THESIS

REACTIVE ELECTROCHEMICAL MEMBRANES FOR THE DEGRADATION OF PER- AND POLYFLUOROALKYL SUBSTANCES

Submitted by

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ABSTRACT

REACTIVE ELECTROCHEMICAL MEMBRANES FOR THE DEGRADATION OF PER- AND POLYFLUOROALKYL SUBSTANCES

Per- and polyfluoroalkyl substances (PFAS) are extremely stable and widely used in consumer goods, industrial processes, and aqueous film-forming foams (AFFFs), and have been shown to pose a serious and ongoing danger to global water security. Due to the general inefficiency of conventional water treatment techniques, sophisticated destructive technologies must be developed. Reactive electrochemical membranes (REMs), which combine filtration with in-situ electrochemical oxidation and reduction for targeted pollutant degradation, have become a potential solution.

Using titanium oxide nanotubes (TiOxNTs) as the anode and cathode material, this thesis explores the creation of an affordable, dual-function REM system. TiOxNTs provide an electrochemically adjustable, mechanically durable, and scalable platform in contrast to costly noble-metal electrodes. The anodic and cathodic performance of TiOxNTs REMs for the degradation of complicated AFFF-contaminated groundwater and model PFAS chemicals (PFOA, PFOS, and PFBA) is comprehensively assessed in this study. Near-complete elimination of UV-absorbing intermediates indicates that TiOxNTs anodes mineralize PFAS by hydroxyl radical-mediated oxidation, exhibiting great stability with low surface fouling, according to electrochemical studies. At the same time, TiOxNTs cathodes demonstrate remarkable reductive activity, which promotes defluorination via surface-activated pathways and direct electron transfer. This is demonstrated by the gradual increase in fluoride ion release and solution conductivity. This work establishes TiOxNTs as a low-cost, highly effective bifunctional material for REMs, offering a scalable and sustainable electrochemical approach for the full breakdown of persistent PFAS in contaminated water sources.

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To friends and relatives who in one way or the other supported me throughout this journey I say thank you. Last but not the least to my partner Oluwatise, I thank you for your unwavering and moral support throughout the dark times, I appreciate the gift of you and look forward to more lofty acievements together.

DEDICATION

This Thesis is dedicated to my late Father, Elder J.O. Adeleye who sacrificed a lot for me.

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INTRODUCTION

1.1 Global Significance of Per- and Polyfluoroalkyl substance (PFAS) Contamination

Per- and polyfluoroalkyl substances (PFAS) represent a diverse group of synthetic chemicals characterized by their unique carbon-fluorine bond, one of the strongest chemical bonds known. This property gives PFAS remarkable stability and resistance to degradation, which is a significant factor contributing to its persistence in environmental matrices and biological systems. Introduced in the 1940s for their oil and water repellent properties, these chemicals are commonly used in a variety of industrial applications and consumer products, including nonstick cookware, water-repellent fabrics, firefighting foam, food packaging, and cleaning products[1].The extensive use of PFAS has led to widespread contamination of natural resources, including groundwater, surface water, and soil. Studies have indicated that these substances can easily migrate through the environment and accumulate in living organisms, leading to bioaccumulation and biomagnification in ecosystems [2]. Per- and Polyfluoroalkyl Substances (PFAS) are widely distributed in the environment due to their chemical persistence and widespread commercial use. Industrial manufacturing and discharge, especially from facilities that have historically produced or used PFAS, is one of the most important sources. These include industries that use PFAS in surface treatment procedures and chemical plants that produce PTFE (Teflon) and other fluoropolymers [3]. Even after treatment, wastewater from these facilities frequently contains leftover PFAS compounds that end up in groundwater and waterways. Additionally, these plants' air emissions contribute to atmospheric deposition, which contaminates surface water and soil downwind. Due to this industrial legacy, "hotspots" of contamination have developed close to manufacturing facilities as well as along related transportation and discharge routes [2-3]. The use and disposal of Aqueous Film-Forming Foams (AFFF), which are extremely effective fire suppressants that have historically been used

by military bases, commercial airports, and industrial fire training facilities, is another significant environmental reservoir for PFAS. High levels of persistent PFAS compounds, mainly perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA), are present in AFFF. These compounds seep directly into the underlying soil and groundwater after use. Both public and private drinking water supplies are impacted by the vast and frequently long-moving contaminated groundwater plumes that originate from these AFFF release sites. The extensive, long-standing use of AFFF continues to be a major cause of serious environmental contamination in the US and around the world, despite the existence of more recent firefighting foam formulations [4-5].

In addition, common consumer goods and municipal waste disposal systems are diffuse, ongoing sources of PFAS contamination. Products like food packaging (grease-proof paper), stain-resistant carpets, and water-repellent apparel are made with PFAS to provide water and grease resistance [6]. The PFAS in these products end up in landfills and wastewater treatment facilities (WWTPs) when they are thrown away. Groundwater may become contaminated by PFAS released by landfills through leachate. WWTPs are mainly used as collection sites; they are not intended to eliminate PFAS. PFAS are separated into the biosolids sewage sludge and treated effluent released into waterways. PFAS are transferred to the soil by the widespread practice of applying contaminated biosolids to agricultural lands, where they can be absorbed by crops and seep into groundwater, completing the cycle of environmental exposure [6-7]. Aquatic ecosystems are particularly vulnerable to PFAS pollution, with studies indicating that these substances can seriously affect aquatic organisms. PFAS have been reported by many scientists to bioaccumulate in fish and other wildlife, which can lead to biomagnification throughout the food web. As these chemicals accumulate at higher trophic levels, their effects can ripple throughout the ecosystem, disrupting natural processes and jeopardizing the survival of species. The implications for biodiversity are profound, as declining populations of sensitive species can alter community structures and decrease ecosystem resilience [8].

Soil serves as a critical reservoir for PFAS, where they can bind to particles and migrate to groundwater sources. This contamination route presents serious risks for human health, partic-

ularly through the agricultural sector. The implications of PFAS to accumulate in agricultural products, emphasizes the potential for PFAS to enter the food chain which does not only threatens food safety but also raises serious public health concerns. Consequently, it is essential to understand the dynamics of PFAS in soil-plant interactions; environmental assessments must take into account the transfer of these substances through various ecological pathways [6-8]. The persistence of PFAS in the environment has raised serious concerns about their long-term effects on ecosystems and human health. Researchers have provided insights into the mechanisms by which PFAS influence ecological health, including impaired reproductive outcomes in wildlife and a compromised immune response. Strict regulations and monitoring of PFAS concentrations in drinking water, imposed by emerging global initiatives, reflect the growing recognition of these substances as a significant environmental threat. As various countries and international organizations begin to combat PFAS contamination, the urgency for action becomes clear, highlighting the need for sustainable solutions to mitigate the widespread effects of these pollutants [9].

Global initiatives to reduce exposure to PFAS highlight the collaborative effort to address the environmental health challenges posed by these contaminants. Efforts such as the U.S. Environmental Protection Agency PFAS Action Plan aim to set standards for drinking water, while the European Union is advancing legislation to restrict the use of PFAS in consumer products. These initiatives demonstrate a growing recognition of the interrelated nature of ecological health and human well-being, signaling the global commitment to sustainable practices that limit the proliferation of PFAS. As new evidence emerges regarding the ecological consequences of PFAS, there is need for robust policy measures integrating scientific findings into public health frameworks, thereby highlighting the urgent need for comprehensive management strategies against this persistent environmental contaminant [10]. The health impacts of per- and polyfluoroalkyl substances (PFAS) have raised considerable concern within the scientific community, particularly due to their pervasive nature and persistence in the environment and the human body. Recent investigations have clarified various potential health risks associated with PFAS exposure, highlighting links to cancer, immune dysfunction and developmental problems. A seminal study by Panieri et al. (2022)

examined the toxicological mechanisms through which PFAS exert their effects on human health. Their research has shown that PFAS can interfere with hormone regulation, immune response and cellular homeostasis, contributing to an increased risk of various health conditions. The study specifically found associations between PFAS concentrations in blood samples and high incidence of liver and kidney cancers. The authors used a comprehensive analysis using data from both animal studies and population-based epidemiological research, highlighting the need for continued investigations into the molecular pathways affected by PFAS exposure [11]. Also, Sebe et al. (2023) contributed to the understanding of health risks related to PFAS by conducting a large meta-analysis of epidemiological studies. Their review indicated a statistically significant correlation between PFAS exposure and various adverse health outcomes, particularly an increased incidence of thyroid disease, decreased response to vaccinations, and developmental delays in children. The study consolidated data from different geographical regions, thus describing a global perspective on the health impacts of these substances and underlining the urgency of preventive measures. Epidemiological evidence has also linked PFAS exposure to immune dysfunction, where studies have similarly shown an impaired immune response leading to increased susceptibility to infection. This is particularly alarming given the public health implications, especially in vulnerable populations such as children and pregnant women. For example, research has indicated that prenatal exposure to PFAS may be associated with reduced birth weight and developmental delays, suggesting long-term consequences on childhood health and development [12]. In addition to cancer and immune effects, emerging literature has increasingly focused on the potential effects of PFAS on metabolic health. A recent review highlighted that exposure to PFAS may contribute to metabolic syndrome, characterized by obesity, hypertension and dyslipidemia, thus intensifying the risk of cardiovascular disease [11-13]. The associations observed in numerous studies raise significant concerns about the long-term health trajectories of people exposed to PFAS, particularly given the increasing prevalence of associated chronic health problems globally. Overall, the research demonstrates a clear need to address the health risks posed by exposure to PFAS. As these substances continue

to bioaccumulate and persist in ecosystems and human populations, negative health consequences are likely to manifest themselves more uniformly, requiring urgent public health interventions.

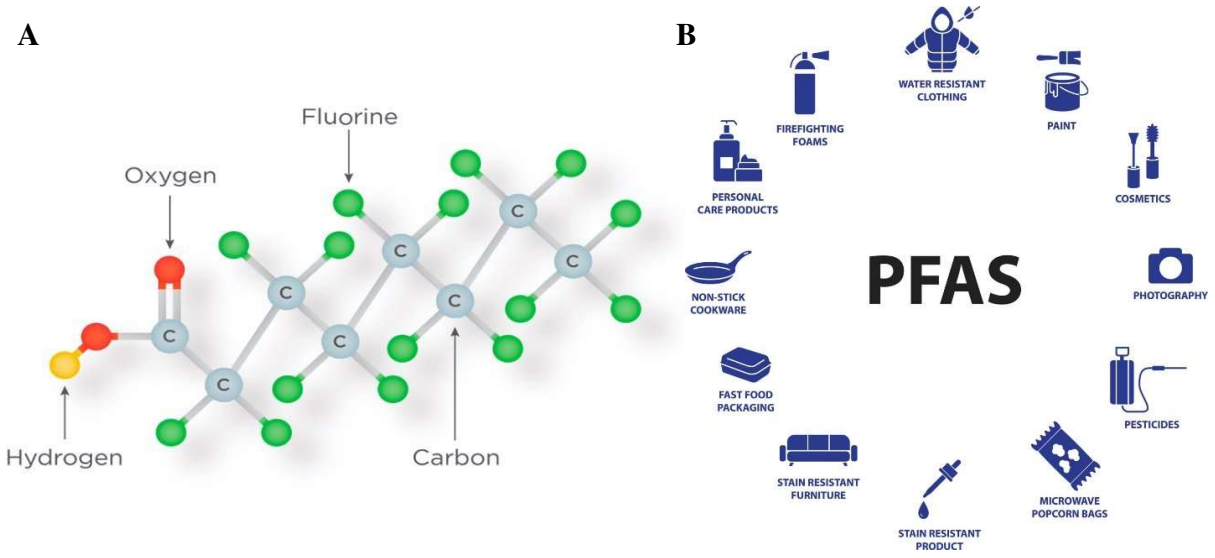

Figure 1.1: A) Molecular Structure of Per fluorooctanoic Acid (PFOA), one of a group of PFAS. Source: AWWA American Water Works Association B) Common household and industrial products that contain PFAS. Source: Syracuse University Environmental Finance Center Network.

The urgency of addressing the implications of exposure to PFAS is further compounded by their classification as "forever chemicals" due to their resistance to natural degradation processes. This nomenclature reflects the long half-lives of PFAS in the human body, where certain compounds can remain for years, potentially leading to chronic health risks associated with long-term exposure [14]. The inability of wastewater treatment plants to effectively remove PFAS from effluents increases the complexity of managing their environmental impact, resulting in a greater dissemination of these substances in aquatic ecosystems and, thus, their entry into the food chain. Global attention has increasingly turned to PFAS due to their broad environmental and health implications. International bodies such as the United Nations have recognized PFAS as a critical issue that requires urgent action. Initiatives such as the Stockholm Convention on Persistent Organic

Pollutants underscore global consensus on the need to monitor, regulate and phase out the use of hazardous substances, including certain PFAS [15]. Additionally, public awareness campaigns and advocacy for stricter regulatory measures have intensified as communities around the world battle PFAS contamination. These efforts underscore the critical importance of sustainable solutions that incorporate the reduction and elimination of PFAS from both production systems and product formulations [16-17]. The prevailing narrative emphasizes not only immediate regulatory action, but also the need for innovative alternatives that are environmentally benign and do not compromise public health. As the body of research continues to grow, it becomes increasingly vital that stakeholders, including policymakers, scientists and the public, collaborate to develop a comprehensive approach to managing the legacy of PFAS and safeguarding future generations.

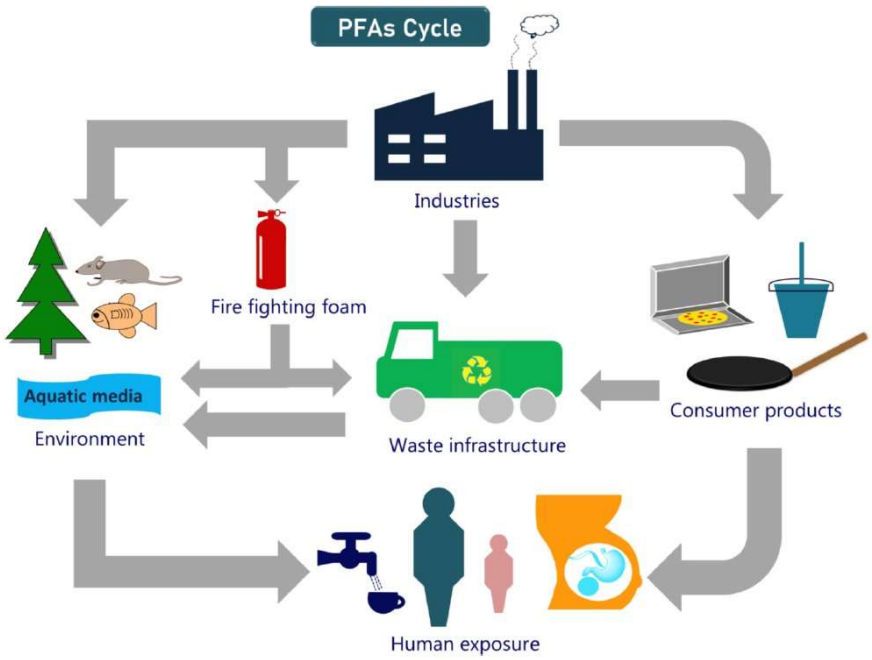

Figure 1.2: Schematic illustration of per- and polyfluoroalkyl substances (PFAS) cycle, from industrial sources through various pathways, eventually leading to human exposure [144].

1.2 Evaluating PFAS Treatment Technologies: A Comprehensive Analysis of Separation and Destructive Methods

Per- and polyfluoroalkyl substances (PFAS) have garnered significant attention due to their persistence in the environment and potential human health risks. The urgency for effective treatment technologies has catalyzed the investigation into various methodologies for PFAS removal from water sources. In this section I examined and compared PFAS treatment technologies, covering both separation and destructive methods, thus providing a broader understanding of their respective advantages and disadvantages.

Separation technologies are often employed as a first line of defense in PFAS remediation due to their ability to selectively separate contaminants from water. Among these methods, adsorption and membrane filtration are noteworthy [10]. Adsorption utilizes solid materials to capture and retain PFAS molecules from water via physical or chemical interactions, frequently employed activated carbon and ion exchange resins are favorable due to their cost-effectiveness, simplicity, and established operational frameworks. However, the disadvantages include the potential for saturation of the adsorbent material, leading to increased operational costs and the need for periodic regeneration or replacement [12]. Another separation technology is Foam fractionation which has emerged as an effective method for the removal of long chain (PFAS) from contaminated water, demonstrating notable advantages, including high efficiency and cost-effectiveness [16-20]. This technique exploits the properties of surfactants to separate pollutants from aqueous environments. Additionally, research indicates that various co-foaming agents can enhance PFAS removal rates, further optimizing this method. However, concerns regarding potential environmental impacts and challenges related to scalability and inability to remove short chain PFAS persist, which may hinder broader application in PFAS remediation efforts [20-22]. Membrane filtration, particularly high-pressure processes, presents another effective separation method. Also technologies such as reverse osmosis and nanofiltration can effectively reduce PFAS levels in contaminated water, achieving retention rates as high as 90 percent [10-12]. The advantage of membrane filtra-

tion lies in its ability to remove a broad spectrum of PFAS compounds efficiently. Nonetheless, this technology also poses challenges, such as membrane fouling, high energy consumption, and substantial investment costs for the infrastructure. These concerns necessitate careful assessment when selecting membrane technologies for PFAS treatment.

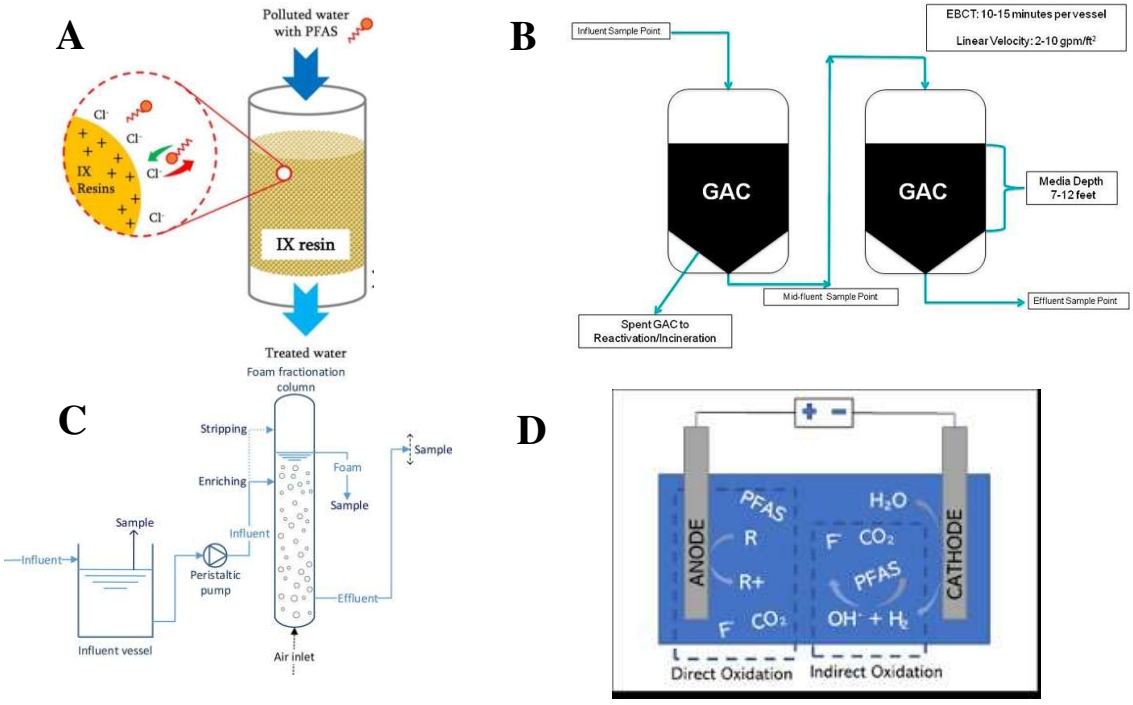

Figure 1.3: Common PFAS remediation technologies A) Ion Exchange Resin System for PFAS treatment [130], B) Granular Activated Carbon (GAC) water treatment system, Source: ITRC/Calgon, C) Schematic of a continuous foam fractnonation system [131], D) Electrochemical oxidation process for PFAS remediation, Source: EPA Innovative reserach for sustainable future.

While separation methods primarily focus on filtering or capturing PFAS, destructive technologies aim to completely mineralize these substances, converting them into less harmful byproducts. Advanced oxidation processes (AOP) represent a significant class of destructive technologies that leverage reactive species to breakdown PFAS molecules [13-15]. Destructive methods such as ozonation or photolysis can degrade even resistant PFAS compounds effectively [16]. However, the implementation of AOPs can be hindered by the requirement for extensive energy input and the potential formation of toxic byproducts during degradation.

Another destructive method, thermal decomposition or incineration, employs high temperatures to decompose PFAS. Although this method can effectively destroy PFAS at both high and low concentrations, concerns have been raised regarding the emission of harmful flue gases and the difficulty of handling PFAS residues post-incineration [12-16]. Moreover, the regulatory frameworks surrounding air emissions from incineration can complicate deployment efforts.

The choice between separation and destructive technologies is crucial and contingent upon specific water quality characteristics and regulatory requirements. Even though separation methods serve as a practical solution for immediate PFAS removal, they often require subsequent treatment to ensure complete remediation. Therefore, hybrid approaches that combine both separation and destructive technologies may emerge as the most effective treatment strategy. Also scientists and engineers should bear in mind scalability and adaptability when employing these technologies within various operational contexts this is because many technologies demonstrate efficacy in laboratory settings, while the translation of these methodologies to larger-scale applications remains a significant challenge. This disparity raises questions about how best to optimize processes like adsorption or AOP to operate efficiently in diverse environmental conditions.

1.3 Navigating the Complexities of PFAS Remediation: Addressing Conventional Limitations and the Urgent Need for Advanced Destruction Technologies

Per- and polyfluoroalkyl substances (PFAS) present significant challenges in remediation efforts due to their unique chemical properties and persistence in the environment. Conventional treatment methods, including adsorption, filtration, and ion exchange, have been widely used to combat PFAS contamination. However, critical examination reveals key limitations inherent in these approaches, highlighting the urgent need for more advanced remediation technologies.Adsorption is one of the most commonly used techniques for the treatment of PFAS, relying on the binding of PFAS molecules to adsorbent materials such as activated carbon or technical sorbents [18]. Despite its popularity, the adsorption process primarily serves to concentrate PFAS contaminants rather than breaking them down. Adsorbents often exhibit varying effectiveness depending on the specific PFAS compounds in question, primarily influenced by molecular size and chain length.For example, longer-chain PFAS have a greater affinity for adsorbent materials, but these compounds are also more resistant to desorption, which often requires periodic replacement or regeneration of adsorbent media [19]. Therefore, although adsorption can effectively and temporarily reduce PFAS concentrations in water, it is not a viable long-term solution because it does not address the fundamental problem of PFAS degradation [20]. Filtration, including membrane filtration and reverse osmosis, aims to physically separate PFAS from contaminated water through size exclusion or charge interaction mechanisms. However, like adsorption, filtration techniques do not chemically dismantle PFAS structures. Research has shown that these methods can be effective in reducing the concentration of certain types of PFAS; however, they often require high operational pressures and produce a concentrated waste stream that may still contain harmful PFAS, requiring additional disposal or treatment steps [21]. Additionally, accumulation of PFAS on membrane surfaces can lead to fouling, significantly increasing operational costs and maintenance needs [22]. Ion exchange is another method that can facilitate the removal of PFAS from

aqueous systems by exchanging PFAS anions with less harmful ions, typically on resin-based media [23]. Although ion exchange has been shown to be effective in capturing certain types of PFAS, its limitations are increasingly recognized. The selectivity of ion exchange resins can vary significantly, leading to incomplete removal of PFAS from contaminated sources, particularly for shorter chain PFAS that do not bind effectively to the resin [24]. This limitation is compounded by the need to regularly replace or regenerate the resin to maintain effectiveness, which can create additional logistical and economic burdens.

