flow were kept constant throughout the whole test. Small bubbles were observed in the reactor for each test, a sign that the reactor was turned on and working. These bubbles were made up of gaseous oxidants and constituents created in the electrochemical oxidation process.

To determine the power setting at which more PFAS and ammonia were destroyed, percent destruction of the contaminants over the whole testing period was calculated. In synthetic wastewater, ammonia test results revealed that ammonia had a greater percent destruction in this system as applied power increased. When the pH was lowered, ammonia decayed to a similar extent in the low/medium power test as in the medium and high power tests. PFAS test results revealed that overall, the MA6 PFAS also had a greater percent destruction in the synthetic wastewater as applied power increased, apart from PFHpA at low power. Running the system at low/medium power, while lowering the solution pH to 5, yielded results comparable to the medium and high power test results. This suggests that low/medium power with a pH of 5 might be an optimal treatment setting for waters with fewer background organics while saving on electrical costs.

Within landfill leachate, the highest destruction of ammonia was achieved with high power. The percent destruction of ammonia in the landfill leachate tests was lower than in the synthetic wastewater tests, likely due the presence of other oxidizable compounds and lower conductivity in the leachate. The high power test achieved the greatest destruction of PFAS in leachate except for PFHxS, which increased. However, the high power test showed the lowest increase in PFHxS. Better understanding of the landfill leachate's composition could provide insight into the observed increase in PFHxS. Longer test times could also be experimented with to potentially achieve higher PFAS degradation in landfill leachate.

The decay rates of both PFAS and ammonia were also calculated as a supplement to the percent destruction data in determining optimal power setting. First order decay rates for PFAS and ammonia were determined through graphical analysis and literature review. The PFAS decay rates for synthetic wastewater and landfill leachate generally increased as applied power

increased, except for the decay rate of PFHpA. The decay rates for the landfill leachate tests are lower than the decay rates for synthetic wastewater tests. This may be attributed to the lower conductivity of the leachate and the oxidizable precursors present in the landfill leachate that were absent in the synthetic wastewater.

An energy analysis was also conducted to determine how Aclarity's EOx system compared to conventional treatment methods for PFAS. Energy usage was compared between GAC regeneration, EOx at medium power, evaporation, and nanofiltration. Aclarity's EOx system used less energy than most treatment methods except for GAC making Aclarity's EOx system a competitive option for PFAS destruction in terms of energy usage.

Conclusion and Recommendations

In synthetic wastewater, medium power or low/medium power with a pH of 5 is satisfactory to make ammonia levels undetectable. For PFAS, low/medium power with a pH of 5 is the best choice for PFAS in synthetic wastewater as it degrades PFAS to a similar extent as the medium and high power but with less electrical cost. In landfill leachate, high power is recommended to degrade ammonia and PFAS to the greatest extent.

By testing a known chemical composition of synthetic landfill leachate, the effects of oxidizable precursors and organics on the electrochemical oxidation of PFAS and ammonia could be studied. A literature review was conducted regarding compositions of landfill leachates to create a recipe for a more realistic synthetic leachate to run further tests.

Optimizing flow to increase the chance of PFAS colliding with the anode would increase PFAS degradation. One design improvement is changing the shape of the reactor housing from a straight tube to a concave shape. Changing the diameter of the housing halfway would create changes in flow, increasing the velocity and encouraging mixing in the system without an added electric component. With this new design, the flow within the housing becomes more turbulent, leading to increased mass transfer. Based on mass transfer calculations, the new design of the reactor housing improves the mixing and diffusivity of a compound by 1.81 times through the system, increasing the rate at which PFAS will be oxidized and degraded.

1.0 Introduction

Per and poly-fluoroalkyl substances (PFAS), a group of over 15,000 compounds, are used in many everyday products such as nonstick pans, fire-fighting foams, and dental floss as well as industrial processes such as chip manufacturing and metal plating. They are useful due to their water, fire, and grease-resistant properties, as well as their strong chemical bonds. They do not break down naturally in the environment or in the human body due to these strong bonds. Their presence in human blood is linked to many adverse health effects including thyroid disease, liver and kidney cancer, fertility issues, and more. Due to the large number of PFAS used, they are hard to regulate. PFAS leach off products into wastewaters, landfill leachates, and groundwater, ending up in our drinking water. There are increasing regulatory efforts and treatment technologies to remedy this issue.

Landfill leachate is a common source of PFAS contamination. Landfill leachate is a byproduct generated from a landfill that can infiltrate groundwater and consequently contaminate surface water. Landfill leachate also contains many other harmful contaminants in high concentrations that are becoming increasingly difficult to treat. Besides PFAS, ammonia is another toxic contaminant found in landfill leachate that poses risk to humans and aquatic life, as well as challenges during treatment.

Electrochemical oxidation (EOx) is an emerging treatment method that can break PFAS down into its elemental components such as CO_2, HF, F_2 and F^-. Aclarity is a company that has a unique EOx system that simultaneously targets many organic components in landfill leachate streams including PFAS and ammonia. Aclarity is continuously working to improve their current system and determine the best conditions under which to run their EOx systems to optimize the extent of PFAS and ammonia destruction.

This project aims to study the simultaneous degradation of ammonia and PFAS in landfill leachate. The goal of this experiment was to run Aclarity's benchtop-scale electrochemical oxidation system at different power settings, holding other variables constant, to determine the optimal power setting at which both PFAS and ammonia are simultaneously degraded at satisfactory rates.

2.0 Background

2.1 PFAS as an Emerging Contaminant

Perfluoroalkyl and Polyfluoroalkyl substances (PFAS), also dubbed forever chemicals, are synthetic chemicals formed of alkyl chains with carbon-fluorine bonds. These chains can have a bond dissociation energy of 544 KJ/mol (Coyle et al., 2020). As a result of this high molecular strength, these compounds are difficult to destroy or remove using conventional treatment methods. These chemical chains can vary between four and twelve carbons long with a different hydrophilic polar head group on the end. PFAS are defined by the length of their carbon chains. Short chain PFAS compounds are classified as less than six carbon for perfluorinated carboxylic acids and less than five carbons for sulfonic acids (Li et al., 2023). Long chain PFAS are defined as having six or greater carbon such as perfluorooctane sulfonate (PFOS) or perfluorooctanoic acid (PFOA) (Buck et al., 2011).

The properties that make PFAS hard to destroy are also the reasons they are so widely used. There are almost 15,000 PFAS found in countless items, from grease-resistant paper and take-out containers to fire-fighting foams meant for extinguishing fuel-based fires. These compounds are known for being heat-resistant, grease-resistant, and water-resistant. The high use of PFAS has led to their detection at measures of ug/L in groundwater, lakes, and streams (Furdui et al., 2008).

PFAS are even found in human blood in levels of ng/L, creating concern in the water treatment community (Gagliano et al., 2020). In the human body, PFAS can have detrimental and lasting health effects. This includes but is not limited to increased risk of thyroid disease, decreased fertility in women, increased cholesterol levels, and a reduction in humoral immune response in children ages five to seven (Grandjean et al., 2012). Different substances have different health effects, making it hard to ban only some of the PFAS. While short-chain PFAS often pass through the body in a couple of days, long-chain PFAS can take years to exit the human body. As a result, PFAS can accumulate in the human body (Xu et al., 2020).

PFAS precursors are also an issue in the environment as they can undergo transformations and create PFAS. Precursors are larger compounds containing a perfluoroalkyl section that sometimes degrade and recombine to form PFOS, PFOA, or short chain PFAS. Along with PFAS, these precursors are used in industrial processes and can be released into the environment through industrial waste and consumer products (Buck et al., 2011).

PFAS are manufactured using two main methods: electrochemical fluorination and telomerization (Buck et al., 2011). Electrochemical fluorination uses electrolysis to rearrange carbon chains of organic raw materials. This is done in anhydrous hydrofluoric acid, supplying fluorine that replaces all hydrogen atoms on the carbon chain, creating certain PFAS (Alsmeyer et al., 1994). Telomerization is a process in which a telogen, usually a perfluoroalkyl iodide ($C_mF_{2m+1}I$) is reacted with a taxogen, usually the polymer tetrafluoroethylene ($CF_2=CF_2$). This reaction yields a mixture of longer chained perfluoroalkyl iodides that can be further reacted to create PFAS like perfluoroalkyl carboxylic acids (PFCAs) (Buck et al., 2011).

2.2 Regulations on PFAS

In 2021, the EPA released the fifth Unregulated Contaminant Monitoring Rule (UMCR 5) as part of the Safe Drinking Water Act, in which they released health advisory levels (HAL) for PFOA, PFOS, and other PFAS. The limits included 10 ng/L of GenX chemicals (a type of PFAS), 0.02 ng/L of PFOS, 2,000 ng/L of perfluorobutanesulfonic acid (PFBS), and 0.004 ng/L of PFOA. The HAL are concentrations in water at or below the limit at which health effects can occur. There was no enforcement on the HAL values as they were only advisory (EPA [1], 2021).

Massachusetts currently has its own PFAS regulations along with federal regulations. These regulations focus on six main PFAS chains known as the MA6. The MA6 is made up of PFOA, PFOS, perfluorohexane sulfonic acid (PFHxS), perfluorononanoic acid (PFNA), perfluoroheptanoic acid (PFHpA), and perfluorodecanoic acid (PFDA). A limit of 20 ng/L or less of combined total concentration of the MA6 in drinking water is enforced to improve public health (MA DEP, 2021). These regulations also mandate sampling requirements such as sampling at every point in the distribution system, confirmation sampling if PFAS is detected, compliance action if detected levels are too high, and routine sampling depending on the testing results (MA DEP, 2021).

In January 2024, the EPA released new PFAS regulations and strategies to better measure PFAS in the environment. EPA method 1633 was finalized to be able to test for 40 PFAS in a variety of solutions including landfill leachate, wastewater, biosolids, and fish tissue (EPA [2], 2024). EPA method 1621, which can screen for substances with carbon-fluorine bonds, was also finalized (EPA [3], 2024).

In April of 2024 the EPA released the PFAS National Primary Drinking Water Regulation; the first enforced regulation on PFAS nationwide. The National Primary Drinking Water Regulation sets maximum contaminant levels (MCLs) for six different PFAS in drinking water. PFHxS, PFNA, and hexafluoropropylene oxide dimer acid (HFPO-DA) have MCL levels of 10 parts per trillion while PFOA and PFOS have MCL levels of 4 ppt. This new regulation also sets a limit for mixtures containing two or more of PFHxS, PFNA, HFPO-DA and perfluorobutane sulfonate (PFBS). The MCL goals for PFOA and PFOS are 0 ppt. Public water systems have three years to complete initial PFAS monitoring and continue with compliance monitoring. Public water systems have five years to implement solutions that reduce PFAS concentration to the levels stated above. (EPA [4], 2024)

2.3 PFAS in Landfill Leachate

PFAS can enter the water cycle in many different ways including landfill leaching, manufacturing discharge, and farm runoff. The PFAS in water is then treated, and in some cases, the treated PFAS-laden substances or streams are taken to a landfill to be disposed of. Due to landfill leaching, the PFAS can end up back in the landfill, contaminate groundwater, and eventually end up back at the treatment plant (State of Hawaii DOH, 2024).

Landfill leachate is a byproduct generated from a landfill that can infiltrate groundwater and consequently contaminate surface water (Parvin & Tareq, 2021). Landfill leachate is created

when water, commonly in the form of rain or melting snow, percolates through a landfill. (EPA [5], 2024) When this water comes in contact with the waste, it causes chemicals to leach out into the water. This leachate can come from hazardous or nonhazardous landfills and must be dealt with differently. Landfill leachate is composed of many harmful chemicals due to the diverse nature of waste dumped such as heavy metals, organics, inorganics, and salts. PFAS is a leading leachate problem because of their high use in everyday products and processes. Since landfill leachate has a wide variety and high concentration of toxic chemicals, these compounds need to be targeted and treated specifically.

Ammonia is another contaminant of concern in landfill leachate besides PFAS. Ammonia, usually in the form of ammonia nitrogen (NH_3-N), is present in very high concentrations at landfills. Ammonia is derived from waste, fertilizers, and natural processes occurring in landfills (EPA [6], 2024). It can be present in a gaseous phase, meaning that it could be emitted into the air, as well as in aqueous phases contaminating groundwater, surface water, and drinking water. Ammonia exerts nitrogenous biochemical oxygen demand (NBOD) because dissolved oxygen (DO) in water is consumed by microorganisms as they oxidize ammonia into nitrite and nitrate. This reduction in DO can lead to a decrease in species diversity in water environments and may even result in mortality of fish (EPA [6], 2024). Therefore, ammonia and NBOD need specialized treatment. Treatment of landfill leachate usually targets ammonia in a separate step; treating it first before targeting other toxic compounds present (Haslina et al., 2021). However, more treatment technologies are finding ways to treat ammonia, PFAS, and other toxic compounds present in landfill leachate in one treatment step.