The challenges associated with these conventional treatment methods raise critical concerns about their effectiveness in the overall fight against PFAS contamination. The reliance on physical separation techniques perpetuates the reality that PFAS compounds continue to persist in the environment, requiring ongoing monitoring and management strategies rather than providing a definitive solution [18]. Additionally, the physical accumulation of PFAS in secondary waste streams only exacerbates the risks associated with disposal or further management, highlighting the inherent limitations of current treatment paradigms. This scenario highlights the urgent need for innovative, advanced and scalable destruction technologies that can effectively break down PFAS compounds. Such technologies could offer transformative potential for long-term PFAS remediation, bridging the gap between current treatment limitations and the need for sustainable environmental solutions., The carbon-fluorine (C-F) bond is a critical factor in understanding the challenges associated with remediation of per- and polyfluoroalkyl substances (PFAS). The strength of these bonds, which are among the strongest in organic chemistry, contributes significantly to the chemical resilience and environmental persistence of PFAS compounds [25]. The stability imparted by the C-F bond makes PFAS resistant to hydrolytic degradation, photolysis, and a variety of biological and thermal treatments typically used in environmental remediation strategies.The energy demands associated with C-F bond breakdown represent another significant challenge. Traditional heat treatments, such as incineration, require high temperatures to facilitate the cleavage of these bonds, which can result in substantial energy costs and raise concerns about the formation of harmful byproducts. The energy-intensive nature of these processes often makes them econom-

ically unviable for widespread application in PFAS remediation [26]. The challenging nature of the chemical inertness of PFAS arises primarily from the properties of the C-F bond itself, which requires considerable energy to break. Traditional remediation methods, such as bioremediation and photolysis, rely on the degradation or transformation of contaminants into less harmful substances, however these approaches lack effectiveness against PFAS due to the robustness of the C-F bond. As noted in the literature, typical environmental conditions fail to provide the energy required for effective breakdown, highlighting a critical gap in conventional treatment methodologies [27]. The inertness of PFAS is further exacerbated by their hydrophobic and lipophobic characteristics, which contribute to their limited reactivity within environmental media [28]. This low reactivity complicates the processes of adsorption, biological degradation and chemical oxidation, making traditional methods such as activated carbon adsorption and reverse osmosis less effective. As a result, PFAS contaminants may evade conventional treatment systems, leading to widespread contamination and necessitating the exploration of alternative remediation strategies [29].

The need for innovative and scalable destruction technologies is critical in PFAS cleanup. Current research efforts focus on developing new approaches such as plasma-based treatments, supercritical water oxidation, and photocatalysis, which show promise in overcoming the limitations imposed by the inertness of PFAS [30]. However, while these advanced technologies have shown potential in laboratory settings, significant challenges remain regarding their scalability to treat groundwater and contaminated soils on a larger scale. Emerging technologies, such as advanced oxidation processes (AOPs) and electrochemical processing, have demonstrated potential benefits in improving the robustness of PFAS due to their ability to generate highly reactive radicals that can disrupt the C-F bond. However, these methods still face practical limitations, particularly in terms of scalability, operational complexity and energy efficiency. The research indicates a critical need for innovative solutions that are not only capable of effectively breaking down PFAS in a sustainable manner, but also scalable for practical use in a variety of settings, from point source remediation to widespread groundwater treatment. The economic implications of energy-intensive

remediation methods also deserve attention, particularly as regulatory pressures increase demand for comprehensive PFAS cleanup. The high operational costs associated with current treatment technologies limit their widespread adoption and scalability, especially in regions where funding is limited. Economically viable and energy-efficient alternatives are urgently needed to make PFAS remediation accessible and effective, particularly in contaminated communities or industrial sites.

Electrochemical methods use the application of electric current to facilitate the oxidation of PFAS compounds. This technique exploits the high energy input to destroy stable C-F bonds, which conventional treatments struggle to target. Various configurations, such as galvanostatic and potentiostatic systems, have shown promising degradation rates and efficiencies. For example, studies have indicated that using reactive electrochemical membranes and advanced electrodes coated with catalytic materials can improve electron transfer processes, subsequently improving degradation rates of PFAS [31]. Furthermore, the flexibility of electrochemical systems allows for scalability, making them suitable for both laboratory and field applications. However, challenges remain, including the generation of harmful intermediates during the degradation process and the need for careful management of operational parameters to optimize performance.

Chapter 2

ADVANCEMENT IN ELECTROCHEMICAL REACTOR DESIGNS FOR PFAS DEGRADATION

Given the persistent nature of PFAS, effective degradation methods are critical for mitigating their environmental impact. Traditional remediation technologies, such as activated carbon adsorption and soil excavation, often fall short in achieving complete mineralization of PFAS compounds. Consequently, innovative and efficient methods for PFAS degradation are under active exploration, with electrochemical approaches emerging as a promising solution. Electrochemical degradation processes leverage the application of electric current to promote chemical reactions that can break down toxic pollutants, thereby aiding in the detoxification and removal of PFAS from contaminated matrices.

2.1 A Comparative Analysis of H-Cells and Flow Cells in Laboratory and Industrial Applications

Electrochemical methods for PFAS degradation can be tailored through various reactor designs, each offering unique operational benefits and challenges. Among these, H-cells and flow cells have gained prominence in both laboratory and industrial applications. H-cells, characterized by their simple two-compartment arrangement separated by an ion-selective membrane, facilitate efficient ion transfer and maintain specific chemical environments conducive to degradation. Their straightforward design allows for the exploration of various electrode materials and configurations, enabling researchers to optimize conditions for PFAS degradation at a small scale.

Conversely, flow cells have received considerable attention for their potential scalability and continuous operation. These systems significantly enhance mass transport and allow for real-time adjustments to operating conditions, such as flow rate and concentration, which can be critical

during large-scale remediation efforts. The inherent design of flow cells can facilitate the integration of advanced materials, such as nanostructured electrodes, which can significantly enhance the kinetics of electrochemical reactions and improve overall degradation efficiency.

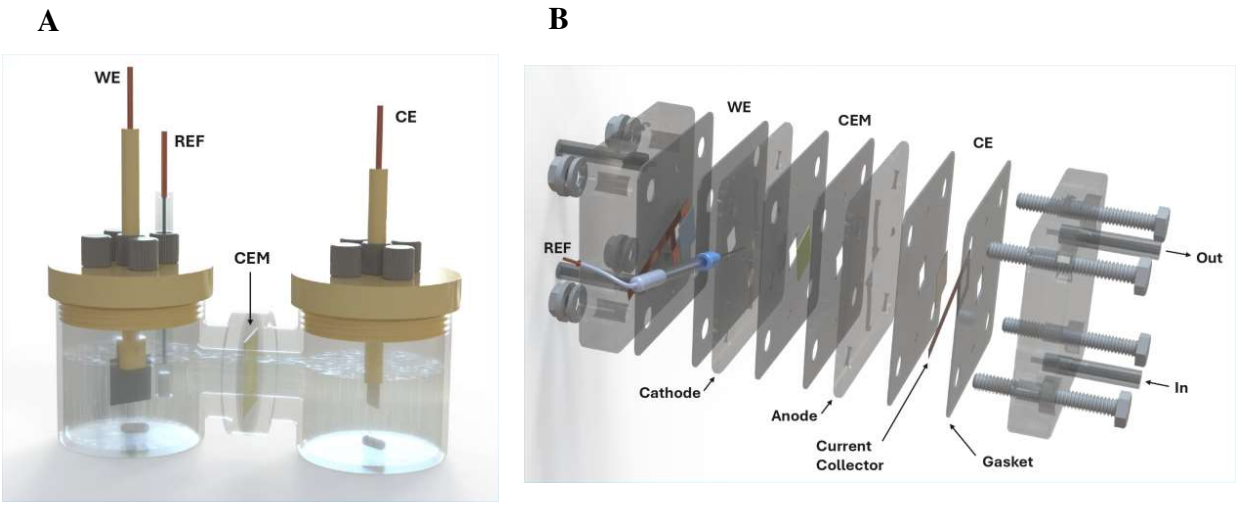

Figure 2.1: Electrochemical Cells. A) H-Cell Separated with a cation exchange membrane (CEM) and showing all the electrodes WE: Working electrode, CE: Counter electrode and REF: Reference electrode B) Membrane Electrolyzer Assembly Flow Cell showing all its components.

2.2 H-Cells

The significance of reactor design cannot be overstated, as it determines the mass transfer conditions and the availability of reactive species at the electrode surface. In laboratory setups, H-Cells and flow cells are among the predominant designs utilized for PFAS degradation. H-Cells, which consist of two electrolyte compartments separated by a diaphragm, enable controlled analysis of electrochemical processes in a static environment [32]. This configuration is advantageous for fundamental studies of degradation kinetics and interaction mechanisms involving PFAS, allowing researchers to exploit potentiostatic and galvanostatic conditions effectively [33]. The simplicity of H-Cell designs facilitates their operation and manipulation, making them suitable for small-scale experiments. However, their limited surface area and potential issues with mass transfer can impede the overall reaction rates, especially when dealing with higher concentrations of PFAS [33-34]. H-cell reactors are one of the traditional configurations utilized in electrochemical studies, primarily due to their straightforward design and ease of operation. The H-cell comprises two chambers separated by a salt bridge, facilitating the electrochemical reactions while allowing for ionic conduction. The design often allows for the utilization of various anodes and cathodes, enabling experiments to explore the efficacy of different materials in PFAS degradation. Notably, H-cells have been extensively employed in laboratory settings for their ability to provide a controlled environment for studying the kinetics of electrochemical reactions. Furthermore, their compact size lends to efficient use of reagents and is conducive to scaling down operations for preliminary testing phases [35-37].

Operationally, H-Cells function by applying a direct current across the electrodes, prompting oxidation and reduction reactions to occur at the anode and cathode, respectively. These reactions facilitate the degradation of PFAS by breaking the persistent carbon-fluorine bonds characteristic of these compounds. The configuration of the H-Cell allows for controlled experimental conditions, including temperature, pH, and concentration gradients, which can be systematically manipulated to study their effects on PFAS degradation rates. This flexibility makes H-Cells particularly advantageous for laboratory-scale investigations. In laboratory settings, H-Cells have been effectively

deployed to evaluate various electrochemical strategies for PFAS degradation. For instance, studies have shown that the use of different electrode materials, such as boron-doped diamond and titanium, can significantly influence the degradation efficiency. Research indicates that optimizing electrode material and surface area can enhance electron transfer rates, thereby increasing degradation performance [38]. Furthermore, researchers have employed H-Cells to examine the impact of varying operating parameters, such as current density and electrolyte composition, on the efficiency of PFAS degradation. One of the most significant advantages of H-Cells is their operational simplicity. The design allows for easy scaling and operational adaptability, making them suitable for both laboratory and industrial applications. Researchers have indicated that they can be easily integrated into existing wastewater treatment systems, facilitating the transition from conventional treatment methods to electrochemical alternatives [38,39]. The minimal moving parts within the H-Cell design also contribute to lower maintenance requirements, which can reduce operational costs, further enhancing their attractiveness for widespread implementation. Additionally, the manageable size and arrangement of H-Cells lend themselves to batch operations, enabling flexibility in addressing varying contaminant concentrations. This adaptability is crucial given the heterogeneous nature of PFAS contamination across different environments. Studies have indicated that the reaction kinetics within H-Cells can be finely tuned by altering operational parameters such as voltage, electrolyte concentration, and temperature, which allows for improved degradation rates tailored to specific PFAS compounds.

However, the use of H-cells is not without disadvantages. The confined volume of the reactor often necessitates a longer reaction time to achieve complete degradation, which can limit throughput. Additionally, the static nature of the solution in H-cells can lead to concentration gradients, which may influence degradation rates and overall efficiency. Also, operational efficiency can decrease over time due to potential fouling or electrode degradation, which necessitates a careful consideration of material selection and reactor design to mitigate such challenges [40]. While H-cells can provide valuable insights and data on electrochemical processes, their scalability to industrial applications remains a challenge due to these limitations. Nevertheless, advancements in

materials science, particularly the introduction of novel electrode materials with enhanced catalytic properties, have shown promise in maintaining the long-term efficacy of H-Cells [40-42].

2.3 Flow Cells

Flow cells, present a more complex design that allows for continuous operation and better mass transport characteristics. By employing a flow of the electrolyte solution across the electrodes, these systems maintain a high concentration gradient and enhance the delivery of reactants to the active sites on the electrodes [43]. This configuration is advantageous for both laboratory studies and industrial applications, as they can be scaled up to treat larger volumes of contaminated water. The dynamic nature of flow cells often results in higher current densities and more efficient degradation of PFAS, as the electrolytic processes are optimized for sustained runs. However, the complexity of the flow system can lead to increased operational costs and the need for advanced engineering solutions to maintain consistent flow rates and prevent fouling of the electrodes [44]. The adaptability of flow cells is one of their primary advantages; they can accommodate modifications in flow rate, electrode surface area, and design configurations to optimize performance for specific PFAS species. Also, the continuous nature of the process can lead to higher throughput and reduced reactor volumes when compared to static systems like H-cells. Operational principles of flow cells for PFAS degradation rely on electrochemical oxidation processes. When a potential is applied across the electrodes, oxidants such as hydroxyl radicals and other reactive species are generated, which can lead to the breakdown of the stable carbon-fluorine bonds characteristic of PFAS. Uniquely, the continuous flow setup allows the introduction of fresh contaminants while simultaneously removing degraded products, reducing mass transport limitations often seen in static systems.

In laboratory applications, flow cells have been utilized in experimental setups to systematically investigate the efficacy of various anode materials and operating conditions on PFAS degradation. For instance, studies employing flow cells have demonstrated that the choice of anode material, such as boron-doped diamond or modified carbon-based materials, can influence the oxidative

capacity and, hence, the degradation efficiency of short- and long-chain PFAS compounds. Such experiments enable researchers to fine-tune operational parameters, including applied potential, electrolytic composition, and flow rate, to achieve optimal degradation outcomes. Moreover, recent advancements in microfluidic flow cell designs have broadened their applicability in research [45-47]. These miniaturized systems not only facilitate controlled experimental conditions for PFAS degradation studies but also allow for the integration of sensing technologies that can monitor real-time degradation progress. Such innovations lead to more comprehensive understanding and quantification of reaction kinetics under varying conditions, a critical factor for both academic research and industrial scale-up considerations.

Despite these advantages, flow cells also possess inherent disadvantages. The complexity of their design can introduce challenges in terms of maintenance and the potential for fouling, which can obstruct flow pathways and reduce efficiency over time. As a result, operational stability becomes a critical consideration when evaluating flow cells for industrial applications, particularly regarding their longevity and the need for regular maintenance [47,48]. Additionally, the initial capital costs associated with flow cell systems may be higher than those for traditional H-cells, potentially deterring adoption in certain contexts.

Ultimately, the choice between H-cells and flow cells must take into account specific project requirements, including the nature of the PFAS to be treated, treatment volumes, economic factors, and operational constraints. The inherent trade-offs between efficiency and operational feasibility necessitate a tailored approach to reactor design selection in electrochemical PFAS degradation efforts, underscoring the importance of ongoing research and development in optimizing these technologies for both laboratory and industrial scale applications.

Chapter 3

INNOVATIONS IN CATALYSTS DISCOVERY, DESIGN, AND SYNTHESIS FOR PFAS REMEDIATION

The environmental concerns surrounding PFAS are multifaceted. Epidemiological studies have linked certain PFAS to a range of health issues, including reproductive and developmental toxicity, liver damage, thyroid disease, and certain cancers. Moreover, the bioaccumulation potential of PFAS compounds poses significant risks to wildlife, disrupting ecosystems and threatening biodiversity. As these substances continue to diffuse into the environment, regulatory bodies across the globe are increasingly focusing on the need for effective remediation strategies to mitigate their environmental footprint and protect public health.

Recognizing the urgent need for effective degradation methods, researchers have explored various technological avenues to address PFAS contamination. Among these, catalytic degradation through Electrochemical advanced oxidation (EAOP) and reduction processes (EARP) offer attractive routes for treating a diverse range of complex water matrices with large variations in the concentration of cations, anions, organics, salts, and recalcitrant pollutants like PFAS. EAOP and EARP have emerged as a promising approach, utilizing catalysts to accelerate the breakdown of PFAS into less hazardous or inert compounds. Catalysts, which can significantly lower the activation energy needed for chemical reactions, play a critical role in enhancing the rate and efficiency of degradation processes. Their ability to facilitate reactions under milder conditions can lead to lower energy requirements and reduced operational costs, making catalytic processes highly attractive for remediation applications. EAOP and EARP provide an effective pathway to selectively target the destruction of micropollutants or emerging trace organic compounds in wastewater through reductive dehalogenation ($e.g.$, 4-chlorophenol) or oxidative mineralization ($e.g.$, PFAS,

1,4-dioxane) [49-51]. EAOP and EARP also offer a pathway to pursue non-targeted destruction of pollutants ($e.g.$, total organic carbon (TOC)). However, the relatively high cost of electrodes, especially for anodic oxidation ($e.g.$, boron-doped diamond), the generation of toxic byproducts in the effluent ($e.g.$, halogenated organics), and the electrode instability and lack of selectivity in complex wastewater matrices have impeded the widespread implementation of electrochemical treatment for large-scale applications [47, 53].

In addition, while significant progress has been made to develop new electrode materials and electrochemical cells to improve activity and selectivity for electrocatalytic treatment, the importance of improving the energy efficiency of electrochemical processes to make this technique economically feasible has been overlooked [47]. Electrochemical anodic oxidation can proceed via two distinct mechanisms. The first mechanism involves the adsorption of reactants ($e.g.$, pollutants) on the electrode surface and degradation or transformation via direct electron transfer [54, 55]. The second mechanism generates oxidizing species or radicals ($e.g.$, $^{\cdot}\mathrm{OH}$, $\mathrm{SO_4^{-\cdot}}$) that degrade pollutants in the bulk solution [56]. One critical approach to improving the selectivity and the energy efficiency ($i.e.$, the ratio of the electricity consumed to degrade pollutants to the total electricity passed through the circuit) of the overall system is to mitigate the undesired reactions ($i.e.$, parasitic/competing reactions) in electrocatalytic processes by identifying the 'sweet spots' for operating electrochemical reactions [57]. Parasitic reactions are broadly defined as any reactions that compete for electron transfer during redox reactions, deteriorating the performance of the desired reaction pathway. For example, in the electrolyte containing chloride ions ($\mathrm{Cl^-}$), undesired anodic reactions result in the generation of toxic disinfection byproducts that compete with desired anodic reactions ($e.g.$, organics mineralization) for giving up electrons at the electrode surface [58-60]. It is important to understand competing reactions in EAOP and EARP and pinpointing operating conditions ($e.g.$, electrode, operating voltage, pH) to minimize those reactions at the positive ($i.e.$, anode) and negative electrodes ($i.e.$, cathode) in complex wastewater matrices. This necessitates conducting a detailed analysis to understand these competing phenomena to achieve superior selectivity and stability in EAOP and EARP. Moreover, the design of electrochemical systems and

catalysts can affect cell selectivity, activity, and stability. Another powerful approach to mitigating parasitic and competing reactions can be accomplished through surface and electrode modifications, promoting selectivity toward desired reactions [61].

3.1 Catalyts Materials for Anodic Oxidation and Cathodic Reduction

The redox potentials of electrode materials can inform the suitability of anodic materials for chemical transformations depending upon the redox potentials of the target compounds in the wastewater. In this section, I focus on parasitic reactions that directly involve electrode materials. Therefore, I assume a pure electrolyte system containing water and target pollutants. The redox potentials of electrodes and target compounds must be carefully examined, and an anodic potential must be chosen so that it maximizes the degradation while preserving the electrode stability for optimal operation. In the aqueous electrolyte, the potential window of electrode materials to generate reactive oxygen species (ROS) must also be considered, which can be complemented by direct electron transfer for chemical transformations. It is noted that the redox potentials of target contaminants must be less positive than the redox potentials of metal electrodes to drive electrochemical anodic oxidation. The thermodynamic potentials to generate ROS at the anode surface ($e.g.$, $\cdot\mathrm{OH}$, $\mathrm{H_2O_2}$) require greater than 1.7 V $vs.$ SHE. This potential window is beyond the stability of most electrode materials presented in Table 3.1, especially for metal electrodes. Therefore, it is not possible to produce ROS on most metal electrodes in aqueous media. Metal ions with more positive reduction potentials ($e.g.$, $\mathrm{Au} \rightarrow \mathrm{Au^{3+}} + 3\mathrm{e^-}$ $\mathrm{E^o}$=1.50 V $vs.$ SHE) are strong oxidizing agents. They tend to get reduced at much faster rates than those with lower reduction potentials [62] (Table 3.1). For metal electrodes, by increasing the potential more positive than their thermodynamic potential ($e.g.$, >0.34 V vs. SHE for Cu), they get oxidized to their ionic forms ($e.g.$, $\mathrm{Cu^{2+}}$) and leach into the electrolyte or form thin oxides surface ($e.g.$, $\mathrm{Cu_2O}$) that are either not conductive or active for degradation as opposed to zero-valent metals. Similarly, metals with lower reduction potentials ($e.g.$, $\mathrm{Fe^{2+}} + 2\mathrm{e^-} \rightarrow \mathrm{Fe}$ $\mathrm{E^o}$=-0.44 V $vs.$ SHE) are strong reducing agents and

may be easily oxidized under anodic oxidation. Therefore, for EAOP applications where strongly anodic potentials are applied, metals with higher reduction potentials must be selected. For example, in the electrocatalytic oxidation of acetic acid to carbon dioxide where the redox potential is 0.11V vs. RHE, the standard reduction potential of the candidate electrode materials in Table 1 must be higher than 0.11 V vs.RHE to drive the oxidation of CH_3COOH [63]. Metal electrodes ($e.g.$, Cu, Ru, Pd, Pt, Ir, Ag) from Table 3.1 might be able to drive the oxidation of acetic acid through direct electron transfer, but they cannot generate ROS as all of them get oxidized before reaching 1.7 V vs. RHE or higher, which is the minimum thermodynamic potential to generate H_2O_2 from water.

While metal-based electrodes are generally not suitable for anodic oxidation, they have been used ($e.g.$, Fe, Al) as common electrode materials for electrocoagulation (EC) [64]. EC is particularly effective for the removal of heavy metals, natural organic matter, bacteria and viruses where contaminants are removed and settled through the generation of Fe^{2+} and Al^{3+} coagulation by applying potentials more positive than the reduction potential of metal electrodes presented in Table 3.1 [65, 66]. Boron doped diamond (BDD) is the most widely used electrode for electrochemical anodic oxidation, which is primarily produced via the chemical vapor deposition method [67]. Boron (B) is the most commonly used dopant in diamond due to its low charge carrier activation energy (0.37 eV) [68]. The electrical conductivity of the BDD is manipulated by the doping level of boron in diamond. At low doping levels ($\sim 10^{17} \mathrm{atoms.cm^{-3}}$), BDD behaves as a semiconductor [67]. At high doping levels of B ($\sim 10^{20}$ $\mathrm{atoms.cm^{-3}}$), BDD shows properties that are similar to metals with electrical resistivities $<$0.1 Ω.cm achieved [69]. In addition, the stability of the BDD electrode at high positive applied potentials is a critical factor, which has led to the use of BDD as gold standard electrodes for anodic oxidation albeit at moderate catalytic activity and selectivity [70-72]. BDD has been studied extensively for electrochemical anodic oxidation due to its high oxygen evolution reaction (OER) overpotential, high stability at relatively high anodic potentials ($>$ 10 V) due to the structural organization of carbon atoms in diamond (sp^3 type hybridization), and decent activity for indirect oxidation of pollutants, such as organic contaminants via genera-

tion of hydroxyl radicals (·OH) by water oxidation (**Fig.3.1**). Since BDD electrodes are known to be inert and lack adsorption sites for direct anodic oxidation, the prevailing mechanism for anodic oxidation using BDD electrodes involves the physisorbed generation of ·OH through one-electron water oxidation reaction (Reaction 1 in Table 3.1) at potentials >2.7 V $vs.$ SHE and subsequent transformation or mineralization of organic compounds by ·OH. However, the high cost of BDD electrodes and their delamination from the substrate at high current densities ($>$ 1 A.cm^{-2}) limit their widespread implementation for electrochemical treatment [73].

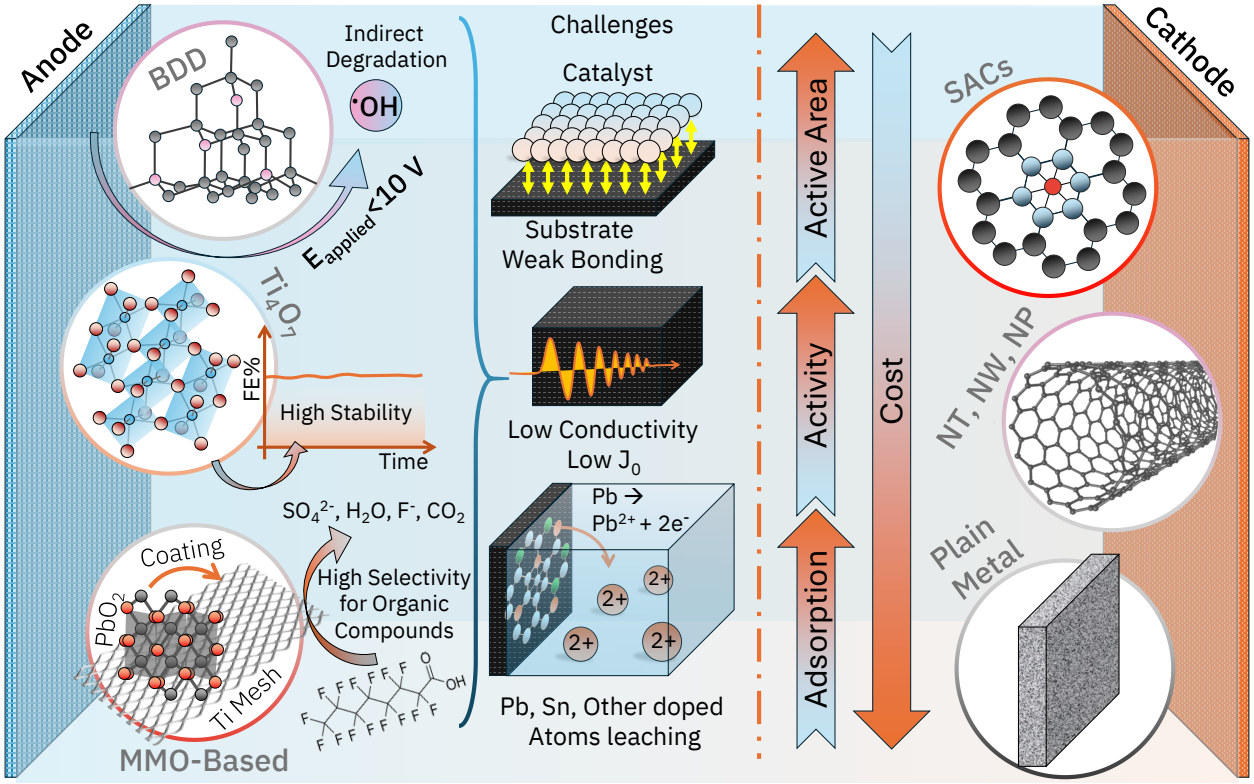

Figure 3.1: Common materials used for anode and cathode in wastewater treatment. BDD shows a high selectivity towards ·OH radicals, while MMO-based materials are highly selective towards organic compound degradation. The Ti_4O_7 catalyst shows both high chemical and electrochemical stability in the wastewater corrosive environment. The anodic catalyst materials typically face challenges such as reliable adhesion to the substrate, low conductivity, and leaching of dopants. The leaching issue is also observed in single-atom catalysts (SACs), these catalysts are especially used for cathodic reactions such as nitrate and nitrite reduction to ammonia. Moving from plain electrode materials to nano-scale materials and SACs increases the activity, adsorption, and active surface area of the catalyst while reducing the cost of the material.

MMO-based electrode materials consist of corrosion-resistant substrates ($e.g.$, titanium, tantalum) covered by a layer of metal oxides ($e.g.$, PbO_2, IrO_2, SnO_2, RuO_2, Table 3.1). Non-active MMO materials such as PbO_2 and SnO_2 have high O_2 evolution reaction overpotentials, a primary parasitic reaction at the anode. Therefore, these MMO-based electrodes exhibit higher selectivity for organic compounds oxidation and mineralization as compared with MMO-based electrodes with a low O_2 evolution reaction overpotentials ($e.g.$, RuO_2, IrO_2, **Fig.3.1**) [74]. Non-active MMO-based materials typically have low electrical conductivities and must be doped with metals ($e.g.$, F, B, Sb) to improve their performance as effective electrodes for anodic oxidation. They are also characterized by their ability to produce high yields of $^{\cdot}OH$. While prior studies using doped SnO_2 have shown decent selectivity for pollutant degradation through direct and ROS generation mechanisms, they generally have short lifetime due to the generation of non-conductive Sn hydroxide at the outer surface of SnO_2, passivating the active sites for pollutant degradation. In addition, doped SnO_2 film delamination from the substrate is another major challenge at anodic potentials >2.0 V [75, 76]. PbO_2 electrodes tend to be more stable at high anodic potentials as opposed to SnO_2. The primary mechanism for anodic oxidation using PbO_2 is through ROS generation ($^{\cdot}OH$) at potentials >3.0 V [77, 78]. Although some studies have demonstrated PbO2 has comparable selectivity with BDD for organic compounds degradation, the leaching of toxic Pb ions into solution poses major environmental challenges for their widespread utilization in water treatment applications (**Fig.3.1**) [79]. Overall, MMO-based electrode materials and BDD have remarkably higher stability than metal electrodes at positive potentials ($>$ 2.5 V) for anodic oxidation. Further research can improve non-active MMO-based electrode selectivity toward pollutant degradation with significantly lower cost than BDD electrodes through dopant or the use of alternative substrates.

The Magnéli phase titanium dioxide (TiO_2) suboxides are attractive electrode materials for water treatment. TiO_2 is an n-type semiconductor with poor electrical conductivity (10^{-9}-10^{-8} $(\Omega.cm)^{-1}$) [80]. However, the electronic properties of TiO_2 can be manipulated by introducing oxygen deficiencies in the TiO_2 lattice structure at elevated temperatures (900°C) under H_2 atmo-

sphere or by doping with other elements ($e.g.$, Nb), resulting in the conversion of Ti(IV) to Ti(III) [81]. The most conductive compounds of Magnéli phases ($\mathrm{Ti_nO_{2n-1}}$) are $\mathrm{Ti_4O_7}$ and $\mathrm{Ti_5O_9}$ with electrical conductivities orders of magnitude higher than $\mathrm{TiO_2}$ (100 $(\Omega.\mathrm{cm})^{-1}$). $\mathrm{Ti_4O_7}$ electrodes are especially ideal candidates for anodic oxidation due to their resistivity to corrosion and the electrochemical stability at anodic potentials >3.0 V, which is suitable to produce $\cdot\mathrm{OH}$ via water oxidation (**Fig.3.1**). It is noted that the oxidation of $\mathrm{Ti_4O_7}$ to $\mathrm{TiO_2}$ at anodic potentials ($>$ 1.5V) must be carefully examined as it results in electrode passivation during anodic oxidation [82]. Doping $\mathrm{TiO_2}$ is an effective strategy to improve the electrical conductivity of $\mathrm{TiO_2}$ while minimizing the possibility of oxidation as compared to $\mathrm{Ti_4O_7}$. For example, Nb-doped $\mathrm{TiO_2}$ through the substitution of $\mathrm{Nb^{5+}}$ with $\mathrm{Ti^{4+}}$ has similar electrical conductivity as $\mathrm{Ti_4O_7}$ and high electrochemical stability for anodic oxidation at potentials $>$ 2.5V. Doping $\mathrm{Ti_4O_7}$ electrodes with various transition metals ($e.g.$, Pd, V) can further improve the catalytic selectivity and durability as compared to bare $\mathrm{Ti_4O_7}$ [83].

Overall, MMO-based electrodes, BDD, and suboxides of $\mathrm{TiO_2}$ are suitable electrodes for anodic oxidation. They exhibit reasonable electrochemical stability and the capability to oxidize contaminants via direct electron transfer and indirect ROS generation ($\cdot\mathrm{OH}$) at potentials >2.5 V. Magnéli phase $\mathrm{TiO_2}$ electrodes are promising candidates for anodic oxidation due to their relatively easy and reproducible method of synthesis, low cost, and high durability and selectivity for electrochemical anodic oxidation. One strategy to improve the selectivity of $\mathrm{TiO_2}$ suboxides is to incorporate single atom metal catalysts into $\mathrm{Ti_4O_7}$ electrodes. It is noted that monolithic $\mathrm{Ti_4O_7}$ electrodes can be utilized as porous electrodes or conductive membranes in flow-through electrochemical systems [84, 85]. The use of single atoms might help minimize the corrosion and oxidation issues at high positive potentials due to the lack of lattice structure to incorporate oxygen during anodic polarization. Single-atom metal catalysts can also help minimize poisoning and deactivation of the catalyst in complex wastewater matrices [86, 87]. The adhesion of single-atom catalytic centers into the base electrode materials ($i.e.$, $\mathrm{Ti_4O_7}$) could be a major challenge yet to be addressed. It is noted that the amount of transition metal used for electrode preparation will

be significantly reduced by using single-atom metal electrodes compared to planar electrodes, assuming similar exposed surface areas. The large-scale production of electrodes is possible through processes such as flow synthesis for nanoparticles and incipient wetness for metal on metal oxide catalysts. Tools such as CATCOST can be used to evaluate the economic viability of large-scale electrode material production based on the synthesis method [88]. In particular, the production of BDD is studied through the hot-filament chemical vapor deposition (HFCVD) process. The stability of metal electrodes strongly depends on the solution pH. MMOs and stainless steel show high stability in acidic conditions, while Pt-based electrodes have a 3-11 pH range [89]. Nickel-based materials are stable at higher pH and dissociate at pH lower than 3.5 [90].

The standard redox potentials of most transition metal electrodes, including those presented in Table 3.1, are suitable to drive cathodic reduction as applying negative cathodic potentials does not change the valence state of metal electrodes. As the stability of electrode materials during cathodic reduction is less of a concern as compared to anodic oxidation, the performance of different electrode materials is primarily assessed by their selectivity and activity in a particular reaction ($e.g.$, oxyanion reduction). Therefore, the major focus in electrochemical cathodic reduction has been devoted to developing new types of electrode materials, including alloys, bimetallic, and trimetallic to enhance the selectivity toward desired reactions. In addition, carbonaceous materials have poor stability during anodic polarization where they are oxidized at potentials $>$0.21 V $vs.$ SHE (Eq. 19 in Table 3.1). However, carbon-based materials are ideal electrode materials during electrochemical reduction as either cathode or a substrate for catalyst-loaded electrodes. They can also be used for promoting the adsorption of contaminants on the electrode surface, particularly for organic pollutants. Carbon nanotubes (CNT), sponge-type porous carbon, and carbon foams are various types of carbon-based materials that offer increased surface areas for pollutants adsorption and degradation.

To improve the selectivity of cathodes or anodes for pollutant degradations, various design strategies, including incorporating selective catalytic centers comprised of materials at nano, subnano or atomic scales onto stable substrates can be adopted. Transition metals ($e.g.$, Fe, Co, Cu,

Pd) are widely used catalytic centers for electrochemical redox reactions in wastewater treatment ($e.g.$, oxyanion reduction, hydrodehalogenation, oxidant generation, mineralization) [91, 92]. For instance, incorporating Fe single atoms onto the conductive substrates ($i.e.$, g-C_3N_4, defect-rich graphene) catalysts to accelerate the rate of organics degradation via Fenton-like systems [93]. Pd single atoms on carbon supports were synthesized and used for electrochemical hydrodechlorination. Even though the use of single atoms has been demonstrated to improve the selectivity over nanoparticle counterparts, the long-term stability of single atoms anchored onto electrodes under complex water matrices yet to be explored (**Fig.3.1**) [94]. It is imperative to design nanostructured or single-atom electrodes that can operate in complex water matrices without fouling or interference by constituents commonly present in wastewater systems (**Fig.3.1**). In addition, developing methods to avoid the leaching of single-atom catalytic centers away from the substrate and into the electrolyte is critical for long-term stability. In this regard, electrodeposition has been shown an effective route to make stable single atoms attached to the substrate for various applications in electrocatalytic treatment [95]. Such is often the case for using polymers in wastewater treatment. While some of the polymers can help with oxidation and reduction due to the alternating single and double bonds between the carbon atoms, they are sometimes used as substrates [96].

Table 3.1: Redox potentials of commonly used transition metal electrodes, mixed metal oxides, and carbonaceous materials in EAOP and EARP.

Reaction no.	Half Cell Reaction	Standard Potential (E^o $vs.$ SHE)
1	$BDD + H_2O \rightarrow BDD(\cdot OH) + H^+ + e^-$	2.71
2	$Au^+ + e^- \rightarrow Au$	1.69
3	$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$	1.68
4	$PbO_2(s) + 4H^+(aq) + 2e^- \rightarrow Pb^{2+}(aq) + 2H_2O$	1.46
5	$MnO_2(s) + 4H^+(aq) + 2e^- \rightarrow Mn^{2+}(aq) + 2H_2O(l)$	1.23
6	$Pt^{2+} + 2e^- \rightarrow Pt$	1.18
7	$Ir^{3+} + 3e^- \rightarrow Ir$	1.16
8	$RuO_4(s) + 8H^+ + 8e^- \rightarrow Ru(s) + 4H_2O$	1.03
9	$Pd^{2+} + 2e^- \rightarrow Pd$	0.915
10	$RuO_2(s) + e^- + H^+ \rightarrow RuO(OH)$	0.94
11	$IrCl_6^{2-} + 4e^- \rightarrow Ir(s) + 6Cl^-$	0.80
12	$Ru^{2+} + 2e^- \rightarrow Ru$	0.80
13	$Ag^+ + e^- \rightarrow Ag$	0.80
14	$Rh^{3+} + 3e^- \rightarrow Rh$	0.76
15	$IrO_2(s) + 4H^+ + 4e^- \rightarrow Ir(s) + 2H_2O$	0.73
16	$Ru^{3+} + 3e^- \rightarrow Ru$	0.6
17	$Ag_2C_2O_4(s) + 2e^- \rightarrow 2Ag(s) + C_2O_4^{2-}$	0.47
18	$Cu^{2+} + 2e^- \rightarrow Cu$	0.339
19	$CO_2 + 4H^+ + 4e^- \rightarrow C(s) + 2H_2O$	0.21
20	$Sb_2O_3(s) + 6H^+ + 6e^- \rightarrow 2Sb(s) + 3H_2O$	0.147
21	$C(s) + 4H^+ + 4e^- \rightarrow CH_4(g)$	0.131
22	$2H^+ + 2e^- \rightarrow H_2$	0.00
23	$SnO_2(s) + 4H^+ + 2e^- \rightarrow Sn^{2+} + 2H_2O$	-0.094
24	$Sn^{2+} + 2e^- \rightarrow Sn$	-0.141
25	$Ni^{2+} + 2e^- \rightarrow Ni$	-0.236
26	$SnF_6^{2-} + 4e^- \rightarrow Sn(s) + 6F^-$	-0.25
27	$Co^{2+} + 2e^- \rightarrow Co$	-0.282
28	$PbF_2(s) + 2e^- \rightarrow Pb(s) + 2F^-$	-0.35
29	$PbSO_4(s) + 2e^- \rightarrow Pb(s) + SO_4^{2-}$	-0.355
30	$Fe^{2+} + 2e^- \rightarrow Fe$	-0.44
31	$Ag_2S(s) + 2e^- \rightarrow 2Ag(s) + S^{2-}$	-0.71
32	$Cr^{3+} + 3e^- \rightarrow Cr$	-0.74

3.2 Parasitic Reactions In Surface Redox Schemes

In electrochemical anodic oxidation, employing an electrode that can suppress parasitic reactions such as oxygen evolution reaction (OER, $2H_2O \rightarrow O_2 + 4H^+ + 4e^- E^o = 1.23$ V $vs.$ RHE) is desired. In addition, the electrochemical cathodic reduction is another pathway to degrade pollutants such as halogenated organics, oxyanions and per- and polyfluoroalkyl subsatnaces (PFAS). Hydrogen evolution reaction (HER) is a primary parasitic reaction at the cathode. As HER and OER are thermodynamically and kinetically favorable on most electrode materials, it is crucial to determine the operating voltage window where these reactions are suppressed to improve the overall energy efficiency of the degradation process. Various cations and anions in real wastewater matrices can induce different parasitic reactions that can be beneficial or detrimental to the overall electrochemical performance of the system. In this regard, chloride (Cl^-) is typically present in the complex wastewater matrices in a wide range of concentrations (100-35000 mg L^{-1}) depending on the type of water ($e.g.$, municipal wastewater, seawater) and reacts at the anode [97] via electrochemical anodic oxidation. Several oxidation reactions can occur during electrochemical oxidation when the anode is subjected to a reasonably high potential. The oxidation of chloride ions to different reactive chlorine species (RCS), such as chlorine gas (Cl_2), hypochlorous acid (HOCl), hypochlorite ions (OCl^-), and most importantly, chlorine radicals (Cl•), is one of the major anodic reactions that occur when Cl^- ions are present. These chlorinated radicals (Cl•) are highly reactive and play a significant role in the indirect electrochemical oxidation of pollutants. They act as strong oxidizing agents by abstracting hydrogen atoms from organic molecules, undergo additional reactions with unsaturated bonds in organic pollutants, act as precursors to other RCS, and help degrade other recalcitrant organic pollutants. In all of these, the organic pollutants are transformed into intermediates, which are then easily oxidized at the anode. Depending upon the pH and applied potential, the electro-oxidation of Cl^- at the anode can take various routes [98]. In a highly acidic region (pH < 3), the free chlorine (Cl_2) evolution reaction dominates over the

other chloride oxidation reactions according to the following equation **(Figs. 3.2A and B)**:

$$2Cl^- \rightarrow Cl_2 + 2e^- \quad (\mathrm{E^o} = 1.36\,\mathrm{V}\ vs.\ \text{SHE, pH = 0}) \tag{3.1}$$

$$Cl^- + H_2O \rightarrow HOCl + H^+ + 2e^- \quad (\mathrm{E^o} = 1.28\,\mathrm{V}\ vs.\ \text{SHE, pH = 0}) \tag{3.2}$$

$$Cl^- + 2OH^- \rightarrow ClO^- + H_2O + 2e^- \quad (\mathrm{E^o} = 0.89\,\mathrm{V}\ vs.\ \text{SHE, pH = 0}) \tag{3.3}$$

Even though competing Cl^- oxidation reactions (COR) are not thermodynamically favorable as compared to the oxygen evolution reaction (OER) **(Fig. 3.2A and B)**, the two-electron requirement in the COR as compared to the 4-electron requirement for the OER might still make COR a kinetically feasible pathway (Eq. 5). As the thermodynamic potential difference between OER and COR is 0.48 V in the alkaline media, for any choice of electrode materials, performing electrolysis in the alkaline electrolytes (pH>8) might suppress COR and promote OER in the oxidative pathway [99, 100].

$$\Delta G^o = -nF\Delta E^o \tag{3.4}$$

In the reductive pathway, $\mathrm{O_2}$ can be reduced through two-electron and four-electron cathodic reduction to produce $\mathrm{H_2O_2}$ and $\mathrm{H_2O}$, according to Eqs. (6) and (7). As $\mathrm{H_2O_2}$ is used as a chemical precursor for wastewater treatment, promoting two-electron ORR to $\mathrm{H_2O_2}$ is a desired reaction pathway. Carbonaceous materials have shown the highest activity for $\mathrm{H_2O_2}$ production from $\mathrm{O_2}$ [101], while Pt-based metal electrodes promote ORR for $\mathrm{H_2O}$ generation [102, 103].

$$\mathrm{O_2 + 2H^+ + 2e^- \rightarrow H_2O_2} \quad (\mathrm{E^o} = 0.67\,\mathrm{V\ vs.\ SHE,\ pH = 0}) \tag{3.5}$$

$$\mathrm{O_2 + 4H^+ + 4e^- \rightarrow H_2O} \quad (\mathrm{E^o} = 1.23\,\mathrm{V\ vs.\ SHE,\ pH = 0}) \tag{3.6}$$

Cations with various reduction potentials can form scale on the cathode surface and deactivate the desired cathodic reduction **(Fig. 3.2 A and B)**. These reactions are not only considered parasitic but can also entirely deteriorate the performance of the electrochemical system if they are not fully

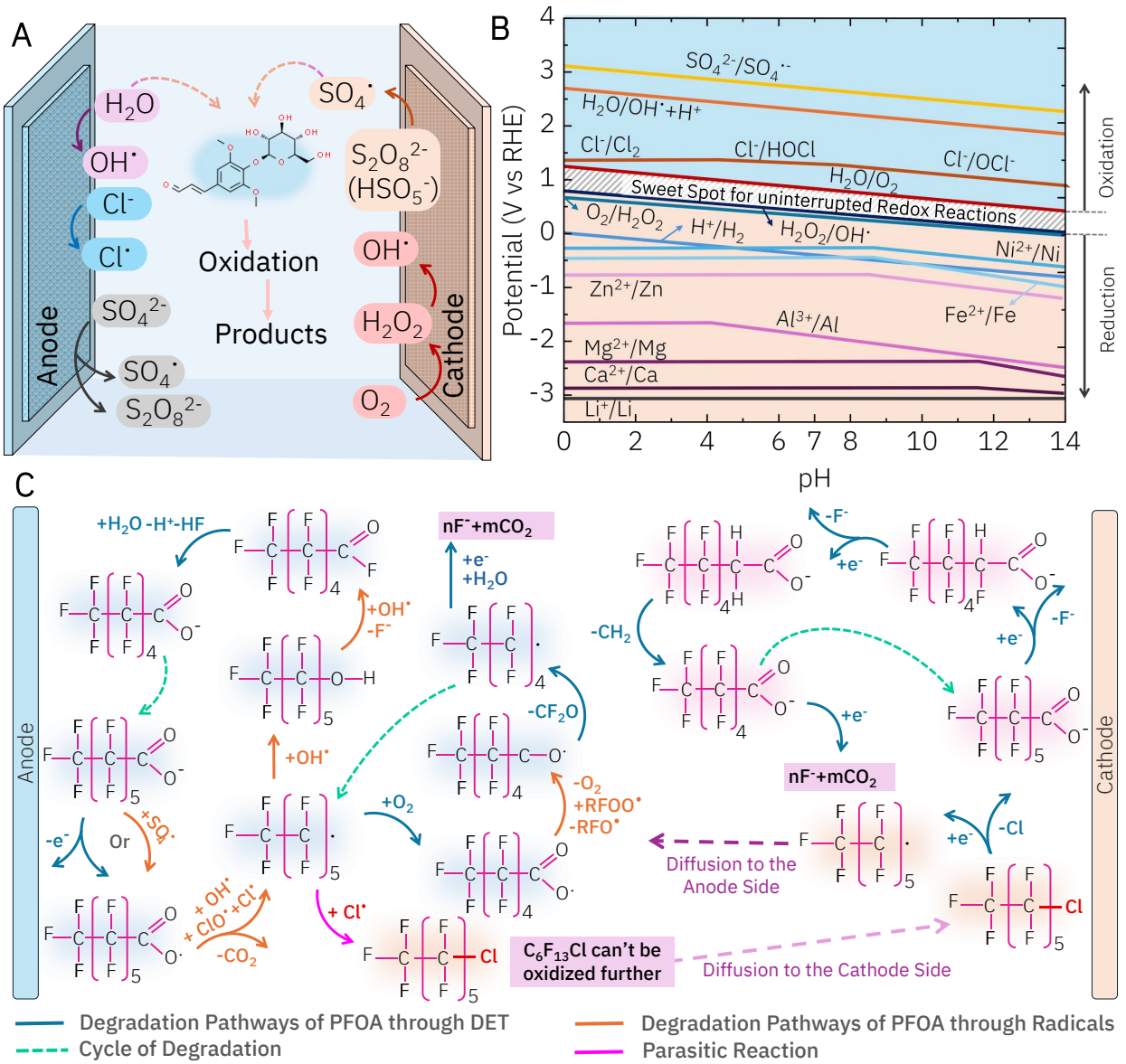

Figure 3.2: A) Favorable redox reactions in wastewater treatment, Reaction pathways for in-situ generated radicals (·OH, $SO_4^{\cdot-}$, $Cl^{\cdot}$) via electrochemical advanced oxidation and reduction processes, B) Parasitic and competing anodic and cathodic reactions in complex wastewater matrices containing various cations and anions, which may result in the formation of toxic byproducts and/or deactivation and poisoning of the catalyst, C) Degradation pathways for PFOA through direct electron transfer (DET) and radicals. Removing the membrane and using a single-cell configuration allows the cathode and anode to cooperate effectively in degrading complex organic molecules such as PFOA. As PFOA is degraded *via* radicals, it may react with Cl·, and the product can't be further oxidized. The produced intermediate species (C_xF_yCl) diffuses to the cathode surface, where it is reduced and loses the chloride. The final product returns to the oxidation cycle.

understood. A prime example of deactivation is the presence of calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions in hard wastewater. Mg^{2+} and Ca^{2+} are particularly problematic to many cathodic reactions that lead to locally alkaline environments, notably oxygen reduction reaction (ORR) and HER. Under such conditions, $Mg(OH)_2$ and $CaCO_3$ can form on the electrode surface, hindering electrocatalytic activity by blocking active sites and increasing interfacial resistance [104]. While some deposits can be removed with periodic flushing or electrochemical methods ($e.g.$, polarity reversal or pulsed electrolysis) [105], other constituents may chemisorb and poison the active sites, which blocks off their access to the necessary reactants and subsequently leads to their deactivation. As these deactivation phenomena ($i.e.$, scale formation) by the presence of various cations and trace metal constituents in the wastewater are observed on most electrode surfaces, it is important to identify the sweet spots where the applied potential is not favoring the formation of scale on the electrode surface **(Fig. 3.2B)**. By carefully monitoring the wastewater constituents and controlling the applied potential, scale formation can be minimized or even mitigated. In the inevitable case of scale formation, when the redox potentials of target compounds ($e.g.$, electrochemical dechlorination of 4-chlorophenol) are more negative than the redox potentials of some of the cations ($e.g.$, Ni^{2+}, Zn^{2+}) presented in Table. 3.1, pulsed electrolysis or polarity reversal are common strategies to extend the lifetime of the electrode material and maintain the electrocatalytic performance.