2.4 PFAS Removal

There are many conventional methods for PFAS removal from water. However, some of these methods for water treatment only remove PFAS from an aqueous phase and place the PFAS in a concentrated stream or a solid phase. These methods include but are not limited to adsorption using GAC, ion exchange (IEX), reverse osmosis (RO) and nanofiltration (NF), foam fractionation (FF), and other proprietary media and sorbents (Appleman et al., 2020).

While these methods are all effective at removing long-chain PFAS from water, some struggle with the removal of short-chain PFAS (Appleman et al., 2020). Short chains can be adsorbed on the fresh surface of GAC and IEX taking up adsorption locations. Long chain PFAS can bump short chain PFAS off the surface and take their adsorption site (Zhang et al., 2023). This can lead to a sudden increase in short-chain PFAS in the effluent.

Reverse osmosis (RO) is a method where pressure drives water through a semipermeable membrane, resulting in two streams: purified water known as "permeate," and a concentrated stream known as "concentrate" or "brine." RO systems have the capability to eliminate various water pollutants like lead, volatile organic compounds (VOCs), PFAS, arsenic, bacteria, and viruses (EPA [7], 2024). Nanofiltration is a pressure driven membrane separation process, with pore sizes ranging from 1-10 nm (Ismail & Matsuura, 2022).

In foam fractionation, PFAS are adsorbed onto the surface of gas bubbles rising through dilute solutions (Smith et al., 2022). This process utilizes the surfactant properties of PFAS. A foamate forms at the top of the solution containing concentrated PFAS which can easily be removed from the solution (Smith et al., 2022). These conventional methods do not lead to the destruction of PFAS, so if the waste is not properly contained or destroyed, the PFAS can eventually end up back in the water system.

There are treatment methods that destroy PFAS including electrochemical oxidation (EOx), supercritical water oxidation, plasma oxidation, photochemical processes, reductive defluorination and sonolysis (Marin-Marin et al., 2023). PFAS destruction methods often take high amounts of energy to break the strong carbon-fluorine bond.

2.5 Electrochemical Oxidation

Electrochemical oxidation technology is one of the newest technologies in PFAS destruction. The technology employs an electrode, consisting of an anode and a cathode, to create strong oxidants in the water to destroy contaminants through oxidation. From an electrical standpoint, the anode is positive and the beginning of the circuit, while the cathode is negative, ending the circuit. The electrode oxidizes constituents in the water with two methods: direct or indirect oxidation. Direct oxidation refers to the direct transfer of electrons which occurs only on the surface of the anode. Indirect oxidation occurs when the electrode creates oxidants such as O_2, OH, or H_2 which oxidize constituents in the bulk solution. Most oxidizable compounds found in landfill leachate like ammonia can be broken down through both direct and indirect oxidation.

PFAS degradation mechanisms in EOx systems are complicated and still debated in the scientific community (Le et al., 2020). Studies have shown that the hydroxyl radical is unable to oxidize PFOS (Shi et al., 2019). Therefore, it seems generally accepted that the first step in PFAS destruction is direct electron transfer on the anode surface. This step is rate-limiting due to the mass transfer of PFAS from the bulk solution to the anode surface, as supported in density-functional theory simulations (Le et al., 2020) (Shi et al., 2019). Therefore, PFAS degradation by EOx is mass transfer limited. The radical created after direct electron transfer is then thought to break apart in a series of reactions with strong oxidants in the bulk solution. Through these reactions, shorter chain PFAS are proposed to be created (Le et al., 2020). Eventually, complete mineralization of PFAS can be achieved, leaving CO_2, F^-, and HF (Schaefer et al., 2020) (Sharma et al., 2022).

Recently, many treatability studies have been published on the destruction of PFAS with EOx systems. These systems use many different methods including various electrode shapes and sizes, electrode housings, electrode materials and coatings, and mechanisms to guide flow to achieve high PFAS destruction with low energy use and cost. Destruction of PFAS can be achieved with flow-by EOx systems where the flow runs parallel by the anode and cathode, or with a flow-through EOx system where the flow runs perpendicular through a porous or mesh anode and cathode (Liu et al., 2022). Another EOx reactor variation to the flow-by system is the tubular reactor, in which a rod-shaped anode sits inside of a tubular cathode (Liu et al., 2022).

Anode material is important in EOx of PFAS as only some materials can degrade these compounds (Shi et al., 2019). Most of the existing studies have been conducted on electrodes made of boron-doped diamond (BDD) or ceramic titanium based materials such as titanium suboxide (Ti_4O_7) (Schaefer et al., 2020). Literature on BDD is more widespread, however these electrodes are more expensive and harder to manufacture than Ti_4O_7 electrodes (Le et al., 2020). With BDD or titanium based electrodes, almost 99% of PFAS removal has been achieved with the lowest energy compared to other materials (Sharma et al., 2022).

Titanium materials specifically have high conductivity, chemical stability, and high oxygen evolution potential (Shi et al., 2019) (Sharma et al., 2022). The ceramic titanium based materials have small pores that provide much more electroactive surface area for the oxidation to occur than nonporous materials. Because of the extra electroactive surface area, electrodes made of these materials can achieve great destruction of PFAS with low energy (Sharma et al., 2022). The titanium based materials have less capacity to create OH radicals, therefore other methods to improve production of OH may need to be applied (Sharma et al., 2022).

The use of electrode coatings such as metal ions like Ce^{4+}, Bi^{4+}, Mn^{4+}, or Yb^{3+} can improve electrochemical activity and improve degradation of contaminants. The use of coatings can increase mineralization of PFAS without having to dose the solution with reagents that would increase mineralization instead (Sharma et al., 2022).

The recent increase in the application of EOx systems for PFAS destruction can be attributed to the technology's many advantages. One advantage of electrochemical oxidation is the possibility for multiple treatment goals such as destroying organics and PFAS simultaneously with the same system (Chaplin, 2019). The process itself also creates fewer harmful byproducts than some treatment options as the electron is a "clean reagent" (Sirés et al., 2014). EOx also operates under normal conditions, not requiring manipulated temperature or pressure (Sirés et al., 2014).

Despite the many promising studies on various EOx system designs, most designs are not ready to be applied in full-scale operation. Most of the EOx studies achieve great PFAS destruction results in synthetic streams with low energy. However, many have found it hard to replicate the results on real landfill leachate and wastewater streams. One difficulty in applying EOx for PFAS degradation in real streams is the low conductivity of many wastewaters and landfill leachates (Sirés et al., 2014). A stream of low conductivity requires added electrolytes such as NaCl, $NaClO_4$, and Na_2SO_4 to achieve higher PFAS degradation and better energy efficiency (Sharma et al., 2022). The pH of a stream can also affect PFAS degradation in EOx systems. Therefore, testing a wastewater or landfill leachate with an unaltered pH may yield less efficient results than testing a tailored synthetic stream (Le et al., 2020). EOx electrodes also foul over time due to the deposition of organics and salts, requiring acid cleaning (Sirés et al., 2014).

Another difficulty in relating results from synthetic streams to real-world application is the high PFAS concentration in synthetic streams. Many EOx systems are tested with high PFAS concentrations, yielding great PFAS degradation and energy efficiency in synthetic streams. PFAS are surfactants so their adsorption onto the anode can be dependent on concentration (Le et

al., 2020). Therefore, testing streams with PFAS concentrations much higher than environmental concentrations may overestimate the EOx system's capability in destroying PFAS with low energy in real streams. This concentration effect leads to much higher energy usage to destroy lower concentrations of PFAS in wastewaters and landfill leachates (Sharma et al., 2022)

The destruction of PFAS through EOx is limited by the mass transfer of PFAS from the bulk solution onto the anode surface (Sharma et al., 2022). Therefore, mass transfer must be improved through reactor design and optimization of flow to improve PFAS degradation. This also causes issues in streams with many types of PFAS and higher concentrations. EOx experiments have shown that PFOS and PFOA were degraded much slower when in a stream together than if only one of the compounds was present due to coadsorption effects (Le et al., 2019). The PFAS fight for adsorption sites, therefore streams with more types of PFAS would show less PFAS destruction overall. Long-chain PFAS specifically adsorb more easily than short-chain PFAS, blocking the short-chains from being degraded (Le et al., 2019). This could be an issue in landfill leachates that contain many different PFAS.

Aclarity is a company located in Mansfield, MA that specializes in electrochemical oxidation of PFAS with low energy in landfill leachate, wastewater, water treatment, groundwater remediation, and more. Their system is also used to destroy ammonia and organic contaminants alongside PFAS. Aclarity uses a unique flow-by tubular reactor, with a ████ based anode with proprietary coatings.

Aclarity has tuned their EOx system to achieve the highest degradation of PFAS, ammonia, and other contaminants, especially in landfill leachate, with the lowest possible energy. However, Aclarity is continuously working to improve their current system and determine the best conditions under which to run their EOx systems to optimize the extent of PFAS and ammonia destruction.

3.0 Methodology

The goal of this experiment was to determine the optimal power setting at which both PFAS and ammonia are simultaneously degraded at satisfactory rates by running Aclarity's benchtop-scale electrochemical oxidation system at different power settings, holding other variables constant. The goal was achieved through three objectives.

The first objective was to test Aclarity's EOx system. The EOx system was run at three different power settings, measuring PFAS and ammonia concentrations throughout each test. Two streams were tested: a synthetic wastewater, and a raw landfill leachate, to compare the effect of organics and other compounds on the degradation of PFAS and ammonia. The second objective was to analyze the EOx system results. This objective was completed by calculating percent destruction and decay rates and performing an energy analysis. The third objective was to determine if there is an optimal power setting to degrade ammonia and PFAS at satisfactory rates. This objective was completed using the analysis done in objective two to determine the best power setting for the system.

3.1 Setup

Aclarity's benchtop-scale EOx system consists of a reactor, a liquid storage tank, a pump, a line of PVC pipe, a globe valve, a pressure gauge, two hose fittings, a stand, a chilling coil connected to a chiller, a power supply box for the reactor, and another power supply for an ultrasonic flow meter on the pipe. Figure 1 shows the system setup, not including the chilling coil and chiller. The two power supplies are also not depicted. The system was assembled in a fume hood and remained for four weeks until testing was completed.
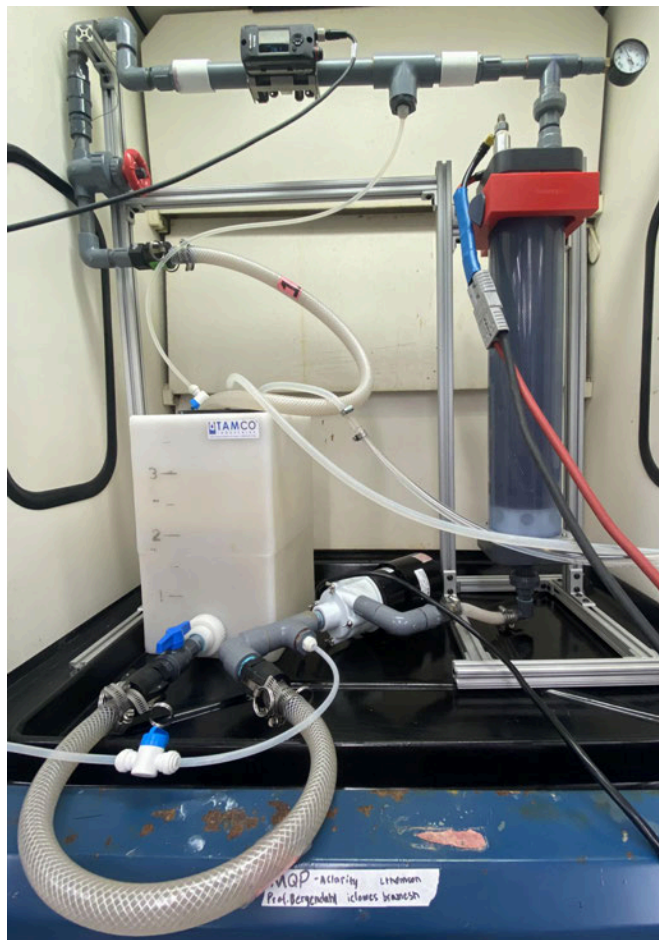
Figure 1. Setup of benchtop-scale EOx system in fume hood

All tests were run in batch mode with water recirculation through the system. For the first three test runs, a PFAS and ammonia spiked synthetic wastewater was tested. To create this wastewater, 12.1 L of reagent grade (RG) water created by running softened tap water through an automated electric still was combined with the MA6 PFAS, NaCl, $CaCl_2$, $MgSO_4$, and ammonia in the form of $(NH_4)_2SO_4$. Table 1 shows the amount of each chemical added to the RG water to make the synthetic wastewater. A fourth test run was created with the same PFAS and ammonia spiked solution and 26.5 mL of 0.01M HCL to lower the pH of the solution to five. Before each test run, the solution was dosed directly in the tank and thoroughly mixed for one hour and 30 minutes by running the solution through the system with the pump. The total volume of each solution was equivalent to three gallons plus 750 mL extra to account for sampling, or 12.1 L total. This total volume was chosen arbitrarily for this study and does not reflect the volume treated by Aclarity on a normal basis.