Certain species, such as sulfide and chloride, are known to form strong complexes with metal-based catalysts, which are dependent on the applied potential. At high negative applied potentials, the poisoning effect is less detrimental to the electrocatalytic performance [106, 107] due to other competing reactions ($e.g.$, ORR) that occupy active sites. Moreover, the nature and extent of these deactivation phenomena are highly dependent on the identity of the catalyst and its operational configuration. One example includes bicarbonate (HCO_3^-), a pH buffer that can mitigate high Nernstian concentration overpotentials [108, 109] and sometimes even promote specific reactions, where it serves as a mediator to enhance the generation of H_2O_2 through hydrolysis with water. On the other hand, bicarbonate exposed to much harsher conditions at the cathode (higher current den-

sities $> 100\,\mathrm{mA.cm^{-2}}$ and overpotentials $> 2\,\mathrm{V_{RHE}}$) can lead to salt precipitation ($e.g.$, potassium carbonate), which can deactivate the electrode and cell [105]. This is further affected by their concentration in the target wastewater and the presence of co-ions; certain metals can complex with carbonates, changing the deactivation pathway altogether. At lower current densities, the conversion rate of $\mathrm{HCO_3^-}$ to $\mathrm{CO_3^{2-}}$ is slower, giving enough time for $\mathrm{CO_3^{2-}}$ to migrate from the cathode surface, resulting in more distributed and lower carbonate concentration and avoiding precipitation. Thus, it is recommended to use pulse electrolysis for industrial-scale wastewater treatment, including bicarbonate, to take advantage of both low and high current densities [105]. It is important to note that $\mathrm{CO_2}$ is the main product of organics oxidation, and the dissolved $\mathrm{CO_2}$ in the wastewater can also be reduced at the cathode surface to generate organic chemicals ($e.g.$, ethanol). While useful commodity chemicals can be produced through the $\mathrm{CO_2}$ reduction reaction ($\mathrm{CO_2RR}$), they are not necessarily desired in the context of wastewater treatment. By tuning the electrolysis time and using cathode materials with low activity for $\mathrm{CO_2RR}$, this can be circumvented.

3.3 Electrochemical Radical Generation for EARP and EAOP

Hydroxyl radicals ($\cdot$OH) can be produced through anodic oxidation (Eq. 3.7) via one-electron water oxidation reaction. In addition, water can be oxidized to hydrogen peroxide through a two-electron transfer process (Eq. 3.8). Electrochemical activation of hydrogen peroxide at the cathode surface can lead to the generation of hydroxyl radicals (Eq. 3.9). Electrochemical activation of strong oxidizers such as hydrogen peroxide, persulfate, and free chlorine, which are often added to wastewater as precursor chemicals, presents an alternative pathway to generate reactive radicals to degrade pollutants **(Fig. 3.2 A)** [110, 111].

Sulfate radicals ($\mathrm{SO_4^{\cdot}}$) have a relatively higher redox potential ($E^o(\mathrm{SO_4^{\cdot -}/SO_4^{2-}}) = 2.60\breve{}3.10$ V vs. RHE) and longer half-life (30 – 40 μs) compared to hydroxyl radicals ($E^o(\cdot\mathrm{OH/OH^-}) = 1.90\breve{}2.7$ V vs. SHE, less than one μs), resulting in strong oxidizing ability and higher pollutant removal capability [111, 112]. Although several sulfate radical-based EAOP research studies have focused on the externally added persulfate (PS) as the precursors of radicals, sulfate radicals can

also be generated directly at the anode in the electrochemical system. This is achieved through the direct oxidation of sulfate anions (Eq. 3.10) via a one-electron transfer process in electrolytes containing sulfate ions. Boron-doped diamond (BDD) and boron/nitrogen codoped diamond (BND) [113] have shown effective oxidation of sulfate anions to sulfate radicals for *in-situ* generation of reactive radical species for contaminant removal.

$$H_2O \rightarrow \cdot OH + H^+ + e^- \quad E^o = 2.73 \text{ V vs RHE} \tag{3.7}$$

$$2H_2O \rightarrow H_2O_2 + 2H^+ + 2e^- \quad E^o = 1.76 \text{ V vs RHE} \tag{3.8}$$

$$H_2O_2 + H^+ + e^- \rightarrow OH^{\cdot} + H_2O \quad E^o = 0.79 \text{ V vs RHE} \tag{3.9}$$

$$SO_4^{2-} \rightarrow SO_4^{\cdot -} + e^- \quad E^o = 3.1 \text{ V vs RHE} \tag{3.10}$$

Sulfate radicals ($SO_4^{\cdot -}$) can also be generated when sulfate anions react with hydroxyl radicals ($\cdot$OH) according to Eq. 3.11. The oxidation of sulfate anions has been reported on the BDD anode surface, with hydroxyl radicals formed through the one-electron water oxidation reaction [114]. The sulfate radicals generated through various pathways also trigger subsequent chain reactions to produce $\cdot$OH by reacting with either water molecules or hydroxide anions (OH^-) at pH greater than 7 in the bulk electrolyte. Thus, sulfate and hydroxyl radicals are the main driving reactive species for degrading organic pollutants in the sulfate radical-based EAOP system, even though other non-radical species have also been reported in persulfate-based electrochemical systems. Peroxymonosulfate (PMS) and peroxydisulfate (PDS) precursors are activated mainly through one-electron cathodic reduction to generate sulfate radicals, facilitating the degradation of organic pollutants [115-117]. PMS and PDS have relatively high redox potentials ($E^o > 1.8$ V), so when pollutants are adsorbed on the electrode surface, those compounds could be directly oxidized

via a non-radical pathway ($i.e.$, direct electron transfer) before the activation of persulfates (Eqs. 3.12,3.13) [118].

$$SO_4^{2-} + \cdot OH \rightarrow SO_4^{\cdot -} + H^+ + e^- \quad E^o = 2.60 \text{ V vs RHE} \tag{3.11}$$

$$HSO_5^- + e^- \rightarrow SO_4^{\cdot -} + HO^- \text{ (or } \cdot OH) \quad E^o = 1.82 \text{ V vs RHE} \tag{3.12}$$

$$S_2O_8^{2-} + e^- \rightarrow SO_4^{\cdot -} + SO_4^{2-} \quad E^o = 2.08 \text{ V vs RHE} \tag{3.13}$$

It is noted that even though side reactions compete for electron transfer at both the anode and the cathode, they could play a positive role if they serve as chemical precursors to generate oxidizing radical agents to degrade contaminants via indirect routes ($e.g.$, H_2O_2) [119]. Besides, the electrogeneration of PDS ($S_2O_8^{2-}$) has been reported in the anodic reaction through multiple pathways, including direct oxidation on the anode surface, oxidation of hydroxyl radicals and sulfate ions, or oxidation of hydrogen sulfate (HSO_4^-) in the bulk electrolyte. The electrogenerated $S_2O_8^{2-}$ can be further activated through cathodic reduction to generate $SO_4^{\cdot -}$ radicals (Eq. 3.13) [120, 121]. Persulfates, including PMS and PDS, are representative precursor chemicals that produce sulfate radicals via cleavage of their peroxide bond. The peroxide bond can be broken through electrochemical cathodic reduction, generating sulfate radicals and/or hydroxyl radicals. For the electro-activation of PS through cathodic reduction, carbonaceous materials such as graphite, carbon nanotubes, carbonized wood, activated carbon fiber, and their combinations [122-124] have been widely employed to investigate their ability to generate radicals and degrade a wide variety of pollutants. These materials are cost-effective, easy to manipulate, relatively reproducible, and corrosion-resistant. Additionally, metal-based cathodes such as platinum , iron, cobalt, aluminum, and mixed metal oxides (MMO) have also been reported for the electro-activation of PS by cathodic reduction [125-128].

PS can also be activated on the anode side. For anodic activation of PS, materials such as iron plates, carbon cloth, blue-TiO_2 nanotubes, graphite felt [118], and BDD electrodes have been used as anode materials. The dominant reactive oxygen species generated anodically were hydroxyl radicals or non-radical species such as singlet oxygen rather than sulfate radicals [129]. In addition to the thermodynamic potential, overpotential is another critical factor that provides insight into the reaction kinetics and dictates the overall applied potential required for driving electrochemical reactions at a certain current density. Developing electrocatalysts with lower overpotential results in faster electrochemical reaction rates and achieving higher current densities.

3.4 Electrochemical Degradation and Mineralization of PFAS

Electrochemical methods to degrade and mineralize PFAS, especially PFOA and PFOS, have gained enormous attention [132]. The primary advantages of this technique include high energy efficiency, scalability, convenient set-up, modularity, easy and discontinuous operability at mild conditions [133, 134]. Additionally, the technique does not require the use of external reagents and can be used at room temperature and atmospheric pressure [135]. For the electrochemical degradation of PFAS, primarily BDD anodes and MMO, also known as dimensionally stable anode (DSA), have been reported in the literature [136, 137]. The BDD, lead oxide (PbO_2), and tin oxide (SnO_2) electrodes are examples of "non-active" anodes. These anodic materials do not get consumed readily during anodic processes, primarily due to their high chemical stability, resistance to oxidation and corrosion at high anodic potentials. Moreover, they have a high oxygen evolution over-potential and can produce a significant amount of ·OH radicals [138, 139]. The addition of metal ions, such as Ce^{4+}, Bi^{4+}, Mn^{4+}, Yb^{3+}, to MMO-based electrodes especially PbO_2 coating improves their electrochemical activity [138]. Recently, there has been growing interest in ceramic electrodes made of sub-stoichiometric titanium oxides (Ti_nO_{2n-1}, $4 \leq n \leq 10$) [140]. For the electrochemical oxidation of PFAS, the Magnéli phase Ti_4O_7 has been the desired anode material because of its chemical inertness, durability, high oxygen evolution potential (>2.5 V vs SHE), and low production costs. Furthermore, Ti_4O_7 could be used to create the reactive electrified

membranes needed for flow-through electrochemical systems that could improve the degradation rates compared to the traditional flow-by or batch-cells due to enhanced mass transport through the membranes [141]. Ti_4O_7 interconnected pores (dia. 1–10 μm) and high overall porosity ($\sim$23%) make this electrode material an ideal choice for electrochemical reactions because the porosity provides increased active sites for the reaction and the macropores can enhance PFAS transport for surface reactions, resulting in improved energy efficiency. Compared to the BDD electrode, which is likely to degrade at higher pH values, Ti_4O_7 electrode is remarkably stable in aggressive media. Because of their large electroactive surface area, ceramic microporous Magnéli phase Ti_4O_7 anodes outperform other anodes in terms of PFOA and PFOS degradation while utilizing the least amount of electrical energy ($i.e.$, 5 and 32 kWh/m^3, respectively) [142]. Ti_4O_7 has a significantly higher electrochemical oxidation capacity than active anodes such as Pt and DSA. But compared to the traditional anode materials (BDD and doped SnO_2), pure Ti_4O_7 has a relatively low interfacial charge transfer rate, resulting in an insufficient amount of hydroxyl radical generation. Consequently, different approaches to improve radical generation using Ti_4O_7 anode can be taken into consideration to attain a higher oxidation efficiency. A trace amount (0.1–2% weight percent) of carbon materials can be added to the Ti_4O_7 anode surface to form a hetero-junction structure. Functional groups that contain oxygen can be essential to the interfacial electron transfer process. Oxidation of carbon groups facilitates electron uptake at the electrode surface, and the appearance of C-O(H) on the surface of carbon material may reduce electron-transfer resistance, significantly accelerating the interfacial electron-transfer process. The presence of carbon materials has been reported to affect the OER as well as the effectiveness of direct and indirect PFAS oxidation. However, their steady oxidation may result in a decrease in the electrode performance [141].

3.5 PFAS Degradation and Mineralization Pathways

Direct electron transfer (DET) from PFAS compounds to the anode surface at potentials above 3.0 V vs. SHE is suggested as the rate-limiting step in the electrochemical oxidation of PFAS [143]. It is followed by an indirect pathway in which an oxidant or radical produced on the anode surface could break down the PFAS species in the bulk. It is suggested that hydroxyl radicals produced by the water oxidation at the anode act as an oxidizing agent to indirectly degrade PFAS. Hydroxyl radicals (•OH) are essential reactive oxidizing species that help break the strong C–F bonds during the electrochemical degradation of PFAS. These radicals are produced at the anode surface during the one-electron water oxidation reaction at high anodic potentials, usually higher than 2.87 V vs. SHE. The generation of hydroxyl radicals (•OH) is often encouraged by non-active anode materials with high overpotentials for oxygen evolution, such as boron-doped diamond (BDD), Ti_4O_7, PbO_2, and SnO_2. In addition, a pH near neutral and slightly acidic promotes efficient •OH generation. Perfluoroalkyl acids' (PFAAs') primary oxidation takes place on a Ti_4O_7 anode at a potential higher than 2.87 V vs. SHE, which is the necessary potential for producing hydroxyl radicals through water electrolysis [134]. The unzipping reaction pathway, which has been suggested by numerous earlier studies, is the most widely used mechanism for the electrochemical oxidation of PFAS. The breakdown process begins with the transfer of electrons from the perfluorinated alkyl radicals to the anode surface [143]. This is followed by the desulfonation of PFOS and the decarboxylation of PFOA because the perfluorinated alkyl radical species are unstable **(Fig. 3.2C)** [138]. Consequently, PFOA and PFOS radicals produce the extremely active C_7F_{15} and C_8F_{17} radicals. There are three possible reaction pathways for these radicals. One is the formation of alcohol through a reaction with a hydroxyl radical, such as $C_7F_{15}OH$ from C_7F_{15}•. Two other possible pathways involve the reactions of C_7F_{15}• with O_2 or H_2O which consequently leads to PFAS degradation **(Fig. 3.2C)** [144]. Intermolecular rearrangement, HF elimination, and hydrolysis can be performed on this alcohol to produce shorter-chain PFOA with one fewer CF_2 group. The identification of CHF_3, CF_4, and C_2F_6 in the gas phase has led to the report of the formation of volatile fluorinated organic contaminants as degradation products. The intermediate CF_3• and CF_3-CF_2•

radicals may react to form these volatile compounds, and it is advised to monitor these volatile species to prevent any potential air pollution [135]. The mechanics of this process, however, are still up for debate and require more research. Electrochemical deflourination of PFAS compounds could occur on the cathode surface. At the cathode, direct electron transfer happens from the cathode surface to the PFAS molecule through reductive dehalogenation, leading to the fluorine and/or chlorine abstraction from the organic molecules. The subsequent intermediates are passed on to the anode, where they get completely oxidized **(Fig. 3.2C)**. The criteria for selecting the best cathode materials for PFAS degradation include excellent electrical conductivity, high surface area, and catalytic activity toward defluorination reactions. Most importantly, the materials must be able to produce adsorbed hydrogen for reductive defluorination and be resistant to chemical and electrochemical corrosion. Materials such as stainless steel, graphite, nickel, copper, and noble metals such as platinum and palladium have been reportedly used as effective cathode materials for PFAS degradation [146], While this process does not result in the mineralization of PFAS, it could contribute to PFAS transformation to smaller chains, followed by anodic oxidation to fully mineralize PFAS through the contribution of both the anode and the cathode in an electrochemical process **(Fig. 3.2C)** [147]. The knowledge of the behavior of PFAS at different time and space, especially their molecular interactions at surfaces and interfaces to long-range dispersion in aquatic and atmospheric systems, has been helpful in understanding PFAS degradation mechanisms. PFAS unique hydrophobic and lipophobic nature sometimes complicates their interactions with aqueous and organic phases. However, understanding their behavior at various spatial and temporal scales is necessary to accurately and reliably postulate the degradation mechanisms. The idea of using computational chemistry methods for PFAS remediation is very promising and its benefits cannot be overstated. Advancing our understanding on PFAS adsorption, destruction, and bioaccumulation could not only contribute to the development of novel materials for PFAS adsorption and degradation but also for the accurate optimization of cell reactors for complete mineralization of PFAS compounds into harmless byproducts.

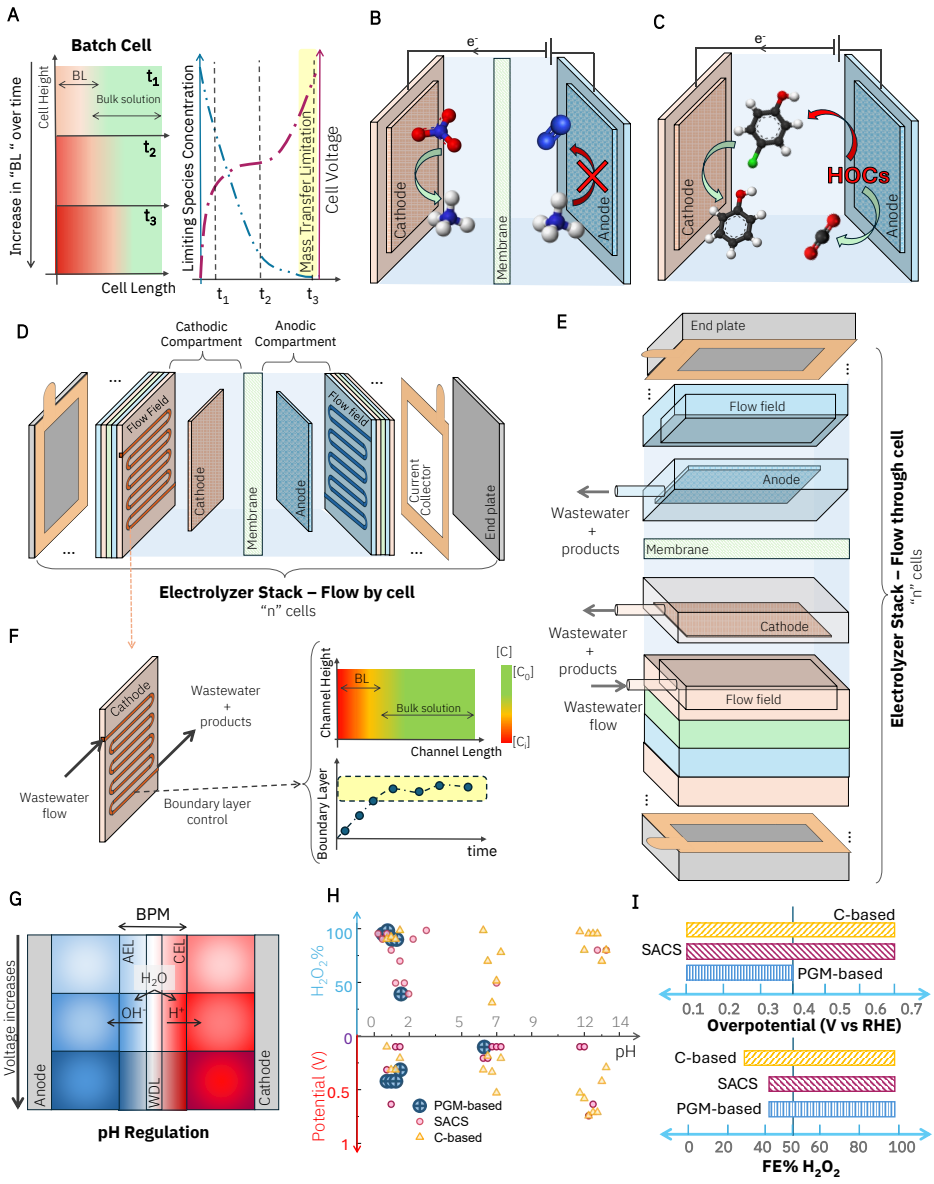

Figure 3.3: A) Growth of the boundary layer in the batch cell leads to the mass transfer limitations and consequently causes a jump in the cell voltage, B) The importance of membrane use in wastewater containing nitrate (NO_3^-) and nitrite (NO_2^-) to avoid ammonium oxidation. The produced ammonium at the cathode surface diffuses to the anode surface and is oxidized to nitrogen gas in the absence of a membrane, C) The advantage of operating an electrolysis cell without a membrane for wastewater matrix, including pollutants such as hydrophobic organic contaminants (HOCs) and Perfluorooctanoic acid (PFOA). D) Flow cell in flow-by configuration: Wastewater flows in the flow channel on the cathode and anode flow fields. While wastewater flows, species take part in redox reactions based on their standard potential, E) Flow cell in flow-through configuration: Wastewater flows in the flow fields and passes directly through the cathode and anode, F) Effect of the flow cell on boundary layer control. The average boundary layer growth is near zero for a flow cell with an optimized flow rate. G) Impact of bipolar membrane (reverse bias) on pH control. As voltage increases, the pH gradient across the electrochemical cell intensifies, H) Effect of pH on the electrode potential and selectivity towards hydrogen peroxide (H_2O_2) formation, I) Sensitivity of overpotential and hydrogen peroxide (H_2O_2) selectivity to variation in pH for catalytic materials.

3.6 Electrochemical Cell Design and Its Effects on Minimizing Voltage and Parasitic Reactions

Different cell designs impact the balance between desired and parasitic reactions, potentially optimizing removal performance and energy efficiency. For instance, a single-cell design offers simplicity and low cost; however, by-products from one electrode can negatively affect the overall system performance. Different flow cell designs, $i.e.$, a flow-by cell with a flow channel between two parallel electrodes vs. a flow-through cell that utilizes microporous electrodes such as mesh, filter, and membrane, impact the electrochemical performance. Different design options can dictate the area of reaction sites and suppress diffusion limitations. It is critical to understand how the flow cell design can contribute to finding a sweet spot wherein desired and parasitic reactions are balanced, a subject that has seldom been addressed in the literature. The traditional electrolysis cell, known as a batch or H-cell, presents inadequate industrial practicality. This is due to the mass transfer limitation that dramatically increases the cell voltage, resulting in a high energy consumption and very low energy efficiency (**Figs. 3.3A, B, and C**). Over time, as reactants are being produced or consumed at the electrode surfaces, the surface concentration of species reach near-zero values, resulting in a huge jump in the Nernstian loss and consequently the cell voltage (**Figs. 3.3A**). Stirring the electrolyte can control species concentration gradients and prevent the mass-transfer limit phenomena to some extent. However, stirring is energy-intensive and does not offer a practical solution for scaling to larger industrial applications. The recent developments in electrochemical cell designs have led to the design of flow cells. In this design, the electrolyte moves through the cell, offering the same effect of mass transfer control as a stir bar (**Figs. 3.3D, E, and F**).