Table 1. Synthetic wastewater composition

Chemical	Stock Concentration	Test Concentration Needed	Amount of Stock Added	Purity of chemical
PFOA	50 mg/L	1000 ng/L	0.227 mL	NA
PFOS	50 mg/L	1000 ng/L	0.227 mL	NA
PFHxS	25 mg/L	500 ng/L	0.227 mL	NA
PFHpA	25 mg/L	500 ng/L	0.227 mL	NA
PFDA	25 mg/L	100 ng/L	0.0454 mL	NA
PFNA	25 mg/L	100 ng/L	0.0454 mL	NA
$(NH_4)_2SO_4$	pure solid	100 mg/L (as ammonia)	4.405g	99%
NaCl	pure solid	1250 mg/L	14.195 g	98%
$CaCl_2$ (anhydrous)	solid, 96%	1250 mg/L	14.195 g	96%
$MgSO_4$	pure solid	1250 mg/L	14.195 g	97%

For the last three tests, raw landfill leachate from a Massachusetts landfill in Mansfield was tested. The starting concentrations of PFAS and ammonia in this leachate sample are included in Table 2, however a complete analysis of the leachate's composition was not done. Before each test, a 12.1 L sample of the leachate was directly transferred into the tank and mixed through the system for 15 minutes.

Table 2. Starting concentrations in raw landfill leachate

Chemical	Starting Concentration			
	Test 1L	Test 2L	Test 3L	Average
PFOA	70.2 ng/L	72.7 ng/L	65.6 ng/L	69.5 ng/L
PFOS	128.0 ng/L	111.0 ng/L	106.0 ng/L	115.0 ng/L
PFHxS	78.3 ng/L	36.8 ng/L	23.7 ng/L	46.3 ng/L
PFHpA	33.7 ng/L	20.4 ng/L	17.6 ng/L	23.9 ng/L
PFDA	31.8 ng/L	13.9 ng/L	8.36 ng/L	18.0 ng/L
PFNA	40.7 ng/L	21.2 ng/L	16.2 ng/L	26.0 ng/L
NH_4	17.7 mg/L	17.1 mg/L	16.8 mg/L	17.2 mg/L

The globe valve was adjusted for both streams to stabilize flow at three gal/min, an arbitrary rate chosen only for the purpose of this study. The temperature of the solution was kept at one designated temperature for all tests and monitored throughout the test and the chiller was adjusted if needed. These parameters were set before the reactor was turned on and were kept constant throughout each test.

Once the test solutions were properly mixed, the power supply was connected to the reactor and set to the proper power mode for the test. Table 3 displays the power applied to each test.

Table 3. Tests and power applied

Test Number	Test Solution	Power
1A	PFAS and Ammonia Synthetic Wastewater	Low
2A	PFAS and Ammonia Synthetic Wastewater	Med
3A	PFAS and Ammonia Synthetic Wastewater	High
4A	PFAS and Ammonia Synthetic Wastewater with pH of 5	Low/Med
1L	Raw Landfill Leachate	Low
2L	Raw Landfill Leachate	Med
3L	Raw Landfill Leachate	High

3.2 Test Run, Sampling, and Analysis

Synthetic Wastewater

Before the reactor was turned on, a 250 mL sample was collected in a beaker for ammonia analysis at time zero. A 1 L sample was also collected in two 500 mL HDPE bottles for PFAS analysis at time zero. Another sample of about 80 mL was collected in a beaker to measure pH, conductivity, and temperature. This 80 mL sample was returned into the tank after measuring. The reactor was connected to the power supply and a corresponding power was applied to start the test. Each test ran for three hours, an arbitrary run time chosen for the purpose of this study. This is not representative of all of Aclarity's tests. Flow rate and applied power were kept constant throughout the test. Ammonia samples were taken every hour for analysis. PFAS samples were taken at time = 0 and time = 3 hours. Each sample's time, pH, conductivity, amperage, and temperature were measured and recorded.

Benchtop analysis of ammonia for the synthetic wastewater was conducted in-house immediately after sampling. Ammonia samples taken for the analysis were diluted accordingly based on estimated ammonia concentrations and the power applied for each test. Next, any chlorine in the samples was quenched with a 1M sodium thiosulfate pentahydrate solution to accurately get an ammonia concentration. The quenching process was done by adding a few drops of the sodium thiosulfate solution and measuring the total chlorine in the sample using the portable Hach DR 1900 spectrophotometer and Hach Method 8167 adapted from Standard Method 4500-Cl (APHA, 2023). This process was repeated until the total chlorine measured was undetectable by the spectrophotometer. Once all the chlorine in the sample was quenched, ammonia analysis was conducted using Hach method 8155 and the portable Hach DR 1900 spectrophotometer adapted from Reardon et al. 1966.

The PFAS samples collected during this synthetic wastewater test were stored in a $4℃$ fridge and then delivered to Alpha Analytical in Mansfield, MA, in an ice cooler within a week after sampling. PFAS samples were analyzed using EPA Method 1633 (EPA [8], 2024). EPA method 1633, testing for 40 different PFAS chains, is the current standard for laboratory testing of PFAS in wastewater from the EPA. This method details any required instruments, testing conditions, sample hold times, etc. to conduct PFAS testing. The use of this method improves precision of data between different laboratories and promotes consistency and comparability of results across many labs and regulatory jurisdictions (EPA [8], 2024).

Landfill Leachate

Before the reactor was turned on, a 250 mL sample was collected in an HDPE bottle for ammonia analysis at time zero. A 1 L sample was also collected in two 500 mL HDPE bottles for PFAS analysis at time zero. Another sample of about 80 mL was collected in a beaker to measure pH, conductivity, and temperature. This 80 mL sample was returned into the tank after measuring. The reactor was connected to the power supply and a corresponding power was applied to start the test. Each test ran for three hours. The flow rate and power applied were kept

constant throughout the test. Ammonia samples were taken every hour for analysis; however, these samples were not quenched with the sodium thiosulfate solution. PFAS samples were taken at time = 0 and time = 3 hours. Each sample's time, pH, conductivity, amperage, and temperature were measured and recorded.

For the landfill leachate tests, ammonia and PFAS samples were sent for external lab analysis. Ammonia was analyzed using Method 350.1 and PFAS was analyzed using EPA Method 1633 (EPA [9], 1993) (EPA [8], 2024). The samples slated for external lab analysis were stored in a 4℃ fridge immediately after sampling and then delivered to Alpha Analytical in Mansfield, MA in a cooler with ice, within a week after sampling.

3.3 Takedown

After all samples were taken during the run time, the power supply to the reactor was shut off and then disconnected from the reactor. The pump circulating the solution through the system was shut off. The system was drained following the Reactor Draining Procedure found in Appendix A. Any test solution drained in this process was placed back into the closed tank. All remaining test solution from the tank was placed in labeled hazardous waste containers. The hoses were disconnected and the reactor was removed from the stand.

3.4 Cleaning

After each test, the reactor was disassembled following Appendix B: SO-1 Reactor Assembly Procedure to extract the electrode. To clean the electrode, it was submerged in an acid bath made of 6% HCl. The electrode was then placed in a bath of RG water to rinse off the acid. Appendix C: Electrode Cleaning Procedure contains more details regarding the cleaning procedure. The reactor was then reassembled following the assembly procedure in Appendix B. A multimeter was used to ensure that the anode and cathode were not touching after assembly, as specified in Appendix D: Multimeter Check Procedure. This step was done to ensure that the electrode was seated in the reactor body properly, maintaining a gap between the anode and cathode. If the anode and cathode were touching, the reactor was disassembled and reassembled to correct the issue and retested with the multimeter.

The acid bath solution was reused for every test and then disposed of as hazardous waste at the end of testing. The rinse water had an acceptable pH of >5 and contained very little acid, therefore it was not classified as hazardous waste and it was disposed of appropriately.

The whole reactor system was reassembled and RG water was run through the system without any power applied to the reactor to flush out any residual contaminants that might have adhered onto the surfaces of the system. Due to very low concentrations of contaminants in the additional rinse water, the water was disposed of appropriately. The system was then ready for the next test.

4.0 Results & Discussion

The collected data was analyzed to determine the impact of different power settings on the destruction of PFAS and ammonia in Aclarity's EOx system. The percent destruction and decay rates were calculated to determine the ideal power settings for the simultaneous degradation of Ammonia and PFAS. An energy analysis was also run to compare the energy use of the EOx system with the energy use of other PFAS treatment options.

4.1 Testing Results

The parameters measured every hour included pH, conductivity, current, and flow. Appendix E: Laboratory Data contains the raw data collected during testing. Between all of the tests, some trends emerged.

The pH had a wide range throughout each test. Most of the tests started with a neutral pH and decreased to an acidic pH after the first hour of testing, then slowly climbed back up to a neutral pH. Test 2A started at a low pH of 4.55, decreased even lower after an hour of testing, and then climbed to a pH of 7. It is believed the starting pH in test 2A was impacted by residual acid on the reactor due to insufficient rinsing while cleaning the electrode after the previous test or a faulty pH probe.

The salinity of the water determines its ability to conduct an electrical current; in this system, the solution's conductivity decreased over the testing time. As conductivity decreased throughout the tests, the amperage decreased accordingly. The conductivity of the landfill leachate solution was much lower than the conductivity of the synthetic wastewater.

Small bubbles were observed in the reactor during each test. These bubbles were gaseous oxidants such as O_3 and other gaseous constituents like CO_2 and F_2 created in the electrochemical oxidation process. The bubbles served as a signal that the reactor was turned on and working. More small bubbles appeared with higher power settings and the amount of bubbles stayed relatively constant throughout the test. We also observed that the bubbles interfered with the ultrasonic flow meter. In tests with higher power settings and more bubbles, the flow meter sometimes malfunctioned and ranged from a reading of zero to six gallons per minute without any manual adjustments to flow. However, the actual flow was dialed to three gallons per minute before the reactor was turned on; therefore the flow was not impacted.

A white soapy film was observed on the electrode after testing. Figure 2 displays this film. This was observed in both the synthetic wastewater and landfill leachate tests. This film was different from a normal scale on the cathode caused by salts.

Image Redacted

Figure 2. Soapy film on electrode

Components such as calcium and magnesium left a residue scaled onto the cathode. This scale is similar to that of boiler scale. The scale was removed from the cathode during acid cleaning of the electrode.

The starting concentration of MA6 PFAS was much lower in the landfill leachate than in the synthetic wastewater. Also conductivity and amperage was lower in the landfill leachate tests. Therefore, the PFAS results between the synthetic wastewater stream and landfill leachate stream are not directly comparable. To make the tests more comparable, a synthetic landfill leachate with higher MA6 PFAS concentrations and conductivity could be tested in this system.

4.2 Destruction of PFAS and Ammonia

To determine the power setting at which more PFAS and ammonia were destroyed, percent destruction of the contaminants over the whole testing period was calculated. Ammonia test results revealed that ammonia has a greater percent destruction in this system as applied power increases. As shown in Figure 3, 100% of the ammonia was destroyed after three hours in all synthetic wastewater tests except the low power test. As seen in the raw data from the synthetic wastewater tests in Appendix E, ammonia was undetectable after one hour in the medium and high power tests. When the pH of the synthetic wastewater was lowered to 5 and the test was run at low/medium power, ammonia also decayed very quickly and was also undetectable after one hour. From these results, ammonia in the synthetic wastewater decays quickly in this system at higher power settings; therefore, medium power is satisfactory, and the power does not need to be increased higher than the medium power. When the pH is lowered, ammonia decays quickly, even at lower power; therefore, low/medium power is satisfactory for decaying ammonia in the low pH solution.

The percentage of ammonia destroyed in landfill leachate tests was lower than in synthetic wastewater tests. As seen in Figure 4, complete destruction of ammonia was not achieved with any of the power settings. This result was expected as landfill leachate contains many other oxidizable compounds. The presence of these oxidizable compounds likely reduces the chance that ammonia will encounter an oxidant and be oxidized. Despite achieving less percent destruction of ammonia in the landfill leachate tests, the same pattern of increased destruction with increased power occurred, just as in the synthetic wastewater tests. Therefore, in both test solutions, a higher power setting is better to destroy ammonia. Within landfill leachate, high power degrades ammonia to the greatest extent.

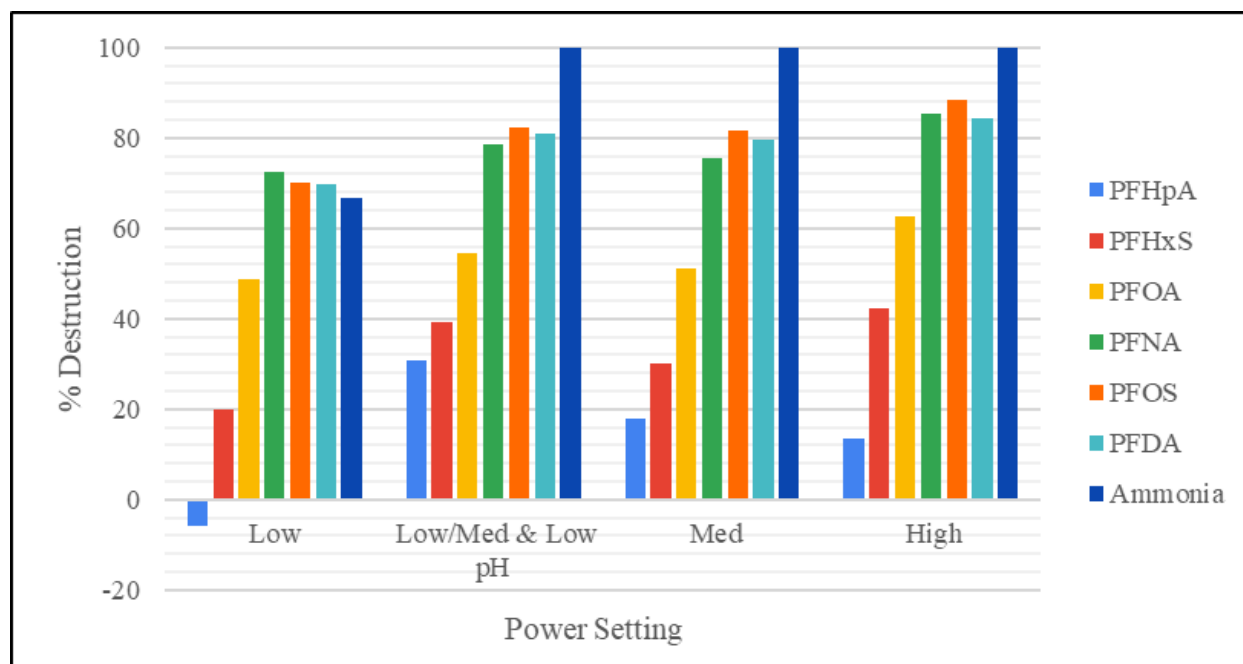**Figure 3.** Percent destruction of contaminants from time 0 to time 3 hours in synthetic wastewater grouped by test voltage
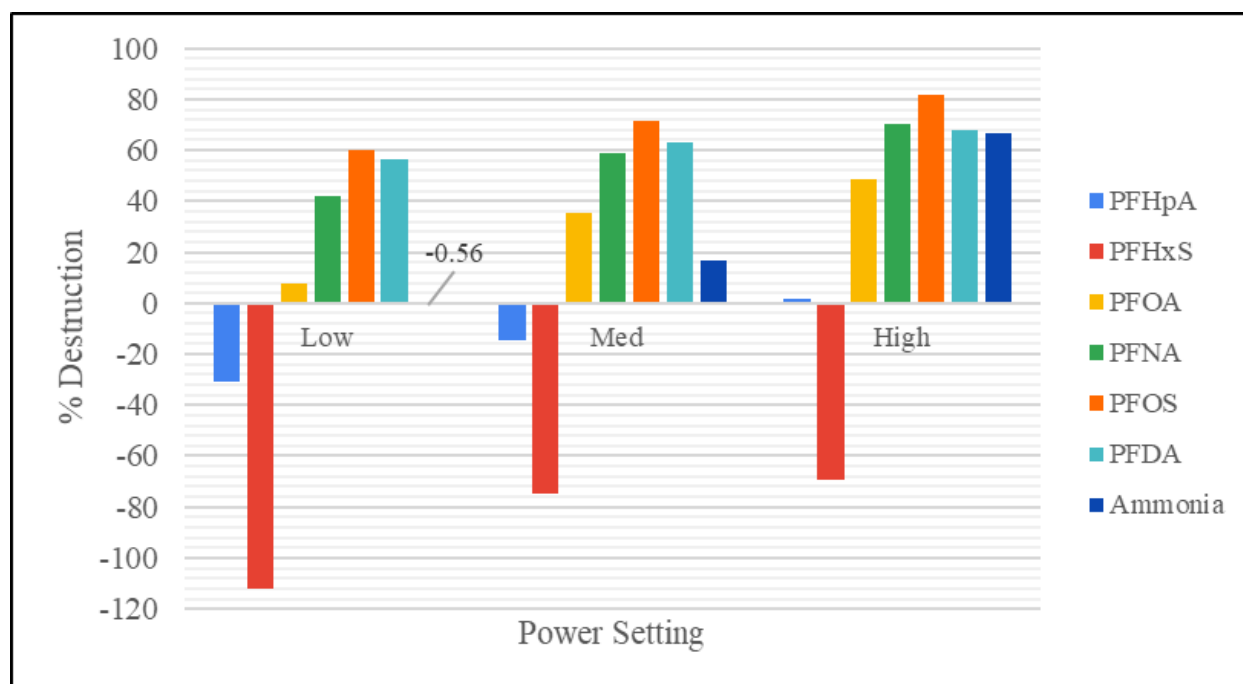

Figure 4. Percent destruction of contaminants from time 0 to time 3 hours in landfill leachate grouped by test voltage

PFAS test results revealed that overall, the MA6 PFAS also have a greater percent destruction in the synthetic wastewater as applied power increases and all other variables are

held constant. The high power test degraded PFAS to the furthest extent in most cases. The only exception was PFHpA. As shown in Figure 3, PFHpA concentration increased at low power. This increase cannot be attributed to any specific cause. However, it is hypothesized that while the longer chain PFAS like PFOA and PFOS are degraded, their components were reconstituted to form PFHpA faster than the EOx system could destroy PFHpA at this power level The highest percent destruction of PFHpA was seen in the low/medium power test with lowered pH. Also, the percent destruction of PFHpA was higher in the medium power test than in the high power test. Therefore, the percent destruction of PFHpA did not follow the pattern of increased destruction with increased applied power.

With a lowered pH in the low/medium power test, the destruction of MA6 PFAS was equivalent to or higher than the destruction in the medium power test. This trend in data suggests that low power and low pH might be an optimal treatment setting for waters with fewer background organics. Since the destruction of PFHpA did not follow the same pattern as the destruction of the other PFAS, lowering the pH may prove to be helpful in destroying PFHpA rather than attempting to increase the power to achieve higher destruction. More tests would need to be run to test this concept, and it is not certain that this outcome will be replicable since only one test was completed.

In the landfill leachate tests, the percent destruction of each MA6 PFAS increased with higher applied power, as seen in Figure 4. Less destruction was achieved in the landfill leachate tests than in the synthetic wastewater tests, which may be attributed to the low conductivity in the landfill leachate.

Compared to the synthetic wastewater tests, the creation of certain PFAS was detected in the landfill leachate tests. As seen in Figure 4, both PFHpA and PFHxS were almost always created during the landfill leachate tests. A full water quality report or a Total Oxidizable Precursor assay was never run on the leachate sample. Therefore, the cause of these increases cannot be pinpointed, only hypothesized. Perhaps as the longer chain PFAS compounds were broken down, their components were reconstituted to form the shorter chain PFHpA and PFHxS faster than the EOx system could degrade them. The leachate also could have contained PFAS precursors that were oxidized in the system and formed PFHpA and PFHxS.

Despite different levels of destruction between the synthetic wastewater and landfill leachate tests, higher power almost always destroyed more PFAS in both solutions. A trend of increased percent destruction of PFAS and ammonia with increased power in this system suggests that a higher power setting is better. The percent destruction of these contaminants is a very important factor in determining which power setting is the best because the goal of running the EOx system is to destroy as many of the contaminants as possible while maintaining energy efficiency.

4.3 Decay Rates

The decay rates of the contaminants over the whole testing period were calculated as an alternative method to determine the power setting at which more PFAS and ammonia were destroyed. A first order decay rate was determined for ammonia and PFAS in both streams through graphical analysis of the concentration data. Appendix F details the analysis to determine the reaction order rate for both ammonia and PFAS.

Ammonia decay rates for the synthetic wastewater for most of the tests could not be calculated since the concentration of ammonia at the end of testing was under range. However, decay rates for the low power and high power tests in the first hour could be calculated. For low power, the decay rate was ███ 1/min as shown in Figure 5. The ammonia decay rate with high power for the first hour was ███ 1/min. As shown in Figure 6 below, ammonia decay rates for the landfill leachate increased as the applied power increased.

The PFAS decay rates for synthetic wastewater and landfill leachate generally increased as applied power increased, except for the decay rate of PFHpA. The decay rates for the landfill leachate tests are lower than the decay rates for synthetic wastewater tests. This may be attributed to the oxidizable precursors present in the landfill leachate that were absent in the synthetic wastewater. The lower decay rates in landfill leachate could also be due to the lower conductivity of the solution.
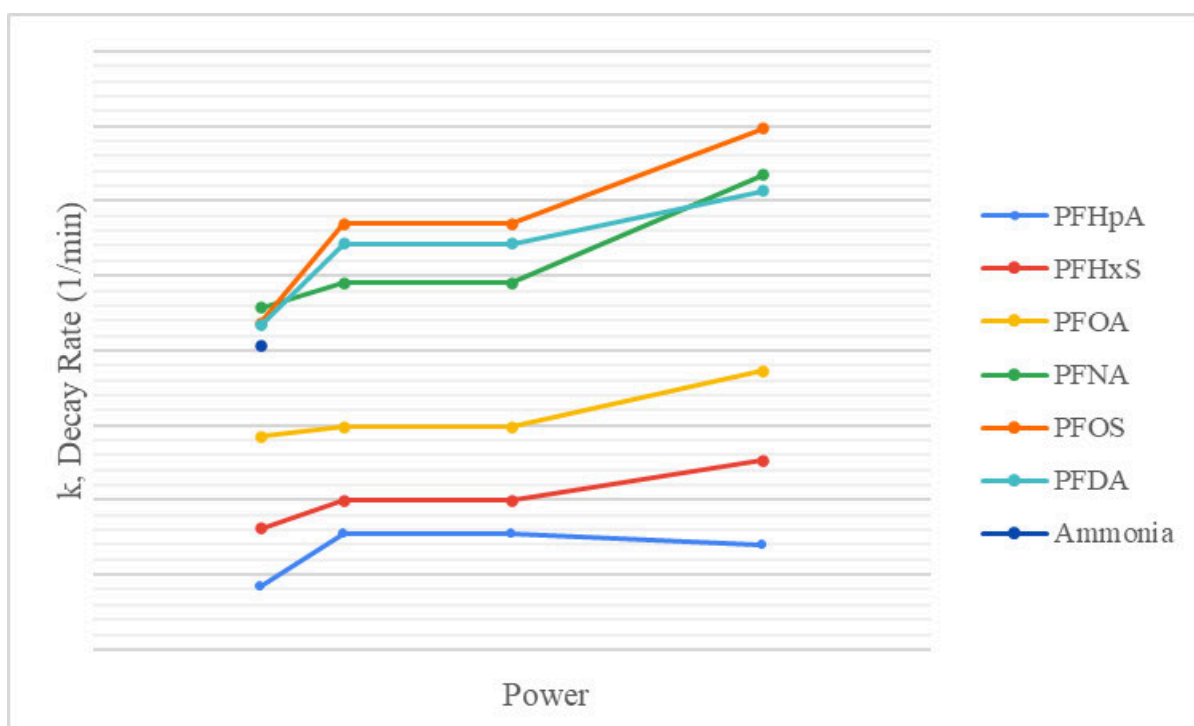
Figure 5. First order decay rates in synthetic wastewater at increasing power
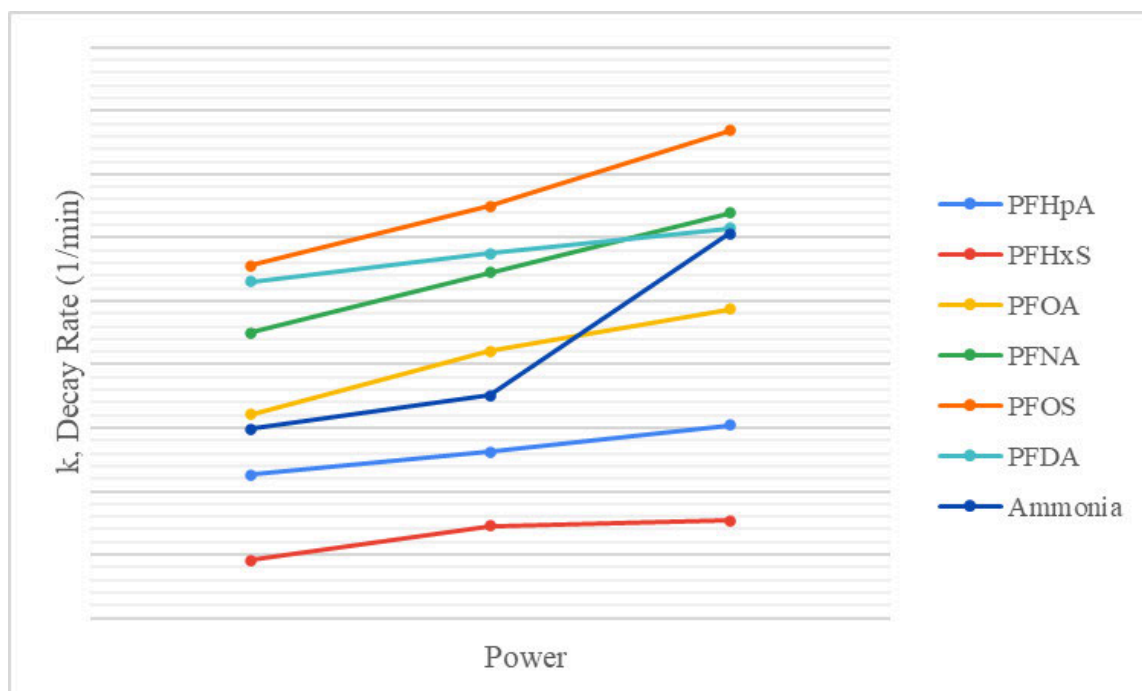
Figure 6. First order decay rates in landfill leachate at increasing power

4.4 Energy Analysis

An energy analysis was performed to compare the energy requirements of Aclarity's system to existing PFAS treatment technologies. The energy efficiency of each power setting run on this system was also analyzed to determine which power setting destroys the most contaminants with the least amount of energy.