Membrane inclusion in an electrochemical cell offers a compartmental cell configuration in comparison to a single-cell design. In some electrochemical systems, the anodic and cathodic compartments have to be separated using a polymer membrane. Under these circumstances, typically, the counter electrode results in the removal of desired products or generates compounds

via electrochemical reactions that decrease the overall selectivity of the working electrode. For instance, in the electrochemical nitrate reduction reaction, if the cathodic and anodic parts are not separated by a membrane, the ammonia produced through cathodic reduction will be oxidized at the anode surface (**Fig. 3.3B**). Therefore, the reactions can be defined as parasitic depending on the goal of the system. This necessitates holistically exploring the electrochemical system design ($i.e.$, combining $vs.$ separating anodic and cathodic reactions) to improve the electrochemical treatment performance for both pollutant degradation and resource recovery. The inclusion of an ion exchange membrane may also lead to a pH gradient between both compartments due to the parasitic HER and OER at the cathode and anode, which leads to additional ohmic loss [147, 148]. Depending on the applied current density, this gradient can lead to very alkaline and acidic conditions at the cathode and anode, respectively. Unless the electrolyte is pretreated, such pH effects can spur the deactivation phenomena, including the cathodic precipitation of Mg- and Ca-based scale [151]. Hence, the use of bipolar membranes may alleviate this pH change during wastewater treatment.

While anodic or cathodic reactions pertaining to water treatment have received thorough treatment in the literature, the interplay between the two has often been overlooked, despite the potential for major synergistic and/or detrimental impacts on overall system performance. For example, in a study investigating the oxidation of phenol at an electrochemically active carbon nanotube filter (CNT) anode, it was found that the removal efficiency of phenol was directly correlated to the flux of H_2O_2 generated at the CNT cathode. Similarly, it was observed 6.3- to 9.7-fold enhancement in the kinetics of phenol degradation by coupling an electro-Fenton (EF) process at the cathode with direct oxidation at the anode in a system employing Ti^{3+} self-doped TiO_2 nanotube arrays as both anode and cathode (**Fig. 3.3C**). For these types of electrochemical systems, while the desired reactions will take place on one electrode surface ($i.e.$, cathode or anode), the other electrode can serve as a complement to promote the rate of formation or degradation. In addition, although cathodic reduction is not typically pursued for organic compound degradation, it can significantly enhance the overall performance [152, 153]. In this regard, electrochemical cathodic reduction for dehalogenation of halogenated organic products generated at the anode, which are often more toxic

than the original organic compound, is a showcase for combining anodic oxidation and cathodic reduction to enhance the system's performance in a single-compartment cell. Here the choice of electrode materials for the cathode is imperative, given the current technological limitations and the electrochemical reactions with significant environmental implications. For instance, in the case of anodic oxidation of phenolic compounds, due to the presence of Cl^- in almost all wastewater streams, a parasitic reaction at the anode is the generation of chlorophenolic compounds, which are hard to oxidize and blocks off the anode surface for further oxidation. Here, the careful choice of cathodic materials, such as Pd-based electrocatalysts for dehalogenation of chlorophenol can remarkably improve the oxidation performance of the anode and the overall performance of the electrochemical system.

Mass transport limitation is one of the most critical challenges that might hamper the desired reaction selectivity or promote parasitic reactions, impacting the overall performance of electrochemical processes [155, 156]. Optimizing cell configuration and operating conditions is a primary strategy to enhance mass transfer. Given the limitations of batch-cell configurations, a flow cell represents a far more practical and viable option for commercial and industrial wastewater treatment options (**Figs. 3.3D and E**). Flow cells have been instrumental in mitigating these mass transfer issues. Recently, there has been a significant focus on designing flow-through systems using porous electrodes ($e.g.$, mesh, membrane) to minimize mass transport losses (**Figs. 3.3E**)) [157, 158]. In this type of reactor, the wastewater flows through the pores (a few nm up to 1 μm pore size) with a high specific surface area electrode that offers move active sites for electrochemical reactions [159]. The flow-through reactors have been reported to have an enhanced reaction rate constant compared to flow by (**Figs. 3.3D**), primarily due to the higher residence time and contact area of pollutants with the electrode surface. As HER and OER are the primary parasitic reactions in electrochemical wastewater treatment systems, the use of flow-through systems can significantly enhance the rate of desired reactions ($e.g.$, pollutant degradation) by flowing the low-concentration reactants (< 50 mM) through the pores of the electrode. For instance, in electrochemical wastewater treatment containing nitrate ions, if the goal is to clean water, the anode

can contribute to oxidizing ammonia generated at the cathode surface to produce benign N_2 gas downstream. One major design that has been widely used in recent years is the inclusion of a gas-diffusion electrode (GDE) for the cathodic synthesis of H_2O_2 [160-162]. Due to the low solubility of O_2 under aqueous conditions, a GDE allows direct delivery of O_2 to the active site without the need for bubbling directly into the wastewater. With proper optimization of operational conditions, these cells can provide high concentrations of H_2O_2 directly in the wastewater for activation and/or further use downstream. Without the use of GDE, H_2O reduction reaction will be the dominant parasitic reaction at the cathode instead of ORR ($i.e.$, desired reaction) as the concentration of H_2O is significantly higher than that of O_2. Using flow cell design provides the possibility of flow rate control to reach to an approximately steady potential and keep the cell voltage at a steady value, making flow cells even more practical for industrial purposes (**Fig. 3.3F**).

Using bipolar membrane (BPM) instead of anion and cation exchange membranes (AEM and CEM) provides us with tools to manage and regulate the cell pH by alternating the cell voltage (**Fig. 3.3G**) [163, 164]. As voltage increases, the ionization of water in the bipolar membrane increases, and the produced H^+ and OH^- ions at the BPM interface could alleviate a more extreme pH gradient occurs in monopolar membranes. This can further assist in managing the reaction mechanisms as species degradation pathways are usually pH-dependent. The Faradaic efficiency and the concentration of H_2O_2 are strictly dependent on the pH of the cell, for almost all types of catalysts, including SACs, carbon-based catalysts, and PGM-based catalysts (**Fig. 3.3H and I**) [165-167]. Although the lowest activation overpotential belongs to the PGM-based materials, SACs and C-based materials can offer the same overpotential in a pH-controlled reaction environment. SACs even offer the same range of Faradaic efficiency for H_2O_2 production as PGM-based material. Although these studies provide valuable insights into catalyst materials discovery for H_2O_2, further studies on crucial radicals generation ($e.g.$, $ClO^{\cdot}$ and $SO_4^{\cdot-}$) and the effect of pH and BPM on the current efficiency will be needed.

Applying high flow rates has been one strategy to mechanically force the removal of bubbles (particularly O_2 at the anode) that otherwise accumulate and increase the interfacial resistance,

resulting in a decrease in the rate of desired reactions ($e.g.$, pollutant degradation) [168]. A higher flow rate can also impact the local microenvironment; high catholyte flow rates can effectively remove OH^- from the electrode surface that will otherwise form metal hydroxides ($e.g.$, $Zn(OH)_2$) with various cations present in the wastewater. This eventually blocks off active sites of the catalyst and deteriorates the rate of desired reactions [169]. Such effects regarding mass transfer and the local electrode environment can be further tuned with appropriate reactor modifications; for instance, minimizing the inter-electrode gap would decrease cell resistance and reduce the length of the mass transport layer at the working electrode and minimize mass transport losses. While using flow-through systems is advantageous for improving the electrochemical performance and decreasing the treatment time, extra attention must be paid to minimizing back-pressure build-up during the operation by manipulating the electrode pore size and other system design parameters, such as the flow rate [170, 171]. In general, a higher conversion rate of the contaminant in question can be attained by lowering the flow rate ($i.e.$, increasing the residence time). The major trade-off with relatively lower flow rates is an overall loss in treatment capacity ($i.e.$, the lower output volume of treated effluent). Hence, it is critical to tune and optimize the flow of the wastewater into the electrochemical treatment cell depending on its specific configuration and tailored reaction pathways.

Considering industrial flow cell designs, an important piece of the stack is the flow field. The geometry of the flow field dictates the current density distribution, pressure distribution, product selectivity, and the total cell potential [172-174]. There are extensive studies on the flow patterns to minimize the voltage of the fuel cell while providing a steady output voltage, but few have investigated the impact of flow patterns on the cell performance in PEM electrolyzers [175, 176]. As wastewater has a complex combination of species, the flow pattern can even play a more important role in controlling parasitic reactions like OER (Removing oxygen gas from the cell). Another important aspect of the flow field is managing the pressure drop along the cell to get a higher collection rate from the electrolysis unit. In addition, the flow field geometry enables the wider flow rate control, which is crucial if we deal with various sources of wastewater matrices.

3.7 Advanced Experimental Characterization in Electrochemical Wastewater Treatment

Advanced analytical and theoretical techniques can be instrumental in discovering and designing high-performance electrocatalysts with superior selectivity and stability [177-179]. These tools also allow researchers to evaluate, characterize, and understand a delicate balance between desired $vs.$ parasitic reactions [180, 181]. Electrocatalytic measurements commonly leverage *ex-situ* characterizations, including electron microscopy ($e.g.$, scanning or transmission), and X-ray spectroscopy ($e.g.$, photoelectron spectroscopy) to characterize catalysts before and after the reaction. In addition, various electrochemical methods ($e.g.$, cyclic voltammetry, electrochemical impedance spectroscopy) are used to *ex-situ* inform the distinct features of the catalyst ($e.g.$, redox peaks, interfacial resistance) after the electrocatalytic treatment. These measurements provide helpful information on catalyst composition, structure, selectivity, and stability toward specific products. However, these techniques cannot provide a comprehensive picture of the electrocatalytic phenomena ($e.g.$, active sites of catalysts or structural changes during the electrochemical reaction) as the catalyst might undergo various changes during the redox reaction.

The state-of-the-art advances in *in-situ/operando* characterization techniques ($e.g.$, vibrational spectroscopy, X-ray spectroscopy) along with density functional theory (DFT) calculations can be leveraged to overcome some of the unique challenges facing electrochemical wastewater treatment, including but not limited to competing electrochemical reactions, fouling, scaling, and corrosion. In addition, *in-situ* and *operando* measurements offer invaluable information regarding parasitic/competing reactions that could only be captured during the treatment. *in-situ* and *operando* characterization techniques complement *ex-situ* measurements by directly connecting the catalyst's physical characteristics ($e.g.$, shape, composition, structure) to the electrocatalytic performance, including the selectivity of the desired reactions $vs.$ parasitic reactions and the stability, **Fig. 3.4**. Particularly noteworthy, the use of *in-situ* electrochemical Raman, infrared, and electron paramag-

netic resonance spectroscopy techniques has been demonstrated for some of the commonly used electrode materials ($e.g.$, boron-doped diamond) in electrochemical wastewater treatment.

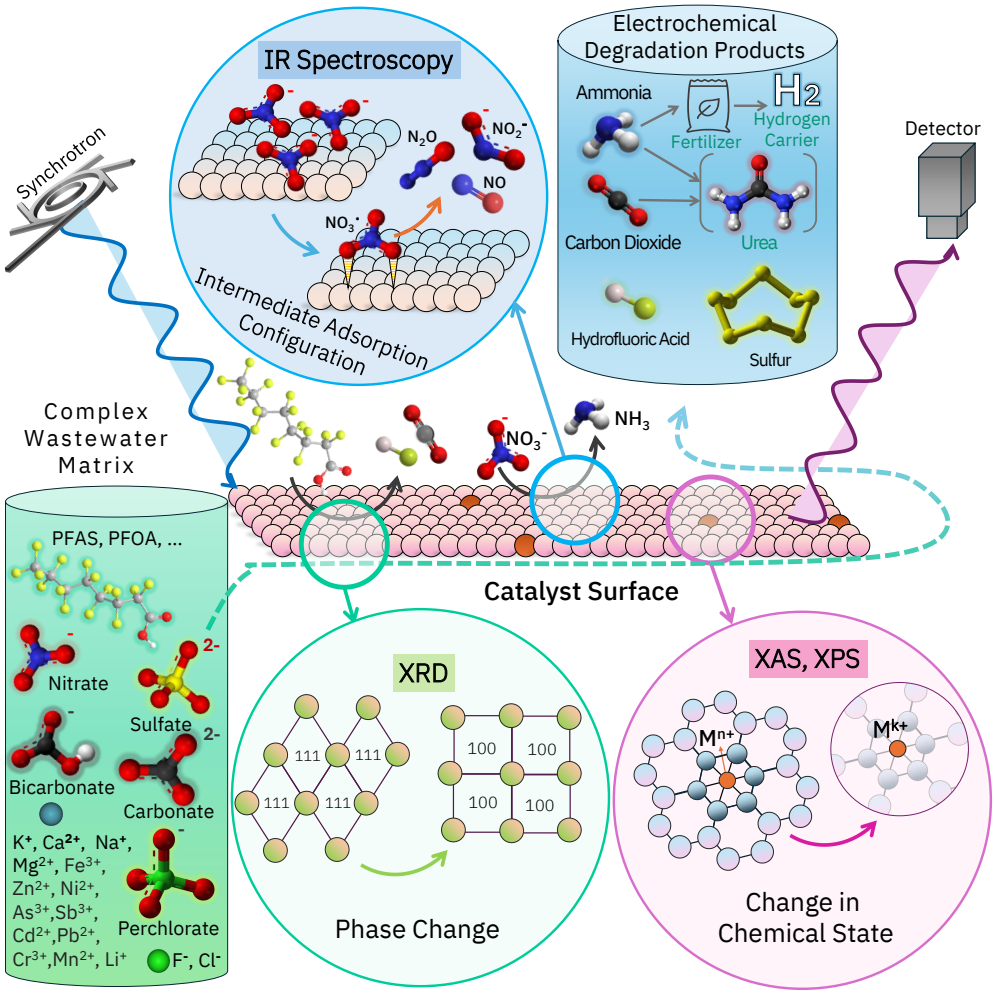

Figure 3.4: The degradation of various common anions and cations in the complex wastewater matrix can be monitored by *in-situ* characterization methods such as XRD, XAS, XPS, and IR spectroscopy. Understanding the intermediate adsorption configurations helps identify the reasons for the selectivity behavior of the catalyst. Specific nutrient recovery is possible by understanding this selectivity behavior. *in-situ* spectroscopy reveals phase change and chemical state change, providing information about the stability of the catalyst and guiding the future material designs.

The overarching goal is to distinguish the desired reaction pathways $vs.$ parasitic reactions on various catalyst materials, ultimately guiding the design and optimization of catalysts with improved performance. While the literature is still infancy in using *operando* spectroscopic techniques to identify reaction pathways in wastewater treatment, these techniques can be widely uti-

lized to determine parasitic reactions and mechanisms for deactivations in the electrochemical treatment of complex wastewater including various anions, cations and particularly heavy metals that can take part in parasitic reactions. The $in-situ$ spectroscopy can shed light on proper catalyst selection according to adsorption configurations, and aid us in redesigning the catalyst-wastewater interface towards more sustainable products for nutrient recovery along with pollutant degradations **(Fig. 3.4)**.

In-situ electrochemical Raman spectroscopy and *in-situ* IR spectroscopy allow monitoring of intermediate species during electrocatalytic treatment by identifying the chemical group of intermediates at the solid-liquid interface (**Fig. 3.4**) [182-184]. This can potentially inform how competing reactions play a role and impact the overall system performance. For instance, *operando* Raman spectroscopy revealed that carbon monoxide (CO) is an intermediate species during CO_2RR on the surface of Ag-covered Cu_2O nanowires [185]. In this tandem system, CO spills over from Ag sites to Cu sites, resulting in an improved C-C coupling to generate C_{2+} products in this hybrid system. Here, *operando* Raman spectroscopy contributed to identifying the desired reaction pathways. *Operando* Raman spectroscopy also helps to track down the local pH gradient near GDE in CO_2RR and inform various reaction pathways. As discussed earlier, the pH can alter the selectivity from desired reaction pathways to parasitic reactions. The same application is observed for nitrate (NO_3^-) reduction. Taking advantage of IR spectroscopy, we can investigate the intrinsic characteristics of catalyst and how it relates to N-O bond breaking to move nitrate reduction reaction to more favorable products such as ammonia (NH_3) instead of nitrous oxide (N_2O) and nitric oxide (NO) (**Fig. 3.4**) [186].

In addition, probe-based techniques ($e.g.$, X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS)) provide spatial resolution to investigate heterogeneous surfaces during electrocatalytic reactions [187]. These techniques provide insights into the local potential in an electric field gradient or probe differences in current density or rate of product generation to identify the active sites or the role of defects (**Fig. 3.4**). XPS is a technique that is sensitive to both the chemical environment and electrostatic potential. Core-level photoelectrons are elementally

specific and can often distinguish the oxidation state and the surrounding ligand environment. As these techniques can provide real-time catalyst surface modifications, they could be potentially useful in understanding the mechanisms by which the reaction pathway is dictated.

In-situ XAS can probe metal atoms' oxidation state and coordination environment at or near reaction conditions, allowing for more accurate structure-selectivity relationships than *ex-situ* methods [188-190]. The main limitation of this technique comes in surface sensitivity, as XAS probes bulk and surface atoms, and bulk signals may interfere with those from the surface. This lack of surface sensitivity can be mitigated if catalysts used are those with small metal clusters or single-atom active sites, as in these cases, most or all metal atoms are on the surface [188]. Similar to *in-situ* XPS, in-situ XAS can be leveraged to connect the catalyst's real-time information to the reactions selectivity (desired $vs.$ parasitic) and performance [191]. *In-situ* XAS can also be used to identify the deactivation mechanisms of the catalyst during the electrochemical treatment ($e.g.$, fouling). *In-situ* XRD (X-ray crystallography) provides valuable insights into the alternation of catalyst phase and structure during complex redox reactions (**Fig. 3.4**). *In-situ* electrochemical electron paramagnetic resonance (EPR) spectroscopy is another powerful technique that provides unparalleled information regarding radicals and species with unpaired electrons during the electrochemical treatment, which can also regulate the reaction pathways.

3.8 Theoretical Characterization in Wastewater Treatment

In addition to experimental studies with the ability to predict pollutant degradation mechanisms [192], theoretical tools are becoming more viable as complementary study tools [193]. Due to the complexity of the wastewater matrix, assessing the reaction mechanisms, catalyst activity, stability, reaction kinetics, and the effect of environmental variables like pressure and temperature is challenging when using solely experimental studies. Theoretical studies such as density functional theory (DFT), molecular dynamic simulations (MD), and Machine learning techniques (ML) can aid us through a better understanding of redox reactions and their interaction with the catalytic material, and other wastewater species (**Fig. 3.5**).

Various variables dictate the cell voltage (potential losses and overpotentials), catalyst activity and stability (**Fig. 3.5A**) of electrolysis cells for wastewater treatment. Machine learning algorithms provide insights into how parasitic reactions, fouling, and catalyst leaching affect the catalytic activity, aiding us in finding the prominent catalyst according to the wastewater composition and the desired products [194]. At the same time, machine learning provides tools for a more controlled wastewater treatment process due to its ability to capture the degradation variables and their computational effectiveness [195]. Artificial Neural Networks (ANNs) have been extensively used in wastewater treatment systems to optimize the freshwater quality and recovery of precious compounds and nutrients [196-198]. The recognition of parasitic reactions and their deteriorating impact on Faradaic efficiency for nutrient recovery reactions like ammonia and sulfur recovery can be modeled and learned through ML methods [199]. This in addition to the ability to foresee the most optimized cell design, flow through or flow by, membrane or membrane-less, the thickness of the membrane, gas diffusion layer, and other design parameters can help us minimizing losses in the whole recovery system instead of only looking at catalyst and electrolyte interactions as we will discuss for DFT and MD simulations [199]. Neural networks offer the advantage of stability analysis for both the catalyst and the stack [200]. Variables like temperature, wastewater pH, corrosive species in the wastewater, and their concentration, and in general, the electrolyte composition can affect the useful life of the catalyst, membrane, and flow fields. Having a tool to predict the

electrolysis system's projected functionality can aid us in achieving better manufacturing plans and performing a more accurate techno-economic analysis for these systems. It can also help integrate essential tools for a well-studied control of variables with drastic effects on the system's life, like introducing a pH control system.

DFT calculations and microkinetic analysis could help correlate the binding energy of the reaction intermediates on the catalyst surface and identify the activation barriers concerning the reaction energies (**Fig. 3.5B**) [201, 202]. Gaining this information is critical for designing catalyst materials, which can promote desired reaction selectivity and suppress the parasitic reactions. For example, in electrochemical nitrate reduction reactions on Fe single atom sites, by calculating adsorption binding energies, DFT calculations uncovered how Fe sites can suppress N-N coupling and improve N* hydrogenation to produce NH_3. For catalytic reactions involving multiple reaction intermediates, the scaling relations indicate that the binding energies of different intermediates are strongly correlated, limiting the possibilities of finding active and selective catalysts by separately optimizing each elementary step. Overcoming this limitation requires decoupling the binding energies of different intermediates, possibly by constructing active sites that can bind various reaction intermediates in different ways or selectively stabilizing some of the reaction intermediates via some external mechanism. Overall, DFT could be a powerful computational tool to unravel the mechanisms that enable the design of new catalysts for electrochemical wastewater treatment and identify various reaction pathways, including desired and parasitic reactions.

MD simulation enables temperature-dependent simulations aiding catalyst, and electrolyte interaction studies. In higher temperatures, the possibility of forming new active sites, enhanced kinetics, catalyst structure alternations, and their effect on the favorable redox reactions can enhance our understanding of the degradation process of complex molecules like PFOA and PFAS [193]. Observing a complex environment including the electrode and catalyst surface, gives us a tool for predicting the active sites and adsorption configurations on the catalyst surface. This knowledge can further facile the ROS radicals formation at electrode surfaces by optimizing the catalyst structure and kinetics (**Fig. 3.5C**).

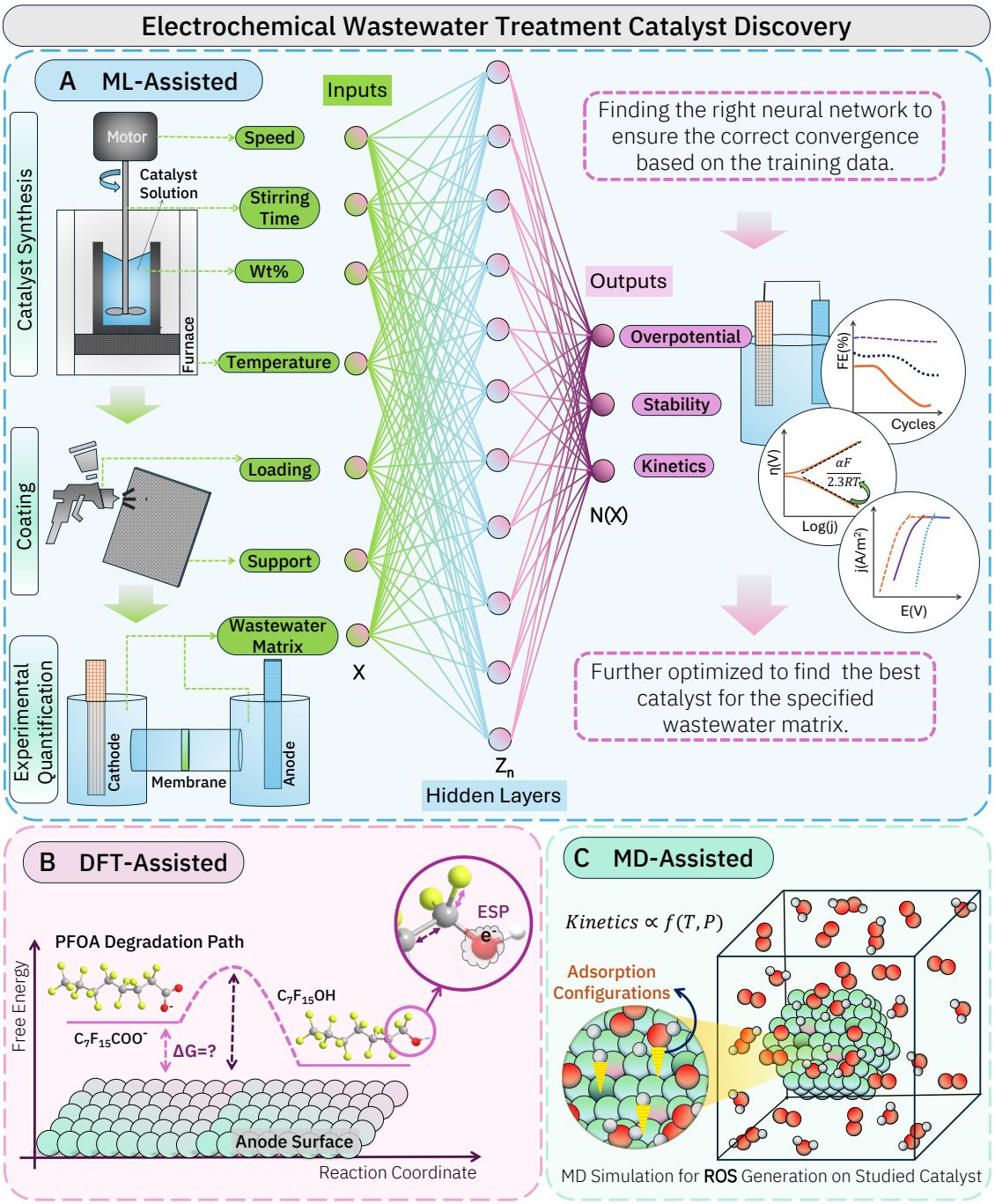

Figure 3.5: A) Using machine learning to predict optimal catalyst synthesis method, material, and coatings based on the wastewater matrix, required kinetics, stability, and cell voltage (Overpotentials), B) DFT calculations are used to predict the degradation mechanisms, C) Using molecular dynamics (MD) modeling helps understand the catalyst interaction with the solution, identifying active sites, adsorption configurations, and kinetics of the catalyst.