The energy usage was calculated for each synthetic wastewater and landfill leachate test by using the average power. With the allotted testing time of three hours and volume of 12.1 L, the energy usage rate was calculated in kWh/L, as shown in Table 4. This energy usage only represents the energy to the reactor, ignoring the energy usage from pumping.

Table 4. Energy usage during testing

Test	Power	Amps (avg)	Watts	Wh/ L	kWh/L
1A	Low	■	55.08	13.66	0.01366
2A	Med	■	162.97	40.41	0.04041
3A	High	■	327.95	81.31	0.08131
4A	Low/Med	■	79.97	19.82	0.01982
1L	Low	■	8.12	2.01	0.00201
2L	Med	■	26.90	6.67	0.00667
3L	High	■	55.65	13.79	0.01379

Due to the low conductivity of the landfill leachate, less power was used during the leachate tests. As shown in the percent destruction results, less power used in the landfill leachate tests contributed to less destruction of contaminants.

Energy efficiency based on the mass of contaminants removed was also considered. The concentration of PFAS and ammonia removed in each test was converted into the mass removed and divided by the energy used in watt-hours. This resulted in a value representing mass removed per watt-hour of energy used in each test for each contaminant. The values for the synthetic wastewater tests are in Table 5 and the values for the landfill leachate tests are found in Table 6. The values highlighted in green represent the most mass of each contaminant removed per watt-hr and the values highlighted in red represent the least mass removed per watt-hour. The asterisks refer to values that were calculated with less than three hours of run time. The ammonia was undetectable by one or two hours in the synthetic wastewater tests, therefore the mass of contaminant destroyed per watt-hr only included the first hour or two.

Table 5. Unit mass destroyed per watt-hr in synthetic wastewater tests

Contaminant (mass unit)	Low	Low/Med (pH 5)	Med	High
PFHpA (ng)	-13.5	58.77	14.45	4.38
PFHxS (ng)	40.51	66.27	21.98	13.22
PFOA (ng)	29.4	24.56	9.46	5.19
PFNA (ng)	37.69	30.86	14.41	7.33
PFOS (ng)	25.96	23.3	12.04	5.33
PFDA (ng)	11.28	12.69	5.94	2.72
Ammonia (mg)	3.69	6.84*	3.27*	2.53*

Table 6. Unit mass destroyed per watt-hr in landfill leachate tests

Contaminant (mass unit)	Low	Med	High
PFHpA (ng)	-3.79	-0.34	0.02
PFHxS (ng)	-32.3	-3.1	-0.94
PFOA (ng)	1.91	2.9	1.84
PFNA (ng)	6.26	1.4	0.66
PFOS (ng)	28.36	8.97	4.96
PFDA (ng)	6.59	0.99	0.33
Ammonia (mg)	-0.04	0.33	0.64

The least efficient, or the least mass removed per watt-hour, was often the highest power setting in the synthetic wastewater tests. The PFAS oxidation reactions are known to be mass transfer dependent, therefore energy may not be proportional to destruction. From the percent destruction results, more contaminants are destroyed with higher power. However, these energy results highlight that destruction of contaminants does not proportionally increase when power and energy usage increases.

These results heavily depend on the compounds existing in the solution and the reactions occurring throughout the test. It is difficult to say one power setting is more efficient (using less energy to destroy a specified mass of contaminants) than the other due to the unknown complex reactions. The efficiency is much less clear in the landfill leachate tests due to the other unknown compounds interfering with the oxidation of the PFAS and ammonia. The differences in

efficiency between the destruction of certain PFAS may allude to the different complex reactions that each PFAS undergoes and the specific difficulties in destroying a broad range of PFAS.

The energy consumption of Aclarity's EOx system was compared to the energy consumption of other technologies used for PFAS removal. Test 2A, the medium power setting with the synthetic wastewater, was chosen as a baseline to compare other treatment methods to Aclarity's EOx. This test was chosen because the synthetic wastewater tests were more controlled due to the known composition of the stream. It also captures the mid-range power usage, therefore the minimum or maximum energy used in the tests would not be compared to the average energy usage of other treatment systems.

The volume of solution treated and the mass of PFAS destroyed in Test 2A were used to calculate energy usage of other treatment technologies to get a comparable energy usage value. Only the main sources of electrical costs for each technology were factored into the energy consumption calculations. More details on the energy analysis assumptions and calculations can be found in Appendix G.

Table 7. Energy consumption comparison between technologies

Treatment Method	Energy Consumption kWh
Aclarity's EOx Medium Power	0.4889
Granular Activated Carbon Regeneration	0.0145
Evaporation	7.596
Reverse Osmosis Pumping	2.001

From the calculations, the only treatment technology that used less energy than Aclarity's EOx was GAC. The GAC used 33.7 times less energy. Therefore, the existing treatment technology seems to be more energy efficient. However, GAC itself does not destroy PFAS while EOx does. Evaporation had the highest calculated energy consumption which was 15.54 times greater than energy for EOx. The energy for RO was 4.092 times greater than the energy for EOx. Therefore, Aclarity's EOx system is a competitive option for PFAS treatment.

5.0 Conclusion & Recommendations

From the data analyzed throughout our experiment, we have determined optimal power settings to create the conditions that simultaneously degrade ammonia and PFAS to the greatest extent in this system. In the future, similar tests should be run with a synthetic landfill leachate that closely replicates collected leachate. This synthetic landfill leachate would provide more control over the content of the solution and show how the presence of oxidizable precursors and other compounds affect the degradation of ammonia and PFAS. During experimentation, the physical properties of the reactor were noted to make changes to the design. These design changes were focused on improving the mass transfer of PFAS onto the anode to improve PFAS degradation.

5.1 Power Setting
Synthetic Wastewater

Ammonia degraded faster with synthetic wastewater as applied power increased. With low/medium power and pH of 5, medium power, and high power, ammonia was undetectable by the end of the three hour tests. If the goal of running the system is to degrade ammonia completely without a time constraint, using low/medium power with a lowered pH or the medium power is a better option to save on electrical costs in the system.

Increased degradation of MA6 PFAS was observed as applied power increased. The most degradation of each contaminant except PFHpA was achieved with high power. However, the low/medium power, while lowering the solution pH to 5, yielded results comparable to those of the high power test. Destruction of most PFAS compounds in the low/medium power test, except PFHpA, were within 10% of the destruction results in the high power test. PFHpA was actually degraded the most in the low/medium power test. If the goal of running the system is to degrade PFAS to a great extent on waters with fewer background organics, using low/medium power with a lowered pH is a better option to save on electrical costs in the system.

Landfill Leachate

Ammonia in landfill leachate degraded faster as applied power increased. While ammonia wasn't degraded fully by the end of any test, the high power test showed the greatest percent destruction. For solutions similar to this sample of landfill leachate containing background organics, high power is the recommended power setting to effectively destroy ammonia. Due to its lower conductivity, the energy usage of the high power test with this landfill leachate sample was lower than the energy in the high power test with synthetic wastewater. Therefore, even with the highest power setting in landfill leachate, electrical costs can still be lowered.

MA6 PFAS in landfill leachate degraded more as applied power increased. The high power test achieved the greatest degradation of PFAS except for PFHxS, which was created. The high power test showed the lowest increase in PFHxS. Therefore, high power is the best power setting to degrade PFAS in this sample of landfill leachate and in these conditions. A better

understanding of the constituents of landfill leachate could provide insight into the observed increase in PFHxS. A realistic synthetic landfill leachate or a landfill leachate with a known composition could be tested to understand which constituents affect PFAS degradation and creation. Longer test times could also be experimented with to potentially achieve higher PFAS degradation in landfill leachate.

Overall Power Setting

In most cases, the trend observed in this system shows increased percent destruction of PFAS and ammonia with increased power. The decay rate for ammonia and PFAS also increased as higher power was applied. Therefore, if the goal is to achieve the highest destruction, a higher power setting such as high power should be used. However, there could be a point at which adding power does not increase the destruction of contaminants because the PFAS destruction reactions are mass transfer limited. Increasing applied power isn't always beneficial due to higher financial and environmental costs. There are potential ways to increase degradation without increasing power, as shown by the low/medium power test results with low pH.

5.2 Next Steps in Testing

A more realistic synthetic landfill leachate solution of known composition should be tested to understand the effects of other constituents on the electrochemical oxidation of PFAS and ammonia in this system. In the tests completed with raw landfill leachate, chemical concentrations besides ammonia and the MA6 PFAS were unknown, making it difficult to pinpoint oxidizable precursors and other PFAS chains. By testing a known chemical composition of synthetic landfill leachate, it is possible to track concentrations and precursors through the test to better understand their effects on the system. Also, by increasing the MA6 PFAS concentrations and the conductivity of a landfill leachate recipe, the tests could be more comparable to the synthetic wastewater tests.

The goal in the creation of a synthetic landfill leachate was to more actively replicate a landfill leachate that the EOx system would treat in a real-world application. To achieve this goal, compounds detected in landfill leachate were pulled from literature, along with previously used compositions of synthetic landfill leachates. The decided recipe shown in Table 8 was chosen to have a variety of heavy metals, organics, inorganics, and salts (A et al., 2017) (VanGulck & Rowe, 2004) (Zhang et at., 2023).

Table 8. Recipe for synthetic leachate

Chemical	Chemical Formula	Concentration (mg/L)
Aluminum sulfate	$Al_2(SO_4)_3 \cdot 16H_2O$	30
Cadmium Chloride	$CdCl_2 \cdot 2.5H_2O$	12
Cupric sulfate pentahydrate	$CuSO_4 \cdot 5H_2O$	30

Chemical	Chemical Formula	Concentration (mg/L)
Nickel(II) chloride	$NiCl_2 \cdot 6H_2O$	20
Iron(III) chloride hexahydrate	$FeCl_3 \cdot 6H_2O$	30
Sodium Chloride	$NaCl$	1000
Ammonium Chloride	NH_4Cl	200
Potassium bicarbonate	$KHCO_3$	200
Potassium dichromate	$K_2Cr_2O_7$	20
Magnesium sulfate	$MgSO_4$	750
Sulfate (acid phase)	SO_4^{2-}	340
Potassium bicarbonate	$KHCO_3$	300
Dipotassium phosphate	K_2HPO_4	20
Propionate	$C_3H_5O_2^-$	10
Acetate	$C_2H_3O_2^-$	15
Sodium nitrate	$NaNO_3$	50
Calcium chloride	$CaCl_2$	200
Urea	$CO(NH_2)_2$	660
Tannic acid	$C_{76}H_{52}O_{46}$	10
Humic acid sodium salt	$C_9H_8Na_2O_4$	100
PFOA	$C_8HF_{15}O_2$	0.001
PFOS	$C_8HF_{17}O_3S$	0.001
PFHxS	$C_6HF_{13}O_3S$	0.0005
PFHpA	$C_7HF_{13}O_2$	0.0005
PFDA	$C_{10}HF_{19}O_2$	0.00001
PFNA	$C_9HF_{17}O_2$	0.00001

Alternatively, another real landfill leachate sample could be tested rather than creating a synthetic leachate. If another real landfill leachate sample is tested, a full water quality report

should be conducted including a Total Oxidizable Precursor assay. Running assessments to know the leachate composition before testing would provide better understanding of the EOx mechanisms and results.

5.3 Improving Mass Transfer via Flow

In the EOx system, PFAS is degraded through direct electron transfer at the surface of the reactor's anode. When there is a lower concentration of PFAS present like in the landfill leachate, PFAS is mass transport controlled. However, the issue in oxidizing PFAS may be the ability of PFAS to contact the anode surface. Optimizing flow to increase the chance of PFAS contacting the anode would increase PFAS degradation.