Chapter 4

Results and Discussion

4.1 Fabrication of Titanium oxides nanotubes (TiOxNTs) on Titanium mesh

In order to be sure that the surface of the Titanium (Ti) mesh is free of contaminants, a pristine Ti mesh was first sonicated in water, acetone and ethanol for 10 minutes each respectively. The cleaned Ti mesh was anodized to create the amorphous TiOxNTs. Platinum was used as the counter electrode in 30 ml of Ethylene Glycol electrolyte containing 2.0 weight percent water and 0.25 weight percent Ammonium Fluoride at a steady voltage of 30 V for three hours. After the anodization process, the anodized Ti mesh was rinsed with ethanol and Deionized water to get rid of any remaining electrolyte, and was put through a two-step reduction procedure. In the initial reduction, a 15 mL 0.5 M Sodium borohydride solution was used for chemical reduction for 8 hours. The resulting mesh was then dried at room temperature after being cleaned three times with Deionized water. The second reduction was carried out by utilizing a tube furnace to thermally anneal nanotube modified Ti mesh at 450 °C for three hours (heating rate of 5 °C per minute to reach 450 °C) in an environment of 95 percent Argon gas and 5 percent Hydrogen gas.

4.2 Treatment Electrolysis

The performance of the TiOxNTs electrode was tested for degradation on different PFAS pollutants namely: Pefluorooctanoic acid (PFOA), Perfluorooctanesulfonic acid (PFOS), Perfluorobutanoic acid (PFBA), and Aquous film forming foam (AFFF) from San Diego, California. The TiOxNT electrodes was applied as Anode and Cathode so as to study oxidation and reduction, while Ag/AgCl (saturated KCl) was used as a reference electrode.

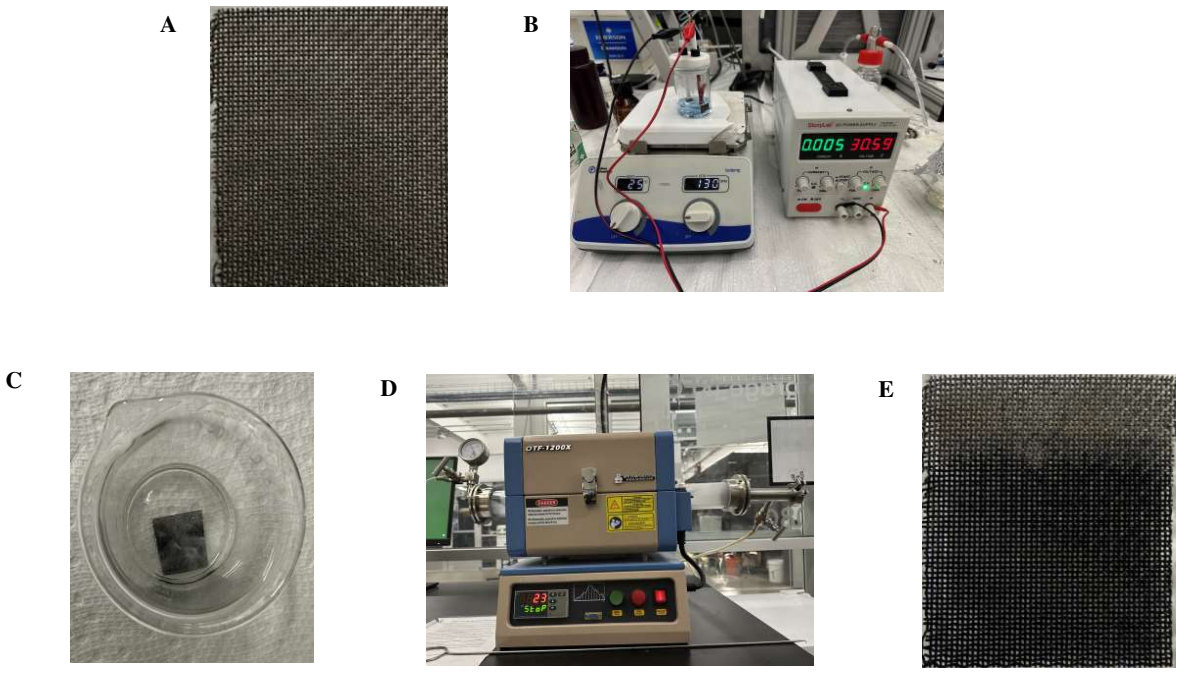

Figure 4.1: Synthesis of Titanium oxide nanotubes (TiOxNTs) on Titanium mesh A) Pristine Ti mesh, B) Anodization process, C) Chemical reduction in Sodium borohydride, D) Annealing in a tube furnace, E) TiOxNTs on Ti mesh after Annealing

4.2.1 PFAS Electrochemical treatment

Electrochemical treatment of 10 ug/L of PFOA, PFOS, and PFBA in 0.5 M Na_2SO_4, and also AFFF mixed with Na_2SO_4 electrolyte in ratio 10 to 90 showed that the TiOxNTs electrode prepared through the two-step reduction method exhibited excellent PFAS degradation performance. **(Fig 4.2)** showed the comparison between the perfomance of TiOxNTs and Platinized Titanium (Pt-Ti) used as anodes and Stainless steel (SS) as cathode Under a constant current density of 75 mA/cm^2, the cyclic voltammetry (CV) evolution shows that the TiOxNTs anode surface is altered during PFOA degradation, with both reductive and oxidative processes being amplified following operation. This could be related to modifications in the material's surface chemistry, intermediate adsorption, or electrochemical activation. Although as seen in **(Fig. 4.2b)** the TiOxNTs anode shows symptoms of altering electrochemical behavior over prolonged operation, it has respectable short-term stability.

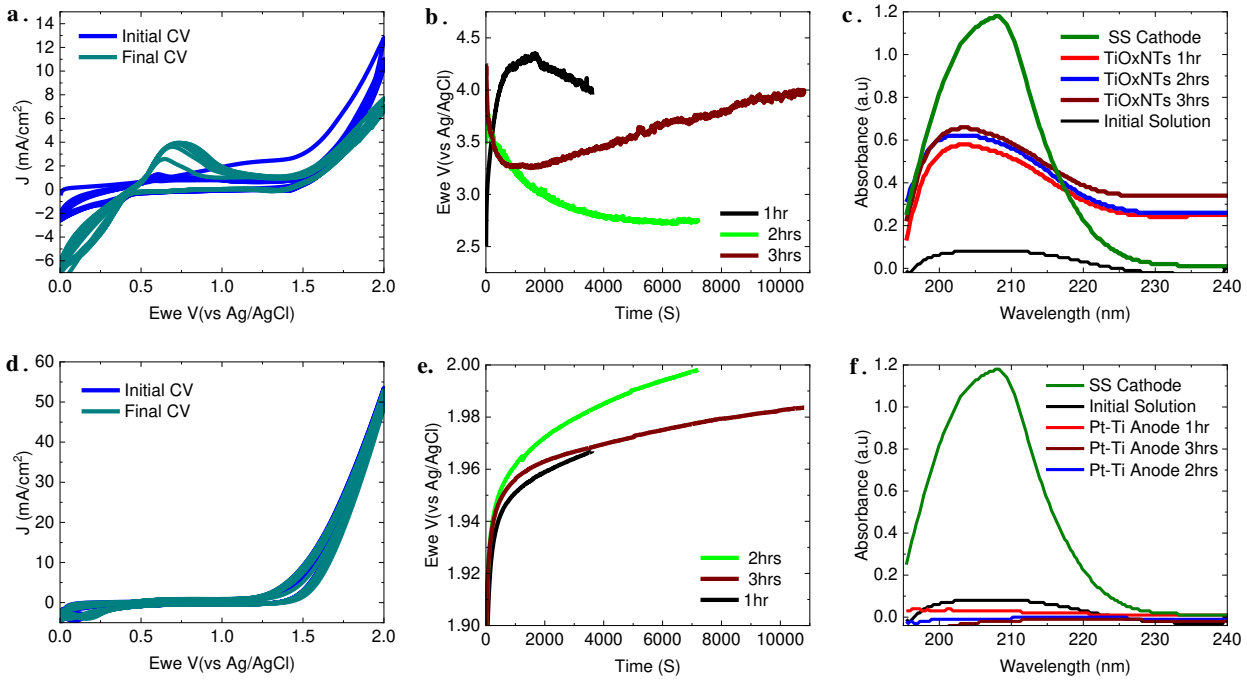

Figure 4.2: a) Cyclic voltammetry (CV) of TiOxNTs, b) Chronopotentiometry (CP) of TiOxNTs, c) UV-Vis of TiOXNTs anode and SS cathode, d) Cyclic voltammetry (CV) of Pt-Ti, e) Chronopotentiometry (CP) of Pt-Ti, f) UV-Vis of Pt-Ti anode and SS cathode

The possible patterns imply that the necessary driving potential changes over time due to surface processes and solution chemistry. Periodic electrode reactivation or potential adjustment may be required for practical PFOA degradation in order to sustain efficiency over extended runs. PFOA breakdown and/or transformation is confirmed by UV-Vis analysis **(Fig. 4.2c)**, however prolonged electrolysis periods cause a buildup of UV-active intermediates. PFOA can be effectively degraded by the TiOxNTs anode, however in order to accomplish full mineralization and prevent the accumulation of absorbent byproducts, the process may need to be optimized. The SS cathode sample's notable absorbance emphasizes how reduction reactions contribute to the formation of observable unsaturated intermediates. When it comes to PFOA breakdown, the platinized titanium anode shows excellent stability and electrochemical inertness **(Fig. 4.2 d-f)**. Instead of direct electrochemical oxidation of PFOA through electron transfer on the Pt surface within the investigated potential range, the degradation process most likely takes place via indirect oxidation mechanisms (e.g., mediated by hydroxyl radicals from water oxidation). This stability of Pt-Ti is advantageous

for long-term operation but may imply lower electrocatalytic activity toward direct PFOA oxidation compared to more active, but less stable, electrodes like TiOxNTs nanotubes. When combined with a stainless steel cathode, the Pt-Ti anode performs exceptionally well for PFOA degradation, removing nearly all UV-absorbing species in a matter of hours **(Fig. 4.2f)**. This suggests deep and efficient mineralization, which makes it a viable solution for long-term pollution removal. Thus Pt-Ti performed better for full PFOA mineralization and steady long-term operation while TiOxNTs provide a programmable and active surface for applications where less expensive materials are needed and intermediate byproducts can be controlled downstream, but there are trade-offs in electrode stability and degradation completeness.

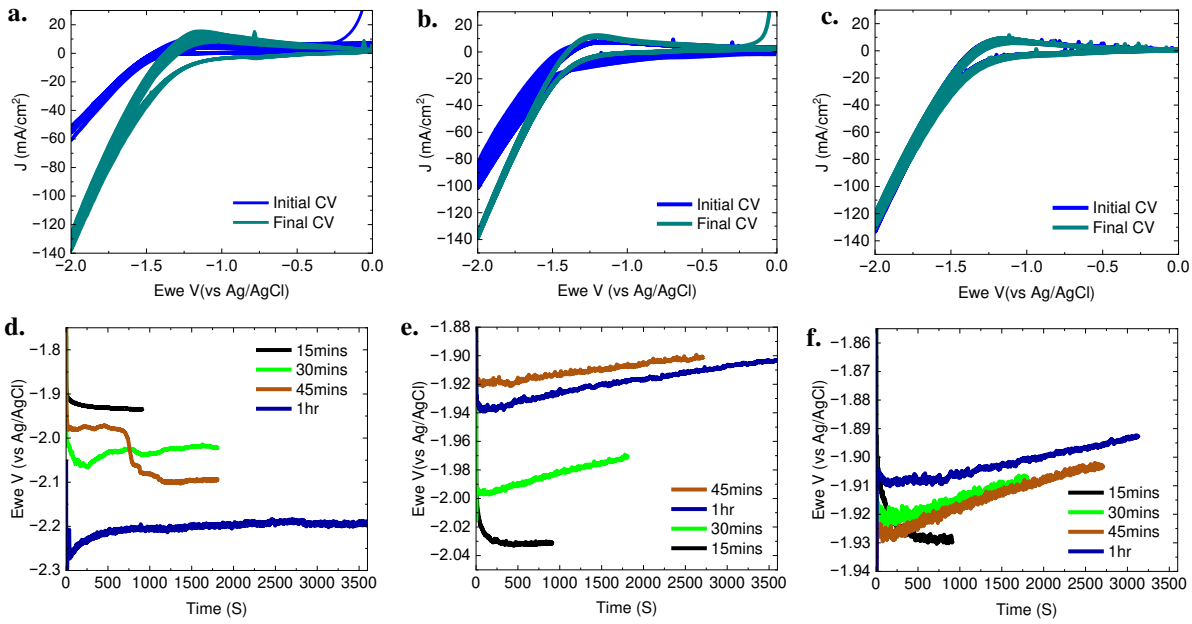

Figure 4.3: a) Cathodic reduction CV of TiOxNTs for PFOA b) Cathodic reduction CV of TiOxNTs for PFOS c) Cathodic reduction CV of TiOxNTs for PFBA d) Chronopotentiometry of TiOxNTs for PFOA. e) Chronopotentiometry of TiOxNTs for PFOS. f) Chronopotentiometry of TiOxNTs for PFBA.

The stability and degradation ability of TiOxNTs in cathodic reduction was also studied. **(Fig. 4.3)** shows the electrochemical data of TiOxNTs as cathode and Ruthenium-Iridum-Titanium (Ru-Ir-Ti) anode, a mixed metal oxides (MMO) electrodes that are more dimensionally stable.

During PFAS degradation, the TiOxNTs cathode experiences strong electrochemical activation **(Fig. 4.3a-c)**, which significantly increases its ability to drive reduction processes. Through enhanced reductive pathways that complement the oxidative reactions at the anode, this activation may increase the overall degradation efficiency. The material has dynamic electrochemical behavior that changes while it operates, which may be useful for adjusting to shifting reaction circumstances during the degradation of pollutants. During PFOA reduction, the TiOxNTs cathode displays time-dependent electrochemical behavior, short runs less than 30 min display cathodic activation i.e a decreasing overpotential, while a Longer runs 45 minutes to 1 hour show a more complicated evolution in the form of surface conditioning and fouling or intermediate accumulation **(Fig. 4.3d)**. The TiOxNTs cathode exhibits outstanding operational stability for PFOS and PFBA, especially in longer runs 45 min and 1 hour where the potential stays almost constant **(Fig. 4.3 e, f)**. The more erratic behavior observed during PFOA reduction is in contrast to this. TiOxNTs are a suitable cathode material for the long-term treatment of sulfonated and short chain PFAS compounds because the results indicate that PFOS and PFBA electroreduction on these nanotubes is a surface-mediated process that stabilizes over time. The UV-Vis data **(Fig. 4.4a)** for the TiOxNTs shows a much higher absorbance at all wavelengths, suggesting that UV-absorbing intermediates are formed when only the cathode is active perhaps in a control experiment or distinct condition. This demonstrates once more how reductive pathways contribute to the production of aromatic and conjugated byproducts or intermediates. According to the ion chromatography data **(Fig. 4.4b-d)** PFOA undergoes reductive breakdown at the TiOxNTs cathode, producing ionic compounds particularly fluoride that boost solution conductivity. For PFOS, sulfate, fluoride, and other ionic fragments were released in a time-dependent manner, an identical defluorination efficiency is suggested by the conductivity trend, which is identical to that of PFOA. This suggest that TiOxNTs are an effective cathode material for the reductive degradation of long-chain carboxylate and sulfonate PFAS, with performance increasing with time as a result of electrochemical activation as seen in the CV and producing quantifiable mineralization products.

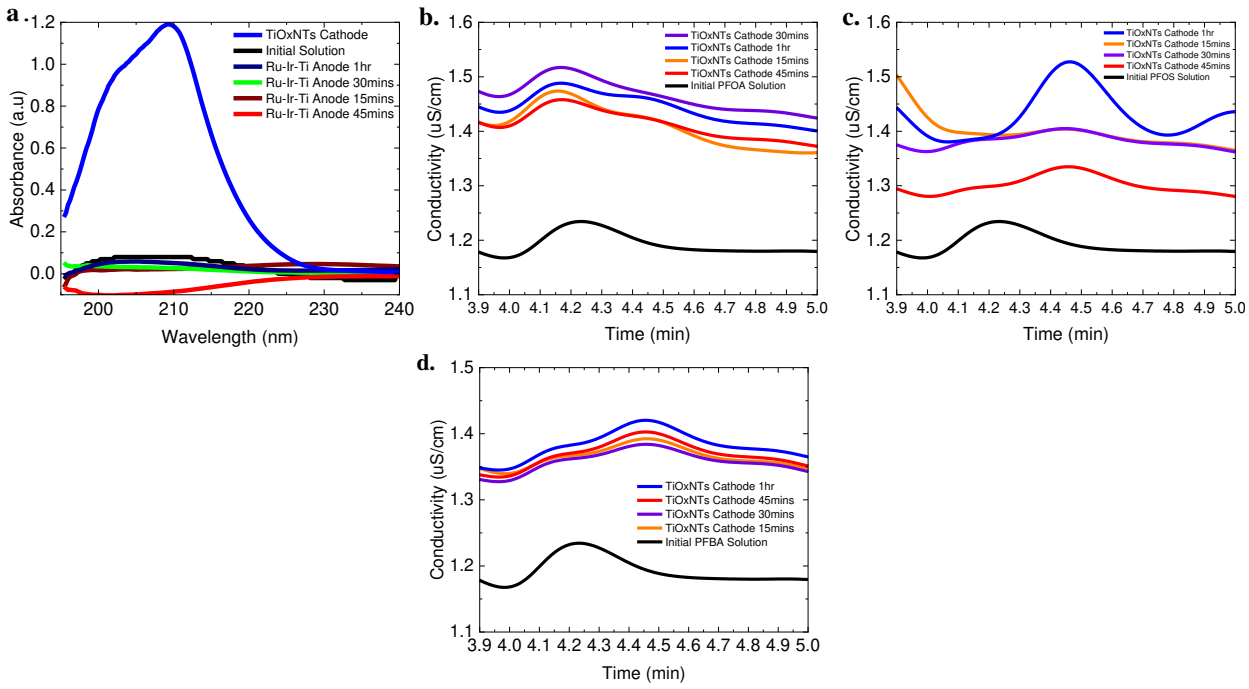

Figure 4.4: a) UV-Vis for PFOA with TiOxNTs Cathode b) Ion Chromatography for PFOA with TiOxNTs Cathode c) Ion Chromatography for PFOS with TiOxNTs Cathode d) Ion Chromatography for PFBA with TiOxNTs Cathode.

The slight rise in solution conductivity even after one hour of treatment shows that the TiOxNTs cathode is far less successful in degrading PFBA than longer-chain PFAS (PFOA, PFOS). This indicates that PFBA is more resistant to reductive defluorination on TiOxNTs surfaces under the investigated conditions and is consistent with electrochemical results demonstrating stable cathode behavior. The outcome reveals a significant drawback that cathode-based reduction might be less appropriate for short-chain PFAS remediation, potentially necessitating the use of alternative materials, potentials, or combined anodic-oxidative techniques.

4.2.2 Batch cell electrolysis of Aqueous film-forming foams (AFFFs)

The electrochemical stabilty and degradation ability of the synthesized TiOxNTs was tested on AFFFs contaminated ground water obtained from San Deigo, CA. In order to enhance its conductivity, AFFFs contaminated ground water was mixed with sodium sulfate solution in ratio 10:90. The TiOxNTs anode exhibits strong stability and no discernible electrochemical surface changes When treating complex AFFF-contaminated groundwater **(Fig. 4.5a)**. Although during prolonged electrolysis, the TiOxNTs anode undergoes progressive passivation. **(Fig. 4.5b)**. This shows that the material deactivates with time under fixed current settings, most likely as a result of fouling or surface blockage by degradation byproducts. Periodic cleaning or possible cycling may be required for long-term therapy applications in order to restore activity.

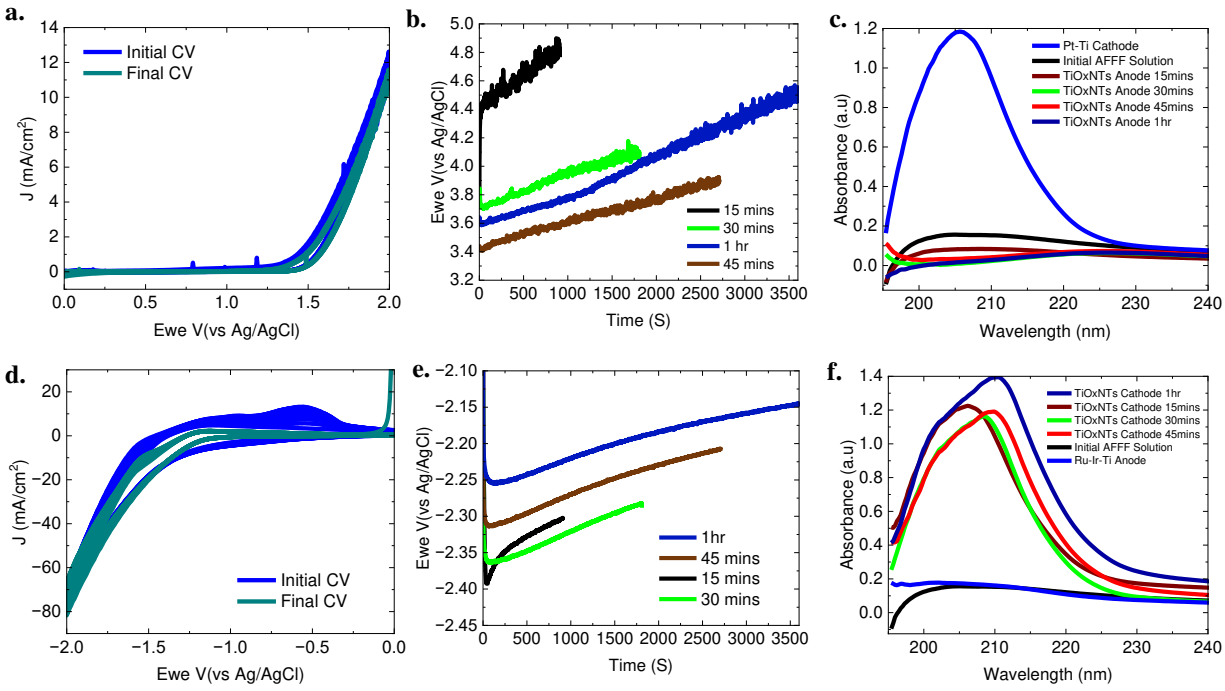

Figure 4.5: a) CV for AFFFs-contaminated ground water with TiOxNTs as Anode b) CP for AFFFs-contaminated ground water with TiOxNTs as Anode c) UV-Vis for AFFFs-contaminated ground water with TiOxNTs as Anode d) CV for AFFFs-contaminated ground water with TiOxNTs as Cathode e) CP for AFFFs-contaminated ground water with TiOxNTs as Cathode f) UV-Vis for AFFFs with TiOxNTs as Cathode.