One method to change flow within the system is to change the shape of the electrode housing. Changing the diameter of the housing halfway through to create a concave shape would create changes in flow, increasing the velocity. This would create a drop in pressure through the concave center, encouraging mixing in the system without an added electric mixing component. Only changing the diameter through the center of the electrode housing also helps to retain a higher volume within the reactor, rather than decreasing the entire diameter. Pumping costs could increase slightly due to the increased pressure as diameter changes. Figure 7 displays the potential design change.
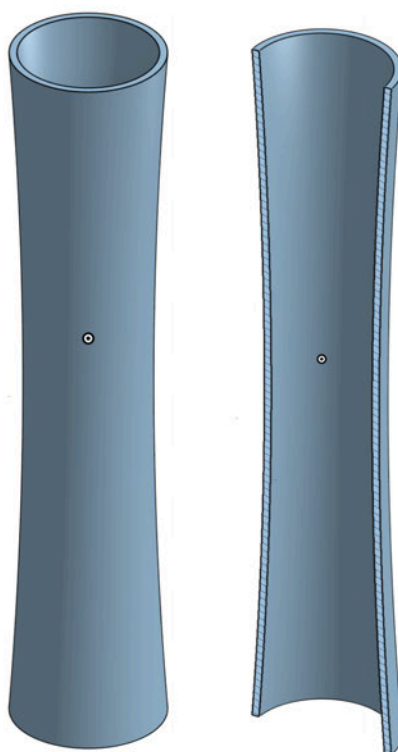

Figure 7. CAD design of a concave reactor housing.

This design should improve mixing throughout the reactor housing because the flow within the housing becomes more turbulent. PVC was assumed as the material of the reactor housing with a height of ███████████████████████████████. The inner diameter of the housing at the entrance and exit is ███ inches, similar to the original design. The inner diameter at the concave part of the housing is ██████ inches, a 20% decrease from the ends.

To quantify the change in the turbulence of the flow within the reactor housing, the Reynolds (Re) number of the annular space in the reactor housing was determined for both the original and the new design. The Re number is utilized to determine if a fluid's flow is laminar or turbulent. The Re of the original design was found using Equation 1 with the original inner diameter of ███ inches. The Re of the new design was found by averaging the Re along nine points of the concave reactor housing as shown in Figure 8. Table 9 shows the calculations for the average Re of the new design. The diameter of the housing used for the Re was calculated by subtracting the diameter of the electrode within the housing from the inner diameter of the housing in its respective location. The electrode was assumed to be a solid cylinder with a diameter of ███ inches to simplify calculations. The fluid flowing through the reactor housing was assumed to be water when determining its fluid properties such as kinematic viscosity. For these calculations, it was assumed that the flow into the reactor housing was undisturbed. The Re was calculated to be ██████ for the original design and ██████ for the new design. The calculations for the Re numbers are shown below.

Equation for Reynold's Number (Re):

$$Re = \frac{4Q}{\pi D \nu} \qquad\qquad \text{Equation (1)}$$

Original Design Calculations:

Q = ██████████████████ ███
ν = ███████████ ███
$D_{entrance/exit}$ = █████████████████████████

$$Re_{original} = \frac{4Q}{\pi D_{entrance/exit} \nu}$$

$$Re_{original} = \frac{\blacksquare\blacksquare\blacksquare\blacksquare\blacksquare}{\blacksquare\blacksquare\blacksquare\blacksquare\blacksquare\blacksquare} = \blacksquare\blacksquare\blacksquare$$

New Design Calculations:

Q = ██████████████████ ███

$\mathcal{V} =$ ▮▮▮▮▮▮

$D_{concave} =$ ▮▮▮▮

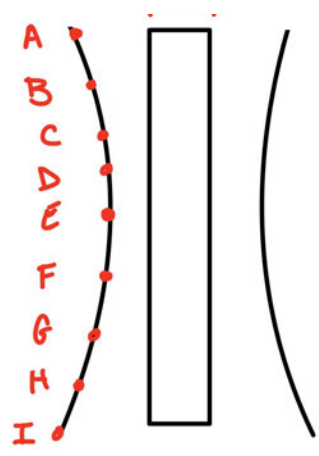$$Re_{concave} = \frac{4Q}{\pi D_{concave} \nu}$$

Figure 8. A depiction of the locations used to find an average Reynolds number for the new design

Table 9. Calculations for average Reynolds number for new design

Location	Diameter			Reynolds
	Diam. of Housing	Diam. of Electrode	$D_{concave}$	
A = I	▮ in	▮ in	▮▮▮▮▮	▮▮
B = H	▮ in	▮ in	▮▮▮▮▮▮	▮▮
C = G	▮ in	▮ in	▮▮▮▮▮▮	▮▮
D = F	▮ in	▮ in	▮▮▮▮▮▮	▮▮
E	▮ in	▮ in	▮▮▮▮▮▮	▮▮

$$Re_{avg} = \frac{Re_A + Re_B + Re_C + Re_D + Re_E + Re_F + Re_G + Re_H + Re_I}{9}$$

$$Re_{avg} = \frac{\blacksquare\blacksquare\blacksquare\blacksquare\blacksquare\blacksquare\blacksquare\blacksquare\blacksquare\blacksquare}{9}$$

$$Re_{avg} = \blacksquare$$

      With the new design, the Reynolds number increased by 3109.5, indicating that the flow through the reactor housing became more turbulent. The mass transfer coefficient (k_x) of PFAS moving through the system was also considered. The mass transfer coefficient is a measure of how a compound diffuses through a membrane, barrier, or fluid. The Sherwood number, the Schmidt number, and the Reynolds number are required to determine the mass transfer coefficient. The Sherwood number is a ratio of the mass transfer of a compound through convection and the mass transfer of a compound through diffusion. The Schmidt number is a ratio of a compound's momentum diffusivity to a compound's mass diffusivity. Because these dimensionless numbers are interconnected in the fundamentals of mass transfer, many correlations can be found between them. Equation 2 shows the convection correlation for the Sherwood number for liquid with turbulent flow through a pipe like the reactor housing. Equation 3 shows the equation used to calculate the Schmidt number where D_{AB} is the diffusivity constant of a particular PFAS compound. Equation 4 shows the equation used to calculate the Sherwood number where L is the characteristic length of the reactor housing and k_x refers to the mass transfer coefficient. Using the mass transfer relationships of the Sherwood, Reynolds, and Schmidt, the mass transfer coefficient was calculated in terms of the diffusivity constant using Equation 4. The calculations were done in terms of the diffusivity constant because this number varies between each PFAS compound and is unknown in this system. For the calculations below, the solution running through the reactor was assumed to be water when determining its fluid properties such as density and viscosity.

Convection Correlation for liquid in pipe with turbulent flow:

$$Sh = 0.218 * Re^{0.83} * Sc^{1/3} \qquad\qquad \text{Equation (2)}$$

Schmidt Number equation:

$$Sc = \frac{\mu}{\rho D_{AB}} \qquad\qquad \text{Equation (3)}$$

Sherwood Number Correlation:

$$Sh = \frac{k_x L}{D_{AB}} \qquad\qquad \text{Equation (4)}$$

Ratio of k_x between new and original design:

$$\text{Improvement Ratio} = \frac{k_x (new\ design)}{k_x (original\ design)} \qquad\qquad \text{Equation (5)}$$

Original Design Calculations:

Re = ▮▮

μ = 10⁻³ Pa-s

$\mu = 10^{-3}$ Pa-s

$\rho = 997$ kg/m³

D_{AB} (m²/s) varies with different PFAS compounds

L = ▮▮▮

$$Sc = \frac{\mu}{\rho D_{AB}}$$

$$Sc = (10^{-3} Pa * s)/[(997 \frac{kg}{m^3}) * D_{AB}] = 1 * 10^{-6} * D_{AB}$$

$$Sh = 0.218 * Re^{0.83} * Sc^{1/3}$$

$$Sh = 0.218 * ▮▮▮ * (1 * 10^{-6} * D_{AB})^{1/3}$$

$$Sh = ▮▮ D_{AB}^{1/3}$$

$$Sh = \frac{k_x L}{D_{AB}} \text{ where } k_x = \frac{Sh \cdot D_{AB}}{L}$$

$$k_x = \frac{(▮▮ D_{AB}^{1/3})(D_{AB})}{▮▮}$$

$$k_x = 2.73 D_{AB}^{4/3}$$

New Design Calculations:

Re = ▮▮

μ = 10⁻³ Pa-s

$\mu = 10^{-3}$ Pa-s

$\rho = 997$ kg/m³

D_{AB} (m²/s) varies with different PFAS compounds

$$Sc = \frac{\mu}{\rho D_{AB}}$$

$$Sc = (10^{-3} Pa * s)/[(997 \frac{kg}{m^3}) * D_{AB}] = 1 * 10^{-6} * D_{AB}$$

$$Sh = 0.218 * Re^{0.83} * Sc^{1/3}$$

$$Sh = 0.218 * ▮▮▮^{0.83} * (1 * 10^{-6} * D_{AB})^{1/3}$$

$$Sh = ▮▮ D_{AB}^{1/3}$$

$$Sh = \frac{k_x L}{D_{AB}} \text{ where } k_x = \frac{Sh \cdot D_{AB}}{L}$$

$$k_x = \frac{(\blacksquare D_{AB}^{1/3})(D_{AB})}{\blacksquare}$$

$$k_x = 4.94 D_{AB}^{4/3}$$

Ratio of k_x between new and original design:

$$Improvement\ Ratio = \frac{k_x\ (new\ design)}{k_x\ (original\ design)}$$

$$Improvement\ Ratio = \frac{4.94 D_{AB}^{4/3}}{2.73 D_{AB}^{4/3}} = 1.81$$

With the new design, the mass transfer coefficient improves by a multiplier of 1.81. Since the mass transfer coefficient is a measure of how quickly a compound is transported through fluid, the new design of the reactor housing improves the mixing and diffusivity of a compound by 1.81 times throughout the system. As a result, this design increases the rate at which PFAS will be oxidized and degraded.

It is also important to note some limitations in this approach to quantifying the improvement ratio. The mass transfer coefficient calculations and the improvement ratio are only approximations. Many assumptions were made that might affect the actual improvement ratio and the mass transfer coefficient when considering the mass transfer of the system. First, the fluid running through the reactor was assumed to be water to easily quantify its fluid properties. However, the synthetic wastewater and the landfill leachate tested were much higher in salinity and other constituents that could affect the density and viscosity of the solution. Next, the new improved design's dimensions, material, and thickness were selected arbitrarily. Experimenting with and changing these parameters can also affect the improvement ratio. Finally, one limitation of this design is a change in the hydraulic residence time (HRT), the average time that constituents are reacting within the housing. The HRT is a function of reactor volume divided by its flow rate. While the flow rate is held constant between both designs, the reactor volume decreases, leading to a lower HRT. This decrease in HRT might impact the PFAS degradation rate, offsetting some of the improvements from the new design. To experimentally verify the improvement, more tests could be run with landfill leachate of known viscosity and density in both the original design and the new design to compare degradation rates.

Another method to improve flow could be to decrease the diameter of the electrode housing, retaining the straight tube shape. Decreasing the diameter of the housing would give less space outside of the reactor for the PFAS to flow. The flow would be contained closer to the

anode, increasing the likelihood that PFAS would make contact with it. However, the HRT would decrease with a smaller volume if the flow rate is kept constant. The system may need to be run longer to achieve levels of destruction similar to the original diameter housing.

A series of reactors could be beneficial for upscaling the system and treating larger volumes of water. Rather than utilizing a batch system in which the reactor housing design would be modified, the water could be treated repeatedly through multiple reactors while maintaining consistent flow within each reactor. The PFAS would have the same mass transfer rate onto each electrode, degrading to a further degree in each reactor through which it flows. This in-series system would take up more space and have higher associated manufacturing and electrical costs because of the multiple reactors. This design choice is an option for a client when considering efficiency versus the cost of the system.

Aeration could be a possibility to disrupt flow if the reactor housing shape is not able to be changed or if any physical changes to the system are not feasible. However, it's important to note that controlling the flow rate with the ultrasonic flow meter currently built into the bench-scale system might prove inaccurate. Aeration bubbles skew the flow readings from the meter without any manual changes to the flow rate. Additionally, PFAS collects at the air-water interface. Leachates usually have a high amount of surfactants which, when aerated, produce a foam that stays on the surface of the water in the tank. This foam can also be saturated with PFAS. The benefit that aeration brings to increasing turbulence may be negated by the impact of concentrating PFAS in solution to the air-water interface of the bubbles.

Capstone Design Statement

This Major Qualifying Project (MQP) consists of a capstone design component that incorporates knowledge and skills from coursework with engineering standards and constraints into a culminating engineering design.

This research addresses the design requirement by looking at ways to improve mass transfer in this EOx system via changes to flow. In this system, PFAS are oxidized and degraded when they come into direct contact with the anode portion of the electrode. It is theorized that improving the flow to enhance the likelihood of PFAS coming into contact with the anode would increase PFAS degradation. This design aims to address this hypothesis by optimizing the flow to encourage mixing throughout the system. To achieve this, multiple changes to the EOx system were suggested in section 5.3. When considering all of these changes, it was decided that changing the shape of the reactor housing was the most practical design to improve mixing and mass transfer of constituents by 1.81 times. This design also ensures that all of the parameters from the original tests can be kept constant in order to effectively compare the change in flow and PFAS degradation.