As seen in **(Fig. 4.5c)** the TiOxNTs is highly effective When treating groundwater contaminated by AFFF, quickly eliminating UV-absorbing organic pollutants without causing intermediates to build up. This suggests successful deep oxidation, which makes it a potential anode material for groundwater remediation affected by PFAS in the real world. When treating AFFF-contaminated groundwater, the TiOxNTs as cathode shows strong stability and no electrochemical surface alterations during operation **(Fig. 4.5d)** and since the cathode continues to function consistently, this is advantageous for long-term field application. During the prolonged reduction of AFFF-contaminated groundwater, the TiOxNTs cathode undergoes significant time-dependent polarization, necessitating increasingly higher potentials to maintain constant current **(Fig. 4.5e)**. This suggests that groundwater elements (ions, organics, precipitates) are probably the source of operational fouling or passivation. Long-term field applications where frequent cleaning or polarity reversal may be required should take into account the cathode surface's deteriorating practical performance under fixed current, even while it remains electrochemically stable in terms of CV response.

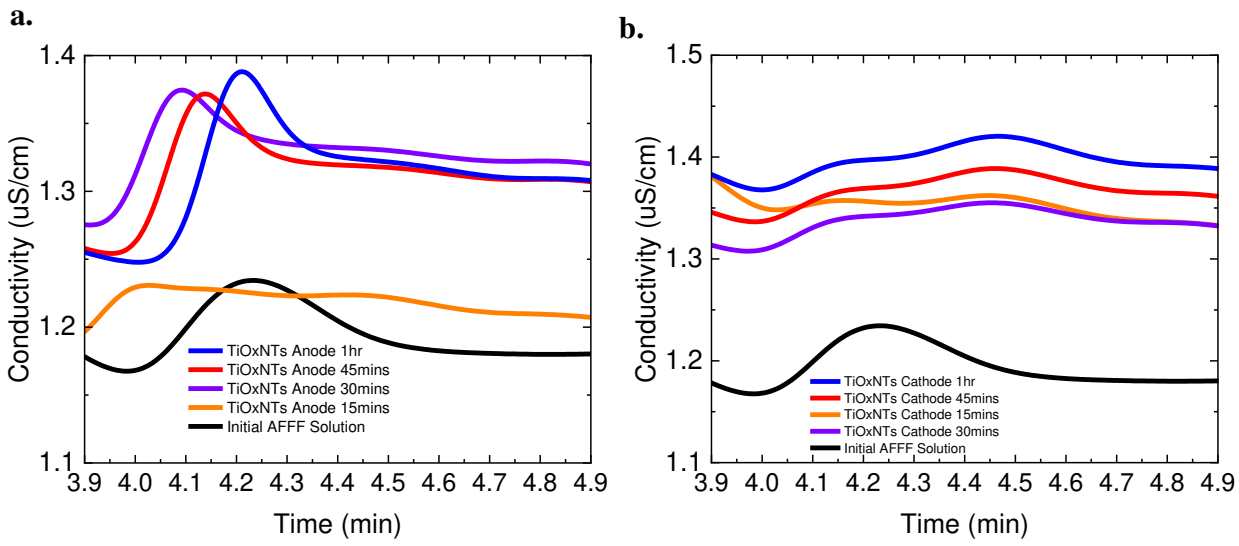

Figure 4.6: a) Ion Chromatography for AFFFs-contaminated ground water with TiOxNTs as Anode b) Ion Chromatography for AFFFs-contaminated ground water with TiOxNTs as Cathode.

When treating groundwater contaminated with AFFF, the TiOxNTs cathode generates and accumulates UV-absorbing intermediates; longer operation times result in more accumulation **(Fig. 4.5f)**. This highlights the requirement for mixed oxidative treatment (e.g., with an active anode like Ru-Ir-Ti) to accomplish complete mineralization and prevent possibly more harmful byproducts.

TiOxNTs efficiently breaks down AFFF pollutants without noticeably raising the solution conductivity **(Fig. 4.6a)**, indicating that the degradation products are either gaseous, precipitated, or adsorbed rather than discharged as soluble ions. This is quite beneficial for ground water because it prevents raising the salinity of the water, and fosters effective cleanup. It was observed that through reductive defluorination, the TiOxNTs cathode efficiently breaks down AFFF impurities, releasing ionic species in the form of organic acids and fluoride **(Fig. 4.6b)** that boost solution conductivity in a time-dependent way. This implies that cathode-only treatment may deteriorate water quality in terms of ionic content, requiring downstream polishing for instance adsorption, precipitation for fluoride removal, even though it also confirms PFAS mineralization.

4.2.3 Batch electrochemical treatment of PFOA prepared in methanol

PFAS is an amphiphilic molecule with the fluorinated tail of its long-chains extremely hydrophobic and poorly soluble in water, which causes micelles or aggregates to form. These hydrophobic tails are efficiently solvated by methanol, guaranteeing a completely homogeneous solution and preventing the molecules from aggregating, which would otherwise lead to imprecise concentration measurements during experimental aliquoting. PFOA stock solution was prepared using methanol and 10ug/L was mixed with 0.5 M sodium sulfate. This was degraded through anodic oxidation and cathodic reduction using TiOxNTs. The current density in the initial CV is comparatively low for the majority of the potential window, suggesting that there is little electrochemical activity at the surface of the new TiOxNTs **(Fig. 4.7a)**. However, the final CV's increased current indicates that the electrode surface becomes more electrochemically active throughout operation, possibly as a result of surface conditioning, modifications to the chemistry of the nanotube, or interaction with degradation intermediates.

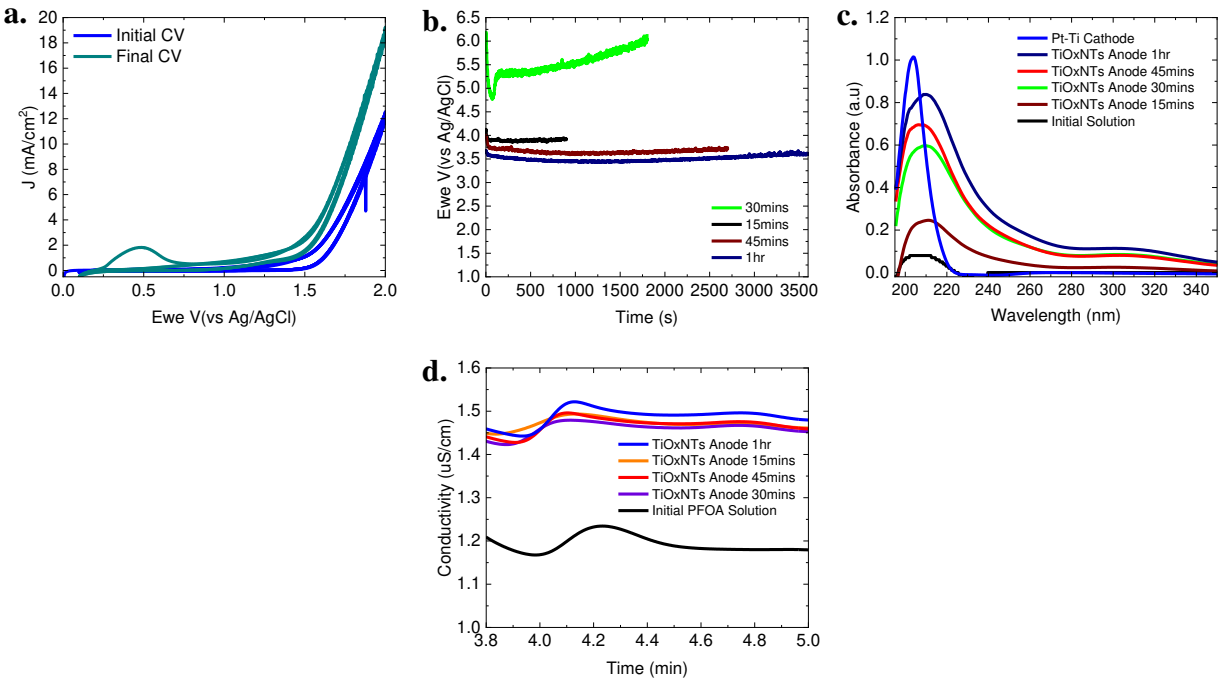

Figure 4.7: a) CV for PFOA solution prepared in Methanol with TiOxNTs as Anode b) CP for PFOA solution prepared in Methanol with TiOxNTs as Anode c) UV-Vis for PFOA solution prepared in Methanol with TiOxNTs as Anode d) Ion Chromatography for PFOA solution prepared in Methanol with TiOxNTs as Anode.

The potential variations **(Fig. 4.7b)** show dynamic interactions between the electrode and the pollutant, with temporary passivation followed by stability as degradation advances. There is a noticeable rise in absorbance in the 200–230 nm range while electrolysis continues (15, 30, 45, and 1 hour) **(Fig. 4.7c)**, and intensity increases with time. This suggests the production of UV-absorbing degradation intermediates at the TiOxNTs surface, which are probably shorter-chain perfluorocarboxylates, fluorinated fragments, or transitory organic species produced by radical-driven oxidation pathways. The successive spectrum shifts signal that PFOA is not only eliminated but is instead undergoing a series of defluorination and breakdown processes that result in intermediate compounds prior to additional mineralization. The solution conductivity rises dramatically as the TiOxNTs Anode promotes the mineralization of the parent PFOA molecule probably by hydroxyl radical production or direct electron transfer. The successful release of smaller ionic species, such as fluoride ions and shorter-chain perfluoroalkyl acids, into the bulk solution is suggested by the

upward shift observed in all treated samples **(Fig. 4.7d)**. After one hour of treatment, the maximum conductivity is reached (blue line), suggesting that lengthier anodic oxidation results in more degradation and a higher concentration of these mobile ions.

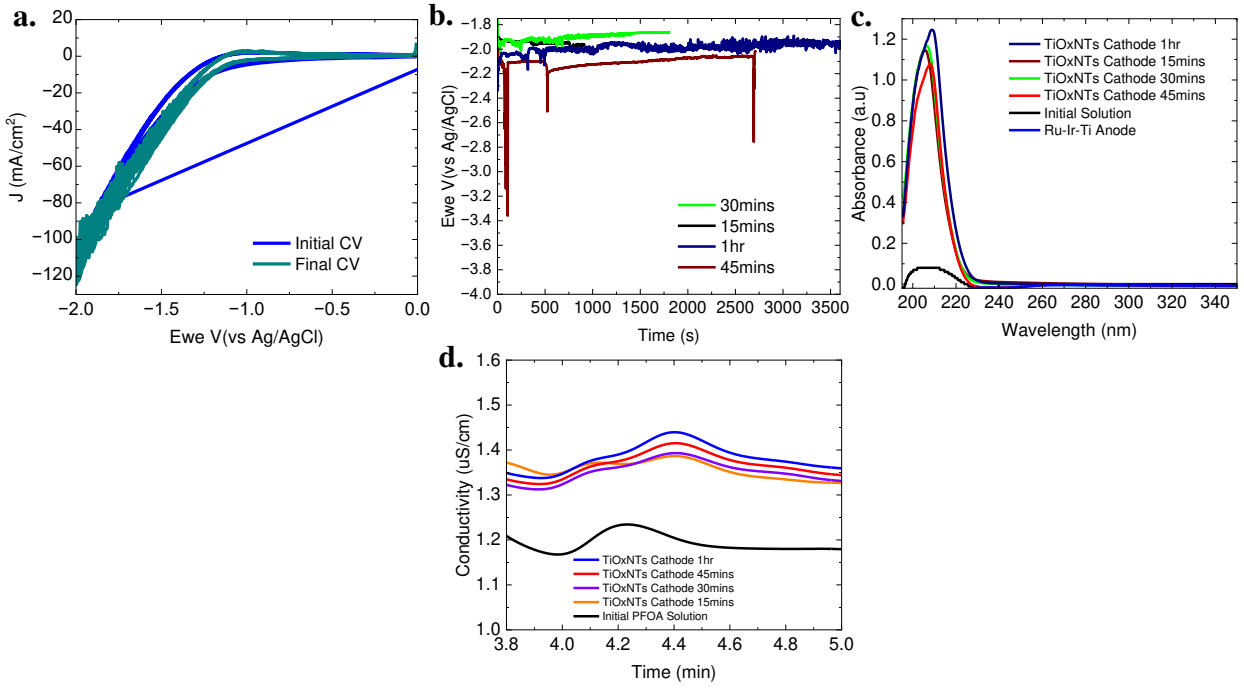

Figure 4.8: a) CV for PFOA solution prepared in Methanol with TiOxNTs as Cathode b) CP for PFOA solution prepared in Methanol with TiOxNTs as Cathode c) UV-Vis for PFOA solution prepared in Methanol with TiOxNTs as Cathode d) Ion Chromatography for PFOA solution prepared in Methanol with TiOxNTs as Cathode.

The CV showed a strong cathodic current at negative potentials **(Fig. 4.8a)**, the primary reduction events in this area are probably dominated by hydrogen evolution (HER), which are important to aid in the breakdown of PFOA. At every point in time (15, 30, 45, and 1 hour), the cathode mostly functions between -1.9 and -2.2 V versus Ag/AgCl **(Fig. 4.8 b)**. This demonstrates that TiOxNTs maintain the highly reducing conditions necessary for the breakdown of PFOA. The overall potential response is constant despite slight fluctuations, indicating that the TiOxNTs cathode retains a respectable level of stability when the current is constant. A prominent absorbance band, typical of PFOA and similar fluorinated organic compounds, is seen in all samples at approximately 200–215 nm **(Fig. 4.8c)**. Electronic transitions linked to the carbon–fluorine functional

groups are represented by this area. From 15 minutes to 1 hour, the absorbance intensity stays relatively constant, suggesting that PFOA is either only slowly broken down or that UV-Vis is not very sensitive to its change. Changes may be obscured by degradation intermediates that absorb in the same area because PFOA lacks strong chromophores. When compared to treated cathode samples, the "initial solution" exhibits extremely low absorbance, which may indicate the creation of UV-active byproducts or scattering effects during electrochemical operation. The increase in conductivity over all treatment intervals **(Fig. 4.8d)**, shows that the parent PFOA molecule is undergoing reductive breakdown and releasing ions like fluoride (F^-) and smaller perfluoroalkyl fragments. Significantly, the conductivity peak is largest for the 1-hour treatment (blue line), indicating that longer cathodic residence durations increase the degree of deterioration. Curiously, the cathode sample peaks show a tiny shift in time (around 4.4 minutes) when compared to the initial solution peak (4.2 minutes). This is probably due to the treated solution's altered ionic strength and chemical composition as the breakdown products manifest.

4.3 Liquid Chromatography Tandem Mass Spectrometry LC-MS/MS

In order to elucidate degradation pathways, confirm the selectivity of TiOxNTs and identify transient intermediates, advanced spectroscopic and chromatographic techniques was used i.e. Liquid chromatography tandem mass spectrometry (LC-MS/MS). TiOxNTs were used as the anodic and cathodic materials to investigate the electrochemical breakdown of PFAS. To assess the degradation efficiency and mechanistic behavior of TiOxNTs against PFAS oxidation and reduction, PFOA and PFOS concentrations were measured over time using LC-MS/MS. Electrolysis was carried out on real wastewater matrix; AFFF-contaminated ground water which contain most of the legacy PFAS in different concentrations for 60 minutes at a constant applied current of 100 mA after the initial concentration of PFOA and PFOS in the solution were determined to be 2.58 µg/L and 12.457 µg/L respectively. When TiOxNTs are used as the anode during electrochemical treatment at 100 mA, the LC-MS/MS results indicate a non-monotonic but generally declining trend

in PFOA content. At first, there was 2.58 µg/L of concentration. The observed concentration rose to 3.57 µg/L after 15 minutes and then significantly dropped to 1.43 µg/L after 30 minutes. At 45 minutes, there was a second increase (5.40 µg/L), and at 60 minutes, the concentration eventually decreased to 1.28 µg/L **(Fig. 4.9a)**. The final concentration, in relation to the initial concentration, reflects about 50% overall elimination, notwithstanding the oscillations. The transient increases suggest that dynamic transformation mechanisms, as opposed to straightforward first-order decay, are responsible for the system behavior. The oxidation of precursor chemicals found in AFFF-contaminated groundwater is probably what caused the initial spike at 15 minutes. Fluorotelomer sulfonates and other PFAS precursors that can electrochemically change into terminal PFOA under oxidative circumstances are found in several AFFF compositions. As a result, early anodic oxidation may produce more detectable PFOA, momentarily increasing its concentration. The steep drop seen at 30 minutes indicates that direct oxidation of PFOA takes over after precursor conversion slows. The ensuing 45-minute rise could be the result of redistribution from intricate groundwater matrices, desorption of surface-bound PFOA from the TiOxNT surface, or ongoing precursor-to-PFOA transformation. The lowest observed concentration occurs after 60 minutes when deterioration once more outpaces production.

Degradation most likely occurs through electro-decarboxylation under anodic polarization, in which the carboxylate group directly transfers electrons to produce CO_2 and a perfluoroalkyl radical. The perfluorinated carbon chain is gradually shortened by subsequent radical reactions, producing shorter-chain perfluorocarboxylic acids such PFHpA, PFHxA, PFPeA, and PFBA. Oxidative transformation may also be facilitated by hydroxyl radicals that are surface-bound. The brief concentration rebound after 45 minutes most likely represents dynamic adsorption–desorption equilibrium or the conversion of intermediate species back into detectable PFOA-like fragments. CO_2 and fluoride ions are ultimately anticipated to be produced by gradual mineralization, with fluoride release acting as proof of C–F bond breaking. Due to advantageous interfacial electron transport and the inhibition of competing oxygen evolution, oxidative decarboxylation and radical-

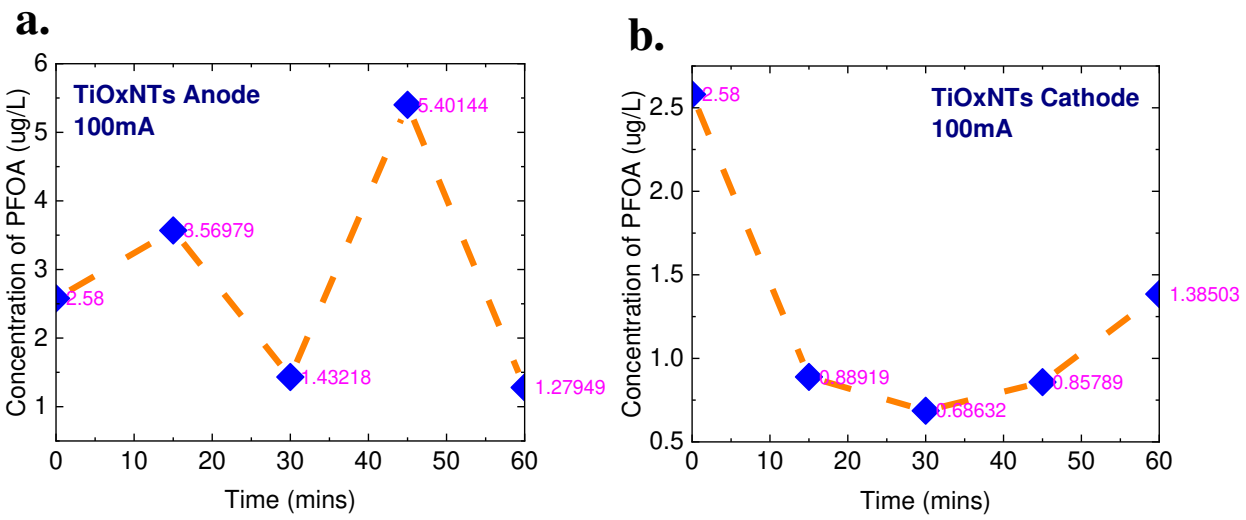

Figure 4.9: a) Degradation profile of PFOA in AFFF-contaminated ground water showing concentration against time with TiOxNTs as Anode b) Degradation profile of PFOA in AFFF-contaminated ground water showing concentration against time with TiOxNTs as Cathode.

mediated chain scission appear to dominate the anodic process, exhibiting significant selectivity toward carboxylated PFAS.

Degradation was considerably faster when TiOxNTs are used as the cathode during electrochemical treatment at 100 mA, within 15 minutes, the starting concentration of 2.58 µg/L decreased to 0.889 µg/L, representing around 65% clearance. After 30 minutes, the concentration dropped even more to 0.686 µg/L, which is around 73% of the original level. At 45 minutes, there was a small increase (0.858 µg/L), but at 60 minutes, there was a more pronounced rise (1.385 µg/L) **(Fig. 4.9b)**. The final concentration still shows about 46% total elimination from the initial concentration notwithstanding this comeback. The general pattern points to quick initial degradation followed by dynamic equilibrium between desorption, transformation, and potential precursor conversion. Effective PFOA adsorption and reductive activation at the cathodically polarized TiOxNT surface are shown by the substantial initial drop. High surface area and interfacial electron transport are made possible by the nanotubular shape. The electron-deficient perfluorinated chain of PFOA can

take on electrons to create a radical anion intermediate when subjected to cathodic bias. Because the powerful electron-withdrawing fluorine atoms stabilize transitory radical entities and allow for subsequent bond breaking, this reductive activation phase is essential. Desorption of previously adsorbed PFOA, redistribution from groundwater matrix components, or conversion of PFAS precursors contained in AFFF into terminal PFOA during treatment could all be the cause of the brief increase in concentration at subsequent time periods.

After that, the intermediates generated in the system might undergo reductive defluorination, especially when protons or water are present. This would release fluoride ions and produce fluoroalkyl products that are partially hydrogenated or have shorter chains. The cathodic route prioritizes electron-driven bond cleavage over hydroxyl radical assault in contrast to anodic oxidation. A more stable degradation profile is suggested by the somewhat smaller concentration fluctuation throughout treatment, which may be the result of faster intermediate conversion and less reformation of the detectable parent chemical. Because of the perfluorinated chain's strong electron-withdrawing properties, which render PFOA vulnerable to reductive activation, TiOxNTs exhibit selectivity in the cathodic mode. All things considered, the cathodic system shows extremely effective concentration reduction by direct electron transfer, decarboxylation, and stepwise defluorination pathways, underscoring its promise as a robust PFAS remediation technique.

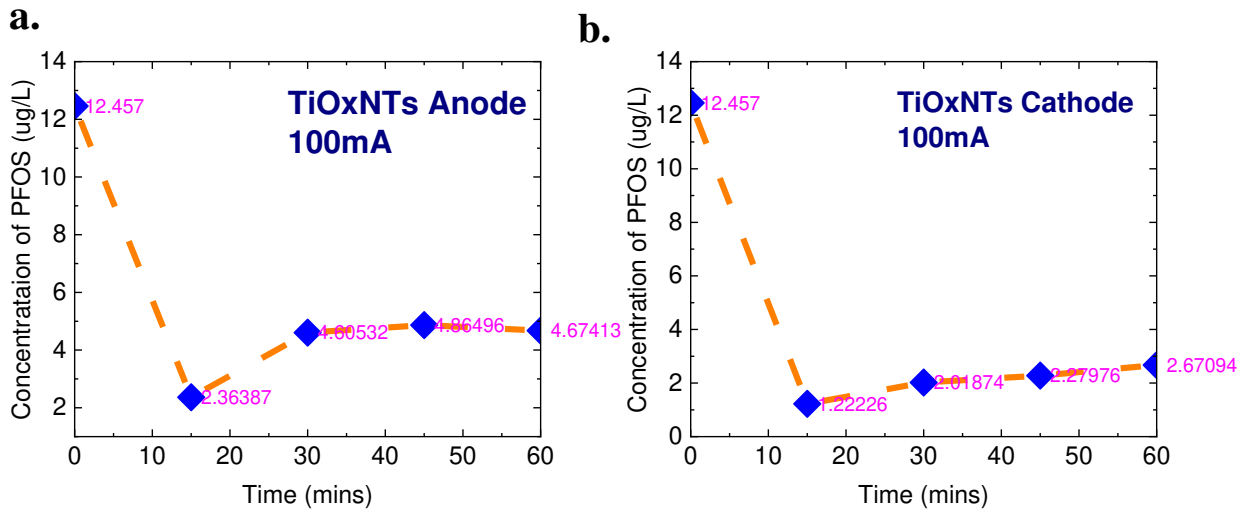

Figure 4.10: a) Degradation profile of PFOS in AFFF-contaminated ground water showing concentration against time with TiOxNTs as Anode b) Degradation profile of PFOS in AFFF-contaminated ground water showing concentration against time with TiOxNTs as Cathode.

During the first 15 minutes, the initial concentration of 12.457 µg/L dropped dramatically to 2.36 µg/L, or about 81% removal, when TiOxNTs were used as the anode at a steady current of 100 mA for the treatment of PFOS in an AFFF-contaminated groundwater (**Fig. 4.10a**). The PFOS levels, in contrast to the PFOA anodic system, then rose to 4.61 µg/L at 30 minutes and stayed comparatively constant at 4.86 and 4.67 µg/L at 45 and 60 minutes, respectively. After 60 minutes, the overall removal rate was almost 62%. This behavior suggests that adsorption–desorption dynamics and intermediate transformation are important factors in the reported concentration profile. It shows rapid initial oxidation followed by partial rebound and stabilization. The quick drop in the first 15 minutes shows that TiOxNTs successfully activate PFOS when anodic polarization is present. Through interaction between the positively polarized anode surface and the negatively charged sulfonate head group ($–SO_3^-$), the nanotubular shape offers a large surface area and promotes the adsorption of PFOS. In these circumstances, direct electron transfer from PFOS to the electrode surface most likely starts the degradation process. But unlike PFOA, PFOS has a sul-

fonate functional group instead of a carboxylate group, which greatly affects how it degrades. PFOS is often more resistant to oxidative circumstances because its C–S bond is stronger and less prone to electro-decarboxylation-type processes. The brief rise in concentration after 15 minutes indicates that adsorption and rapid surface oxidation have a significant impact on the first removal phase, but slower bulk-phase transformation and potential release of adsorbed PFOS back into solution are involved in subsequent stages. The conversion of AFFF's precursor chemicals into PFOS by electrochemical treatment is another tenable hypothesis. The apparent recovery in the observed levels can be attributed to the conversion of sulfonamide-based PFAS precursors into terminal PFOS through electrooxidation. Mechanistically speaking, oxidative routes involving direct electron abstraction and the creation of radical intermediates are probably how anodic degradation of PFOS on TiOxNTs occurs. The C–S bond may be broken or perfluoroalkyl radicals may be produced after initial activation, which may involve electron transfer from the sulfonate molecule. In the end, full mineralization would produce CO_2, F^-, and sulfate species; however, because of the stability of the C–S bond and the potent electron-withdrawing action of the perfluorinated chain, PFOS mineralization is often slower than that of PFOA. Instead of the dominance of hydroxyl radical, surface adsorption and direct electron-transfer capacity appear to control TiOxNTs' selectivity for PFOS under anodic circumstances. However, unlike PFOA, PFOS does not easily undergo electro-decarboxylation because of the absence of a carboxylate group. This explains the plateau seen following the first fast phase and the decreased overall degradation efficiency. Although the transformation rates are slower and may be constrained by the rate of C–S bond cleavage and intermediate oxidation.

Overall, the LC-MS/MS data show that TiOxNT anodes may considerably lower PFOS concentration, especially in the early stages of treatment; however, compared to PFOA, persistent mineralization seems more difficult. Desorption dynamics, slower oxidative transformation pathways, and precursor conversion are probably all involved in the rebound behavior. To properly demonstrate the degradation mechanism and confirm real defluorination, fluoride ion measurement and the identification of shorter-chain sulfonates or carboxylates would be necessary.

A complicated, aqueous and electrode phase trend that highlights the dynamic interaction between adsorption, desorption, and partial degradation is revealed by the LC-MS/MS investigation of PFOS degradation utilizing a TiOxNTs cathode **(Fig. 4.10b)**. Within the first 15 minutes, the PFOS concentration fell from 12.457 µg/L to just 1.222 µg/L, demonstrating an amazing close to 90% removal effectiveness. The fast adsorption of PFOS onto the high-surface-area TiOxNTs cathode is the main cause of this steep drop. Rapid partitioning from the aqueous phase to the electrode interface is made possible by the cathodic polarization, which probably increases the electrostatic attraction between the positively charged TiOxNTs surface and the negatively charged PFOS sulfonate headgroup. However, as the succeeding data show a reversal in concentration patterns, this first elimination cannot be exclusively attributed to degradation. Unexpectedly, the PFOS levels rose from 15 to 60 minutes, reaching 2.671 µg/L. This rebound implies that the adsorbed PFOS was not completely mineralized but rather desorbed back into solution, possibly as a result of local pH variations, surface charge changes, or competition from other AFFF components and degradation intermediates. The cathodic transition of PFOS precursors, which are frequently found in AFFF formulations, could also be the cause of the increase. Under reductive conditions, these precursors can break down and reform PFOS. This draws attention to a crucial drawback: although TiOxNTs can start reductive defluorination and have great selectivity for PFOS adsorption, they are unable to achieve full mineralization within the experimental timescale. The cathode preferentially targets the sulfonate group for reductive cleavage, releasing sulfate ions and starting chain shortening, demonstrating the selectivity of TiOxNTs for sulfonate-containing PFAS like PFOS. The degradation route is not complete, nevertheless, as evidenced by the persistence of PFOS and the probable emergence of shorter-chain perfluoroalkyl carboxylates (PFCAs) as intermediates. These results highlight the need for a coupled anodic oxidation step to fully mineralize the adsorbed intermediates and stop the re-release of parent compounds or the buildup of hazardous byproducts, even though TiOxNTs cathodes are efficient for quick PFOS sequestration and initial defluorination.

Also, electrolysis was carried out on a solution that contains 0.5M Na_2SO_4 and PFAS (PFOA) for 60 minutes at a constant applied current of 100 mA with TiOxNTs used as anode and Platinized

carbon on carbon fiber paper as cathode. The initial concentration of PFOA in the solution was determined to be 23.83 µg/L and within the first 15 minutes of treatment, a sharp drop in PFOA content was noted **(Fig. 4.11a)**. In particular, the concentration decreased from 23.83 µg/L to 0.481 µg/L, which is equivalent to a clearance effectiveness of around 98%. This dramatic drop suggests that TiOxNTs offer extremely active anodic sites for PFOA oxidative transformation.

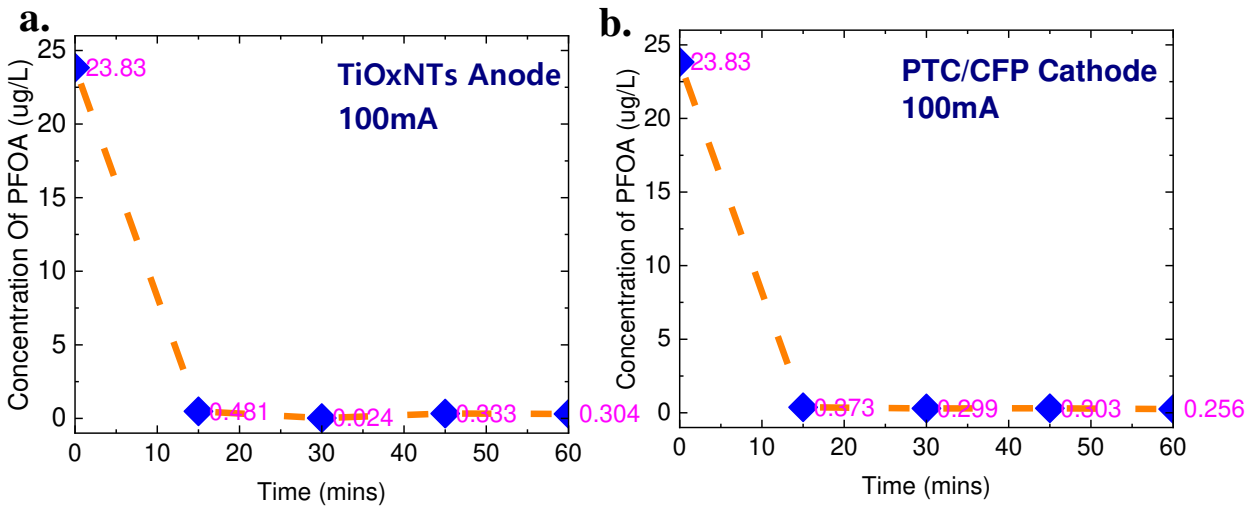

Figure 4.11: a) Degradation profile of PFOA showing concentration against time with TiOxNTs as Anode b) Degradation profile of PFOA showing concentration against time with Platinized Carbon on Carbon fiber paper as Cathode.

The concentration further dropped to 0.024 µg/L after 30 minutes, indicating a nearly 99.9% degradation, this is suggesting the potent capacity of TiOxNT anodes to quickly destroy PFAS at levels that are environmentally significant. Interestingly, PFOA concentrations at 45 and 60 minutes were 0.333 µg/L and 0.304 µg/L, respectively, showing modest increases in detected concentration with longer treatment periods. The desorption and transformation of intermediate fluorinated byproducts, which may temporarily regenerate detectable PFOA-like fragments, or analytical variability at sub-µg/L detection limits are probably the causes of this slight comeback.

The excellent removal efficiency demonstrates TiOxNTs' selectivity as anodic materials for the degradation of PFAS. Numerous synergistic characteristics of TiOxNTs can account for this selectivity. First, the adsorption of PFOA molecules at the electrode–electrolyte interface is improved by the nanotubular architecture's extraordinarily high electroactive surface area. Strong interactions with the TiOx surface are made possible by the hydrophobic perfluorinated tail and the carboxylate headgroup, which efficiently concentrates PFOA close to reactive anodic sites.

Second, a higher percentage of the applied current can accelerate oxidative PFAS transformation because TiOxNTs have a comparatively high oxygen evolution overpotential, which inhibits competing side reactions. Furthermore, TiOxNT anodes encourage the production of reactive oxygen species that aid in the dissolution of the extremely stable carbon–fluorine bonds, including surface-bound Ti–O• species, hydroxyl radicals (•OH), and other oxidative intermediates.

4.3.1 Degradation pathways and products of TiOxNTs anodic oxidation

Direct electron transfer and radical-mediated chain shortening are expected to be the electrochemical processes that lead to the breakdown of PFOA on TiOxNT anodes. The carboxylate group is anodically oxidized in the first step, producing a PFOA radical species:

$$C_7F_{15}COO^- \rightarrow C_7F_{15}COO\cdot \tag{4.1}$$

This unstable radical rapidly undergoes decarboxylation:

$$C_7F_{15}COO\cdot \rightarrow C_7F_{15}\cdot + CO_2 \tag{4.2}$$

Shorter-chain perfluorocarboxylic acids (PFCAs) are the outcome of the reaction between the generated perfluoroalkyl radical and oxidative species in solution. As a result, a progressive shortening mechanism drives degradation:

$$PFOA(C8) \rightarrow PFHpA(C7) \rightarrow PFHxA(C6) \rightarrow PFPeA(C5) \rightarrow PFBA(C4) \rightarrow TFA(C2) \tag{4.3}$$

This pathway exemplifies the distinctive "unzipping" phase of PFAS oxidation, in which long-chain PFAS undergo gradual conversion into shorter-chain intermediates before fully mineralizing.

Finally, additional oxidation results in defluorination, which produces inorganic byproducts such as carbon dioxide (CO_2) and fluoride ions (F^-). As opposed to partial transformation or only adsorption, a crucial sign of complete PFAS breakdown is the release of fluoride ions.

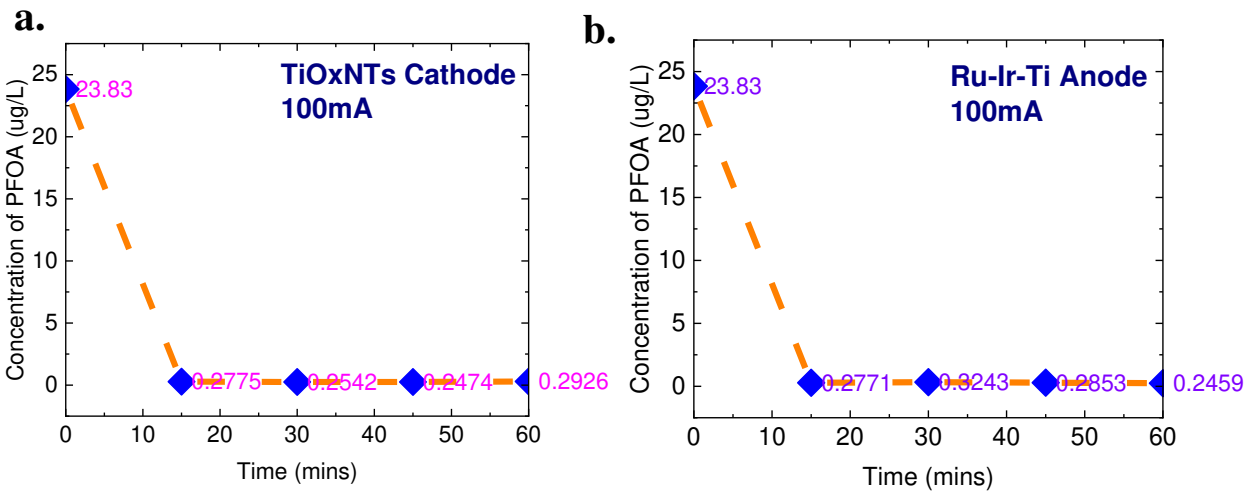

Figure 4.12: a) Degradation profile of PFOA showing concentration against time with TiOxNTs as Cathode b) Degradation profile of PFOA showing concentration against time with Ru-Ir-Ti as Anode.

In the same vein, TiOxNTs were used as the cathodic electrode to assess the reductive defluorination of perfluorooctanoic acid (PFOA). Using galvanostatic electrolysis and an applied current of 100 mA, LC–MS/MS was used to track the temporal evolution of the PFOA concentration. The solution's initial PFOA concentration was 23.83 µg/L, and samples were taken during the course

of a 60-minute treatment session. Within the first 15 minutes of cathodic treatment, a notable decrease in PFOA content was noted **(Fig. 4.12a)**. From 23.83 µg/L to 0.2775 µg/L, the concentration dropped precipitously, indicating a clearance effectiveness of roughly 98.8%. Even in reductive operating circumstances, this quick initial fall indicates that TiOxNT cathodes are quite effective at facilitating the transformation or removal of PFOA from aqueous solution.

The concentration was comparatively constant for the duration of the experiment after this first drop. PFOA concentrations were 0.2542 µg/L, 0.2474 µg/L, and 0.2926 µg/L at 30, 45, and 60 minutes, respectively. According to these findings, the majority of the PFOA was eliminated during the initial electrolysis stage, following which the system achieved a quasi-steady residual concentration at sub-µg/L values.

4.3.2 Degradation pathways and products of TiOxNTs cathodic reduction

As seen by the high removal efficiency and selectivity for PFAS transformation attained by TiOxNTs under reductive electrochemical conditions. This behavior is caused by a number of variables. First, TiOxNTs' nanotubular shape offers a large surface area and lots of active sites for the adsorption of PFOA. The hydrophobic fluorinated tail of PFOA can encourage buildup close to the electrode surface, allowing for localized electron transfer processes even in cathodic operation.

Second, reductive processes are preferred over oxidative radical production by cathodic polarization. Cathodic systems can encourage electron-driven defluorination by forming reactive reducing species, such as hydrated electrons (e^-_{aq}) or surface-bound hydrogen radicals (H•), in contrast to anodic systems, which mainly depend on hydroxyl radicals (•OH). By weakening the C–F link, these reductive species can start the transition of PFAS. However, given that reductive breaking of the strong C–F bonds is still kinetically difficult, the persistence of low residual PFOA concentrations raises the possibility that cathodic systems may be less successful for full mineralization.

Anodic oxidation and cathodic degradation of PFOA are fundamentally different processes. Degradation is anticipated to occur via hydrodefluorination and electron transfer pathways under

reductive conditions as opposed to oxidation driven by decarboxylation. Cathodic reduction could occur through several pathways.

Pathway 1: Reductive Electron Transfer

PFOA may undergo direct electron transfer at the cathode surface:

$$C_7F_{15}COO^- + e^- \rightarrow C_7F_{15}COO^{2-} \tag{4.4}$$

This intermediate is very unstable, and C–F bond cleavage can occur particularly at the terminal positions.

Pathway 2: Hydrodefluorination via Hydrogen Radicals

Adsorbed hydrogen species are often generated through cathodic water reduction:

$$H_2O + e^- \rightarrow H\cdot + OH^- \tag{4.5}$$

The fluorinated carbon chain may then be attacked by Hydrogen radicals:

$$C - F + H\cdot \rightarrow C - H + F^- \tag{4.6}$$

Partial defluorination and the creation of hydrogen-substituted intermediates are the results of this pathway.

Stepwise shortening of PFAS chain may also take place, but more slowly than in anodic systems. Nevertheless, inadequate transformation from cathodic degradation frequently yields partially defluorinated fluorotelomer-like compounds or persistent short-chain PFCAs. In contrast to anodic oxidation, the degradation behavior under cathodic circumstances points to a distinct selectivity tendency. Strong adsorption initially removes long-chain PFAS, e.g. PFOA very quickly, but short-chain intermediates degrade more slowly, leaving behind persistent amounts of intermediates.

Chapter 5

Conclusion

Titanium oxide nanotubes (TiOxNTs) have been shown in this thesis to be a very promising and affordable bifunctional material for reactive electrochemical membranes (REMs) intended to break down persistent per- and polyfluoroalkyl compounds (PFAS). TiOxNTs REMs use complimentary oxidative and reductive pathways when used as both an anode and cathode to destroy PFAS effectively and steadily. While the cathodes allowed for reductive defluorination, which broke strong C–F bonds and released fluoride ions, the anodes enabled the near-complete mineralization of PFAS and similar organic pollutants through the formation of hydroxyl radicals. The device demonstrated exceptional electrochemical stability, fouling resistance, and reliable performance in a variety of PFAS chemicals and intricate environmental matrices, including groundwater contaminated by AFFF. TiOxNTs REMs bridge the gap between laboratory innovation and real-world water remediation by combining filtration with in-situ electrochemical degradation, providing a scalable, energy-efficient substitute for costly noble-metal electrodes and traditional treatment techniques.

5.1 Future Recommendations

Future research should concentrate on improving TiOxNTs conductivity and catalytic activity via heterojunction formation with other metal oxides or doping (for example, with carbon, nitrogen, or transition metals). While maintaining cost-effectiveness, composite architectures that combine TiOxNTs with conductive polymers or reduced graphene oxide may further enhance charge transfer and reactive species formation. In order to assess the long-term efficacy of TiOxNTs REMs in continuous-flow designs under actual water treatment circumstances, pilot-scale investigations are required. To ascertain operational viability for municipal or industrial applications, research should focus on hydraulic optimization, energy consumption analysis, and membrane fouling in high-turbidity waters. It is recommended to utilize sophisticated in-situ spectroscopic and chro-

matographic methods (such as online LC-MS, FTIR, and EPR) in order to quantify radical fluxes, identify transitory intermediates, and clarify degradation processes. Reactor design optimization and treatment efficiency prediction may be aided by kinetic models that integrate fluid dynamics, mass transport, and surface electrochemistry.

To measure the environmental impact of the production, use, and disposal of TiOxNTs REM at the end of its useful life, a thorough lifecycle assessment (LCA) should be carried out. Further investigation into electrode regeneration procedures and wasted membrane recyclability will increase the technology's potential for the circular economy.

5.2 Future Work

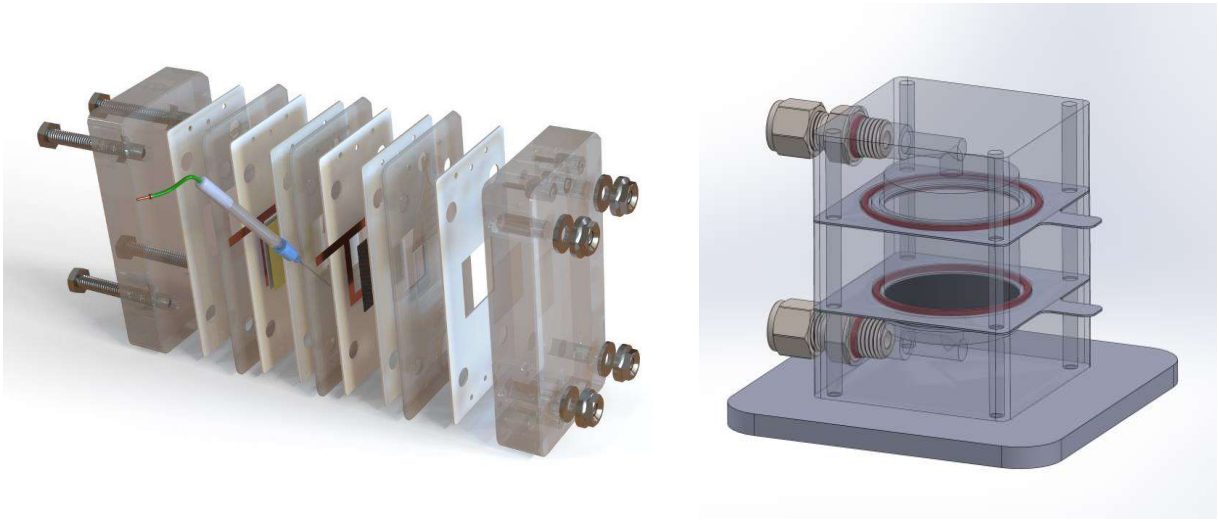

Figure 5.1: Novel Modular Electrochemical Reactors.

In order to address the inherent drawbacks of traditional batch systems for PFAS remediation, we developed a modular three-electrode flow-through electrochemical reactor. Although useful for proof-of-concept research, traditional batch reactors are limited by mass transfer, concentra-

tion polarization, uneven current distribution, and challenges in managing oxidative and reductive conditions separately. Due to the transport toward planar electrode surfaces, PFAS degradation in these systems is often diffusion-limited, leading to partial mineralization and delayed kinetics. Long-term efficiency and reproducibility are further diminished by other issues such as electrode passivation, pH shift, and gas bubble accumulation. These restrictions limit the application of laboratory results to real-world groundwater treatment methods by severely impeding scalability and energy efficiency.

The continuous flow-through arrangement of the reactors architecture **(Fig. 5.1)** immediately tackles these issues. Contaminated groundwater is pushed through specially designed flow channels that keep close contact with the electrode surfaces rather than depending on stagnant bulk mixing. This hydrodynamic improvement enhances overall mass transfer coefficients, guarantees constant PFAS molecule replenishment at reactive sites, and significantly decreases the thickness of the diffusion boundary layer. Improved degradation rates and increased process efficiency follow from quicker reaction kinetics and increased current consumption. Additionally, the specified flow routes lessen the possibility of localized depletion zones and concentration gradients. Uniform current distribution across the electrode surfaces is facilitated by engineered flow fields on the cathode and anode sides. To avoid isolated hotspots, reduce parasitic side reactions, excessive oxygen evolution, and preserve constant degradation selectivity, uniform current density is crucial. Uneven current distribution commonly results in ineffective scaling and decreased performance in bigger batch systems. In contrast, this reactor's structural plate-and-frame design guarantees electrical homogeneity and controlled hydrodynamics, both of which are essential for PFAS treatment that is scalable and repeatable.

True three-electrode operation is made possible by the reactor body's reference electrode port, which permits accurate monitoring of each electrode potential and exact potentiostatic or galvanostatic control. Because it removes the uncertainty associated with two-electrode designs, this feature is especially crucial for mechanistic studies and optimization of PFAS breakdown pathways. A methodical assessment of energy consumption, current efficiency, and oxidative and reductive pro-

cesses is made easier by precise potential control. The reactor allows complementary anodic and cathodic paths to operate simultaneously from the standpoint of degradation. While the cathodic compartment can encourage reductive defluorination through direct electron transfer pathways, the anodic compartment can propel radical-mediated oxidation and electro-decarboxylation of long-chain PFAS compounds. Compared to single-zone systems, this dual-reactive-zone methodology improves overall mineralization potential and provides a more thorough method of PFAS destruction as opposed to partial transformation.

In conclusion, this flow-through electrochemical reactor is a major step up over batch studies conducted in laboratories. The system offers a practical and flexible platform for groundwater PFAS remediation by combining improved hydrodynamics, bipolar membrane pH control, gas diffusion capability, uniform current distribution, accurate electrochemical monitoring, and modular scaling. To further confirm the reactor's practicality and techno-economic competitiveness, further study will concentrate on kinetic modeling, long-term durability assessment, thorough fluoride mass balance validation, and pilot-scale demonstrations.

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