This design idea, which was modeled in CAD, consisted of adjusting the diameter of the reactor housing at its midpoint to create a concave shape of the reactor housing. The change in diameter would create a pressure drop and increase the velocity, encouraging mixing throughout the system. To quantify the increase in turbulence of the flow, the Reynold's number of the original system and the new design were calculated. The Reynold's number increased from ███████ to ██████ indicating the flow's turbulence also increased. Accordingly, the mass transfer coefficient, a measure of a compound's diffusion through a liquid, was also calculated to demonstrate an increase in diffusivity with this design. The improvement ratio of the mass transfer coefficient between the new design and the original design was 1.81 just by changing the shape of the reactor housing.

The feasibility of this design is supported by its synthesis and analysis. In synthesis, the design to change the reactor housing was decided drawing upon engineering principles and knowledge from previous coursework. The analysis of the design applied the engineering tools and principals in a quantitative way to predict the improved performance of the EOx system.

Professional Licensure Statement

Licensure is very important in an engineer's career. Professional Licensure, a legal requirement under certain conditions, ensures that an engineer has the skills and credentials to do any kind of engineering work. Professional Engineers (PE) are highly trained licensed engineers who provide quality work and uphold all values of their profession. PEs demonstrate competency in their field of study by maintaining and improving their skills throughout their career.

There are four steps to take for one to obtain a professional engineer's license. First, an individual must graduate from an engineering program accredited by the Accreditation Board for Engineering and Technology (ABET). An individual is eligible to take the Fundamentals of Engineering (FE) exam shortly before or after graduation from an ABET accredited program to get an Engineer-In-Training (EIT) certification. To gain professional engineering experience, the EIT must practice in the field under direct supervision of a PE for four years. After these four years, the EIT is then eligible to take the Principles and Practice of Engineering exam and become a PE themselves.

The FE and PE exams are administered by the National Council of Examiners for Engineering and Surveying (NCEES) and the EIT and PE certifications are awarded by Professional Credential Services (PCS).The Environmental FE exam covers topics in math, statistics, ethics, professional practice, materials, fluid mechanics, thermodynamics, environmental chemistry, water, wastewater, air quality control, etc. The Environmental PE exam covers highly specialized topics in water, air, solid and hazardous waste, environmental health and safety, site assessment and remediation, and other associated topics in engineering.

With a PE license, PE's can prepare, sign, and seal engineering documents for public and private clients. PE's uphold their work to the highest level of standard and take responsibility for the work they provide. Professors who teach engineering are required by law in many states to hold a PE license. PE's also have enhanced career opportunities due to their licensure and can streamline the process of getting other professional licenses. Finally, holding a PE license establishes client confidence, builds trust, and enhances the reputation of the PE and their firm.

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Appendix A: Reactor Draining Procedure

The reactor setup was drained in a specific sequence to avoid spilling the contaminated streams. First, the pump was turned off and the top of the reactor was unscrewed from the pipe to allow air into the reactor housing. The solution was allowed to drain out of the reactor until it reached equilibrium. The reactor was then removed from the stand and fume hood and raised above the tank, allowing any more solution to drain out of the reactor, tube, or pump, and back into the tank. When all the solution had drained, the valve to the tank was closed. The reactor was disconnected from the pump and held over a beaker to collect any remaining solution in the reactor housing as shown in Figure A1. The pump was tipped over a beaker to drain the solution from the pump and its connected tubes. All solution collected in beakers was placed back into the tank. The tank solution was emptied into hazardous waste storage containers. The hazardous waste was labeled appropriately and environmental health services were notified to remove the waste.

Figure A1. Draining reactor over beaker

Appendix B: SO-1 Reactor Assembly Procedure

Redacted for sponsor confidentiality

Appendix C: Electrode Cleaning Procedure

The reactor and setup were cleaned after each test. A 6% HCl solution was created with RG water and HCl, and was stored and reused during all testing. A PVC pipe large enough to fit the electrode completely was capped on one end, as shown in Figure C1. The pipe was secured in sand in the center of a five gallon bucket and the pipe was filled with the HCl solution.

Figure C1. PVC capped pipe for acid bath

The reactor was disassembled after each test to extract the electrode, using the SO-1 Reactor Assembly Procedure in Appendix B. The electrode was submerged in the HCl and was agitated occasionally to help remove scale and other contaminants. A tub was filled with RG water. After a specified time, the electrode was transferred from the HCl to the tub of RG water to be rinsed. The electrode was agitated in the tub for five minutes. The pH of the RG water in the tub was tested to determine how to safely dispose of the rinse water. The reactor was then reassembled following the SO-1 Reactor Assembly Procedure. The entire system was reassembled and RG water was pumped through the system with the reactor off, for approximately 30 minutes. The system was drained according to Appendix A and the rinse water was disposed of appropriately.

Appendix D: Multimeter Check Procedure

To ensure that the reactor was rebuilt properly, a multimeter was used to test for resistance between the anode and cathode of the electrode. First, the multimeter was dialed to 20k Ohms. Next, each of the leads were placed on the anode and cathode respectively. The multimeter was then checked to see if it read 1. If the multimeter read under 1, the anode and cathode were touching then the reactor was rebuilt. If the multimeter showed numbers under 1 before reaching 1, the anode and cathode were at risk of touching and the reactor was either rebuilt or the electrode was loosened and tightened from its housing again to resolve the issue. If the multimeter read 1 or showed numbers above 1 before reaching 1, the anode and cathode were not touching and the reactor did not need to be rebuilt.

Appendix E: Laboratory Data

Table E1. Laboratory data from synthetic wastewater and landfill leachate tests

Test Solution	Power	Time (hour)	pH	Temperature (C)	Conductivity (mS/cm)	Flow (gal/min)	Current (amp)	Ammonia Concentration (mg/L)
Synthetic Wastewater		0	7.3	█	█	3.0	█	90.09
		1	3.36	█	█	2.9	█	70.07
		2	2.15	█	█	3.0	█	50.05
	Low	3	3.41	█	█	3.0	█	30.03
		0	5.05	█	█	3.0	█	76.00
		1	2.94	█	█	3.0	█	0.00
	Low/ Med, pH 5	2	6.93	█	█	3.0	█	0.00
		3	7.47	█	█	3.0	█	0.00
		0	4.55	█	█	2.9	█	104.26
		1	6.63	█	█	3.0	█	0.42
		2	7.13	█	█	2.9	█	0.00
	Med	3	7.02	█	█	3.0	█	0.00
		0	5.90	█	█	2.9	█	100.25
		0.33	2.54	█	█	3.0	█	40.16
		0.66	6.54	█	█	3.0	█	3.12
		1	7.17	█	█	3.0	█	0.00
		1.33	7.29	█	█	3.0	█	0.00
		2	7.45	█	█	3.0	█	0.00
	High	3	7.47	█	█	2.9	█	0.00
Landfill Leachate		0	6.85	█	█	3.0	█	17.70
		1	7.12	█	█	3.0	█	17.70
		2	6.54	█	█	3.0	█	17.20
	Low	3	7.32	█	█	3.0	█	17.80
		0	6.48	█	█	3.0	█	17.10
		1	6.77	█	█	3.0	█	16.20
		2	6.86	█	█	3.0	█	15.10
	Med	3	7.03	█	█	3.0	█	14.20
	High	0	7.50	█	█	3.0	█	16.80

Test Solution	Power	Time (hour)	pH	Temperature (C)	Conductivity (mS/cm)	Flow (gal/min)	Current (amp)	Ammonia Concentration (mg/L)
	High	1	7.20	■	■	3.0	■	14.00
		2	7.03	■	■	3.0	■	9.93
		3	7.16	■	■	3.0	■	5.58

Table E2. PFAS concentrations at time 0 and 3 hours in each test

Test Parameters			Concentration of PFAS (ng/L)					
Test Solution	Power	Time (hrs)	PFHpA	PFHxS	PFOA	PFNA	PFOS	PFDA
Synthetic Wastewater	Low	0	3710	3320	984	849	602	263
	Low	3	3930	2660	505	235	179	79.2
	Low/ Med, pH 5	0	6330	5650	150	1310	945	523
	Low/ Med, pH 5	3	4730	3440	681	281	168	99.9
	Med	0	3880	3490	887	912	705	356
	Med	3	3190	2440	435	224	130	72.4
	High	0	3800	3710	986	1020	717	384
	High	3	3280	2140	369	149	83.8	60.6
Landfill Leachate	Low	0	33.3	78.3	70.2	40.7	128	31.8
	Low	3	44	166	65	23.7	51	13.9
	Med	0	20.4	36.8	72.7	21.2	111	13.9
	Med	3	23.4	64.3	47	8.78	31.5	5.16
	High	0	17.6	23.7	65.6	16.2	106	8.36
	High	3	17.3	40.1	33.5	4.78	19.6	2.69

Appendix F: Determination of Reaction Order for Ammonia and PFAS

To determine the decay rates of ammonia and PFAS in Aclarity's EOx system, the reaction order kinetics of ammonia and PFAS were first determined through graphical analysis. This graphical analysis method plots concentration of ammonia versus time in different ways according to a reaction order to see which graph yields a more linear slope with a higher R^2 value. The slope of these graphs also represent the decay rate constant, k. Figures F1 and F2 below show concentration of ammonia plotted versus time for the synthetic wastewater and landfill leachate. These plots depict a zero order reaction rate for ammonia.
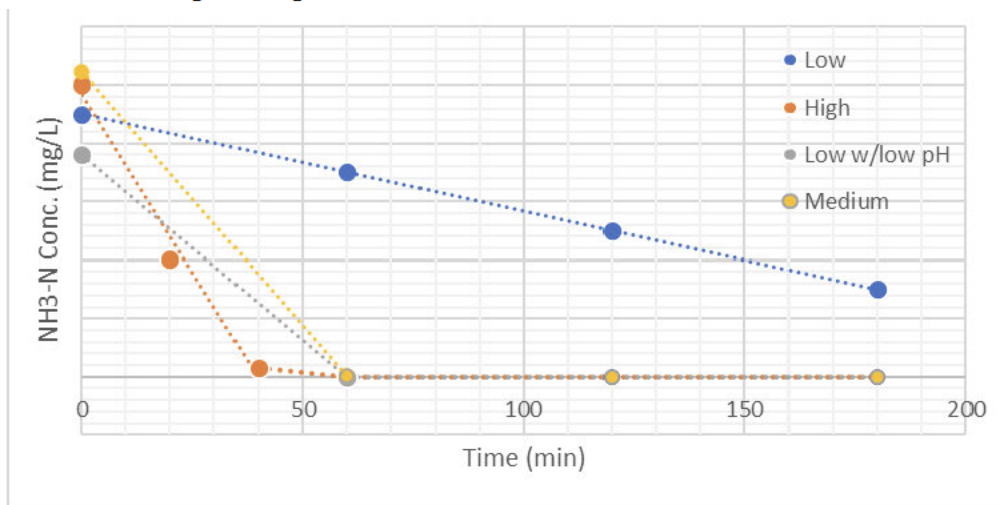
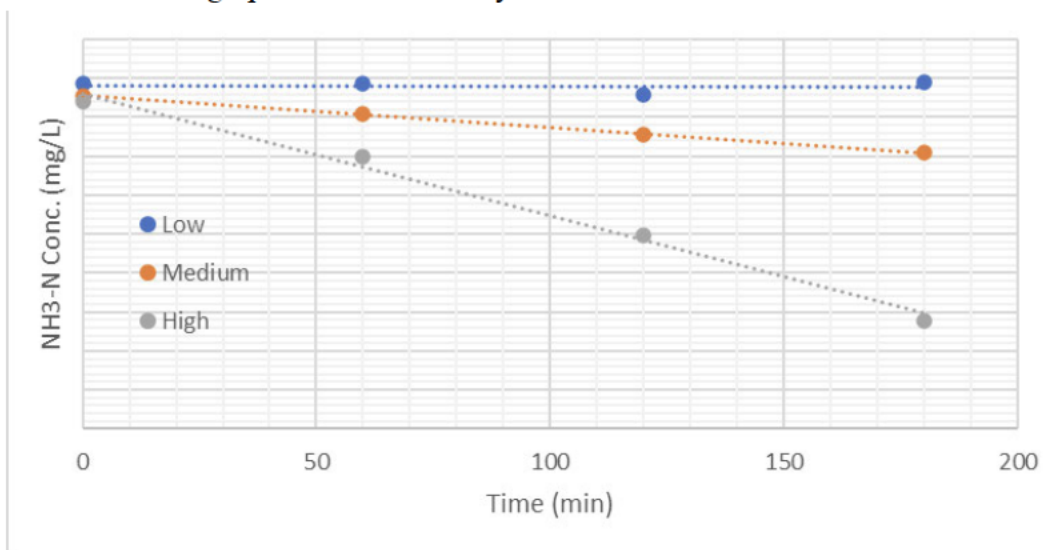**Figure F1.** Zero order graph of ammonia in synthetic wastewater

Figure F2. Zero order graph of ammonia in landfill leachate

By only plotting concentration and time of ammonia throughout both streams, representing a zero order plot, the plots already yield constant linear decays. However, more data points are required to effectively consider this reaction as a first order reaction. Figures F3 and

F4 below show concentration of ammonia plotted versus time in terms of a first order reaction for the synthetic wastewater and landfill leachate.
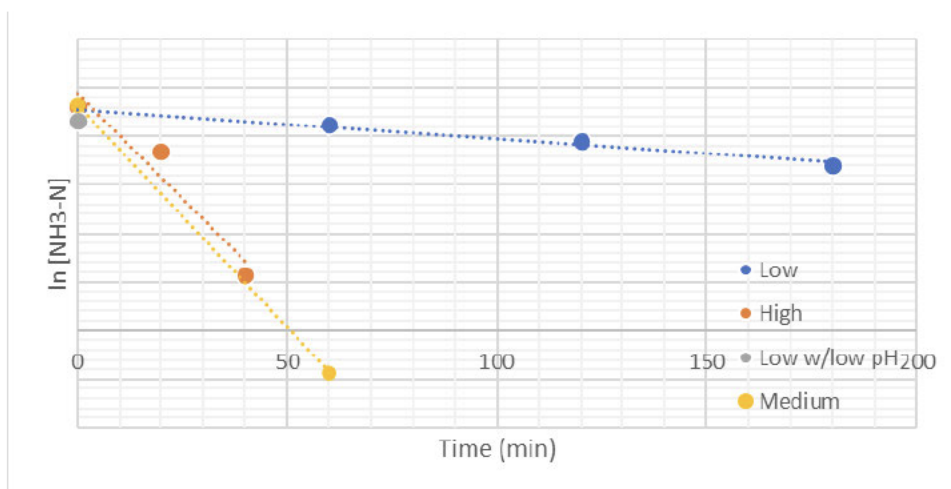

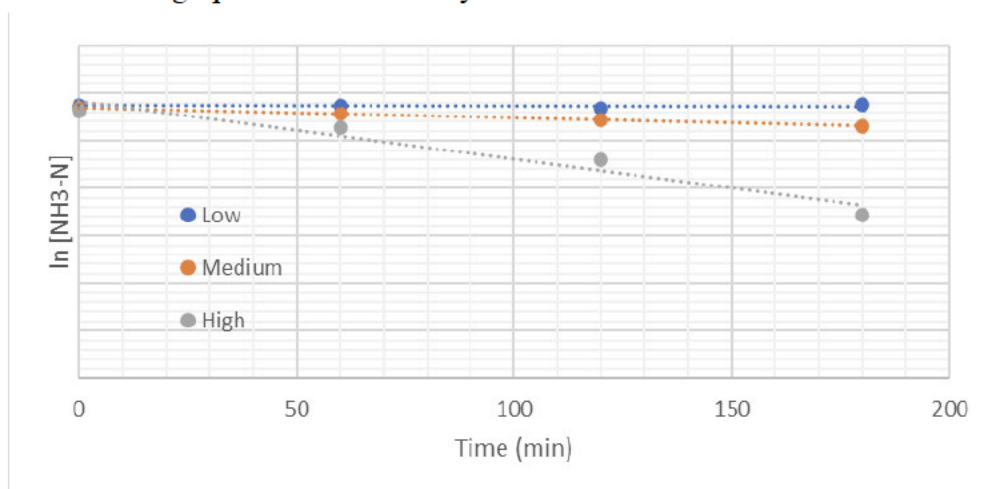**Figure F3.** First order graph of ammonia in synthetic wastewater

Figure F4. First order graph of ammonia in landfill leachate

Graphs F3 and F4 also show linear decays for ammonia in synthetic wastewater and landfill leachate. The zero order reaction graphs are more linear than the first order reaction graphs. However, a first order reaction requires the concentration of ammonia be plotted in a natural log order. Due to this, the data points are limited to effectively consider first order as the reaction rate for ammonia.

Graphs F5 and F6 below show the concentration of ammonia plotted versus time in terms of a second order reaction for the synthetic wastewater and landfill leachate. These plots are not very linear and not suitable for the data record in this experiment. Therefore, ammonia degradation for both synthetic wastewater and landfill leachate is not second order.
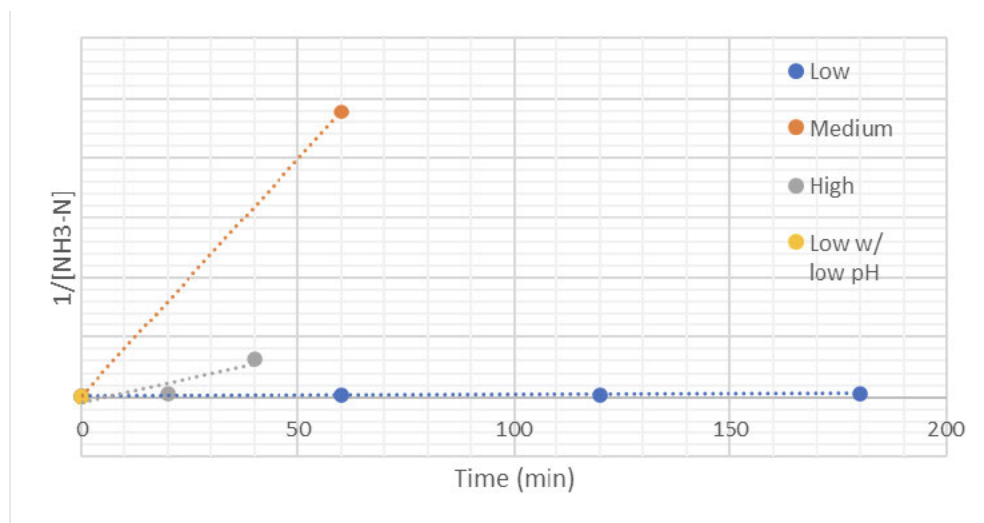
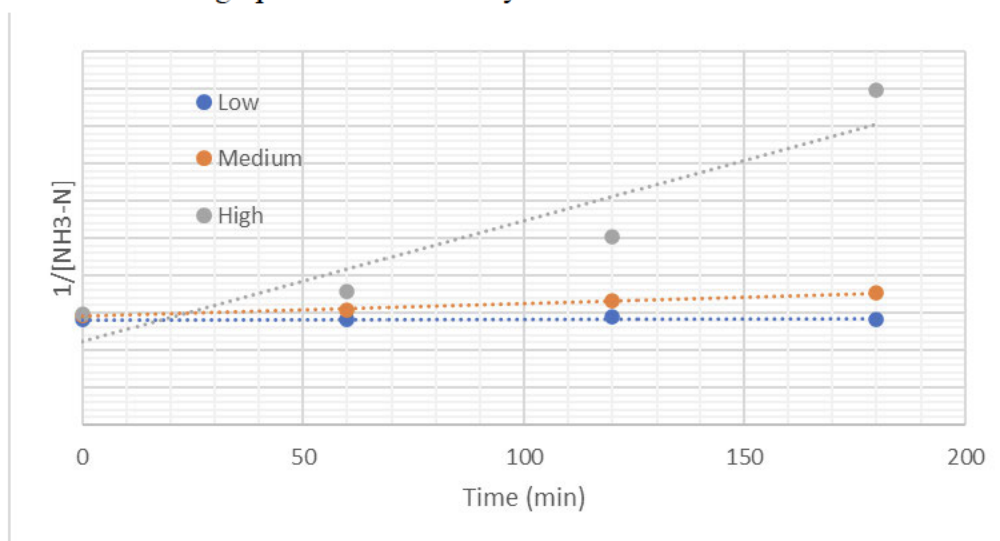**Figure F5.** Second order graph of ammonia in synthetic wastewater

Figure F6. Second order graph of ammonia in landfill leachate

Since data points were limited, an educated guess can be made about the reaction order of ammonia in both streams in this research. This data suggests that the reaction order of ammonia is between zero order or first order. Literature can be used to confirm the reaction order of ammonia in synthetic wastewater and landfill leachate. Most studies in electrochemical oxidation indicate that reactions in landfill leachate are first order with respect to ammonia (Wilk et al., 2021). Therefore, it can be surmised that the ammonia reaction order in this study is most likely first order.

As for determining PFAS reaction order, a graphical analysis is not suitable since there are only two data points for the degradation of PFAS: at the beginning and at the end. Therefore, we can turn to literature to help deduce the reaction order of PFAS in synthetic wastewater and landfill leachate. Research seems to indicate that when PFAS is in abundance, the degradation rate is constant and limited by the direct electron transfer at the surface of the anode (Yanagida et

al., 2022). Therefore, in streams like the synthetic wastewater which contain a high dose of MA6 PFAS, the reaction order is zero order. However, in this research there were increases in PFHpA at low power. The cause of these increases cannot be pinpointed, only hypothesized. Perhaps as the longer chain PFAS compounds were broken down, their components were reconstituted to form the shorter chain PFHpA. Therefore, the reaction is concentration dependent and a first order reaction in this specific recipe for synthetic wastewater. When PFAS concentrations are low, like in the sample of landfill leachate, the reaction in EOx becomes concentration dependent and the reaction order becomes first order (Yanagida et al., 2022). This hypothesis is reflected in the data, therefore PFAS degradation in this sample of landfill leachate is a first order reaction.

Appendix G: Energy Analysis Calculations

The specifics for the medium power test on synthetic wastewater were used to calculate energy usage of other treatment methods under comparable conditions. In the medium power test, 39.652 µg of total MA6 PFAS was removed.

EOx, Medium Power Synthetic Wastewater Test 2A:

The power remained at medium for the duration of the test. ██████████████████████ ██ was used to calculate the energy consumption over the test. The energy consumption only took into account the energy consumed by the reactor.

Energy Consumption by the reactor over the three hour test:

$$\blacksquare\blacksquare\blacksquare\blacksquare \frac{\blacksquare}{\blacksquare} = 0.488895\ kWh$$

Activated carbon:

Activated carbon has an adsorption capacity of 7.5 µg of PFAS per gram of carbon (Burkhardt et al., 2022). It was assumed that this value applied to all MA6 PFAS, despite each having unique adsorption rates. It was also assumed that the carbon was completely saturated or exhausted. Only the energy required to regenerate the carbon was considered, ignoring pumping costs and other electrical costs. The fuel energy required to regenerate 1 lb of carbon is 4250 BTU (Cohen et al., 1973).

Energy requirement for regeneration of carbon in kWh/g:

$$\frac{4250\ BTU}{1\ lb\ carbon} * \frac{1\ kWh}{3412.14\ BTU} * \frac{1\ lb\ carbon}{453.592\ g\ carbon} = 0.002745976\ \frac{kWh}{g\ carbon}$$

Grams of carbon required to remove 39.652 µg of total MA6 PFAS:

$$\frac{1\ g\ carbon}{7.5\ µg} * 39.652\ µg\ PFAS\ Removed = 5.286879\ g\ carbon$$

Energy to regenerate required carbon:

$$0.002745976\ \frac{kWh}{g\ carbon} * 5.286879\ g\ carbon = 0.0145176\ kWh$$

Evaporation:

The specific latent heat capacity for water is 2260 J/g. It was assumed that the solution had the same properties as water, evaporating with the same amount of energy. The volume of water to be evaporated is 12.1L, the same volume that was treated in the EOx tests.

Conversion of specific latent heat capacity in J/g to kWh/L:

$$2260\ J/g * \frac{1\ kWh}{3.6*10^6\ J} * \frac{1000g}{1L} = 0.627777\ kWh/L$$

Energy to evaporate the volume of water:

$$12.1L * \frac{0.627777kWh}{1L} = 7.5961017kWh$$

Reverse Osmosis:

The Dupont BW30 Pro-400 membrane is used in water treatment. Therefore, we chose this membrane to calculate the energy usage for the removal of PFAS from water. From the manufacturer, the maximum operating pressure is 41 bar, or 4100 kPa (Dupont, 2022). An arbitrary pressure was chosen at 3000 kPa. The maximum feed rate for this specific membrane is 17 m³/hr or 0.0047 m³/s (Dupont, 2022). The flow rate was kept constant from the EOx tests, therefore a flow rate of 3 gal/min or 0.000189 m³/s was used in the calculation. Only the pumping power was used in the energy calculation, which is the highest power requirement in RO. Efficiency of pump power to the water was assumed to be 85%.

Power for RO in watts:

Power = Flow Rate * Average Pressure

$$P = (0.000189 \ m^3/s) * (3 * 10^6 \ Pa) = 567.99 \ W$$

85% Efficiency:

$$567.99 \div 0.85 = 668.22 \ W$$

Power for RO in kWh:

$$668.22W \cdot \frac{1 \ kw}{1000 \ W} \cdot 3hrs = 2.00 \ kWh$$