

HARNESSING REDOX ELECTRO-SORBENTS AND REACTIVE SEPARATIONS FOR
EFFICIENT PFAS REMEDIATION IN WATER SYSTEMS

BY

PAOLA A. BALDAGUEZ MEDINA

DISSERTATION

Submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy in Chemical Engineering
in the Graduate College of the
University of Illinois Urbana-Champaign, 2024

Urbana, Illinois

Doctoral Committee:

Assistant Professor Xiao Su, Chair
Professor Hong Yang
Professor R. Mohan Sankaran
Professor Hyun Joon Kong

ABSTRACT

Per- and polyfluoroalkyl substances (PFAS) are persistent environmental contaminants with profound health and ecological implications. Redox-polymer materials have emerged as promising solutions for PFAS remediation, offering tailored electrochemical approaches to tackle the challenges posed by these persistent micropollutants. In this study, we present innovative strategies utilizing redox-polymer materials for efficient PFAS removal and destruction. Our investigation begins with the selective electrochemical separation and mineralization of PFAS, particularly GenX, using a redox-copolymer composed of poly(4-methacryloyloxy-2,2,6,6-tetramethylpiperidin-1-oxyl-co-4-methacryloyloxy-2,2,6,6-tetramethylpiperidine) (PTMA-co-PTMPMA). The copolymer's amine functional groups enhance affinity towards anionic PFAS, while redox-active nitroxide radicals enable controlled adsorption and desorption under electrochemical conditions. Optimized electrochemical parameters yield enhanced kinetics and substantial uptake capacities (>475 mg/g). Further exploration focuses on evaluating PTMA-co-PTMPMA for targeted electrochemical removal of PFAS contaminants, emphasizing regeneration capabilities and transitioning to continuous flow cell configurations. The study elucidates electrochemical mechanisms governing PFAS capture and release across diverse pH and water matrices, showcasing the copolymer's efficacy under varying environmental conditions. Additionally, we investigate redox-active metallopolymer to enhance electrochemical reversibility and electrosorption uptake in PFAS remediation. Synthesized metallopolymer with tailored redox potentials demonstrate superior PFAS capture and regeneration efficiencies, highlighting structure-property relationships impacting electron density and contaminant affinity. Innovative PFAS remediation techniques are then showcased, including up-concentration and utilization of PTMA-containing polymers as adsorbents. Integration of advanced oxidative

processes with boron-doped diamond (BDD) electrodes achieves complete defluorination post-up-concentration, demonstrating energy-efficient solutions for comprehensive PFAS treatment. Through these investigations, this thesis underscores the efficacy and versatility of redox-polymer materials in addressing complex PFAS contamination scenarios. These findings contribute significant insights towards advancing sustainable and efficient PFAS remediation strategies crucial for safeguarding public health and environmental integrity.

ACKNOWLEDGMENTS

I am grateful to Prof. Xiao Su for his guidance and support throughout my research journey. His advice helped me fulfill my academic ambitions and develop professionally, presenting our groundbreaking research at international conferences and connecting with scientists worldwide.

I also sincerely appreciate Prof. R. Mohan Sankaran's guidance in our collaborative efforts and his continuous advice during my time at UIUC. Prof. Hong Yang played a pivotal role in my thesis development and was an outstanding teaching mentor, nurturing my growth toward a future in academia. I am equally thankful to Prof. Hyun Joon Kong for his insightful feedback and guidance during my thesis, along with all the committee members who contributed to my academic journey.

I like to thank my mentors Kwiyoung Kim, Necip Üner, and Ellen Wang Althaus. Kwiyoung's mentorship taught me professional behavior and how to navigate challenging situations while maintaining a fulfilling personal life. Necip emphasized the value of collaborative research, a lesson I will always carry into my professional career. Ellen, thank you for your unwavering support and belief in my potential. Your encouragement propelled me towards achieving my goals.

Special thanks to the Su group members. In addition to Dr. Johannes Elbert, for guiding me with new ideas. Thank you to my undergraduate students, Angelique, Valentina, and Danielle, for their invaluable contributions to our research projects and for allowing me to share my scientific knowledge and skills.

I am immensely proud and thankful of the mentoring program I created with Federico Cifuentes-Urtubey, Julie Lorenzo, and Tasha Mamaril, which has helped Hispanic scientists

transition into graduate school more smoothly. Our efforts in Engineering Education at UIUC are worthy, and I look forward to further expanding and harnessing Hispanic scientists' potential.

To my dear friends—David, Yash, Jemin, Christian, Jenny, Eric, Ohsung, Tove, Tsai-Wei, and Azza—thank you for making my PhD experience at UIUC unforgettable. Our weekly 8:00 pm Friday Dinners were always the highlight of my week, providing comfort during challenging times.

Nayeong, Anaira, and Angela, your friendship means the world to me. Our adventures together have created cherished memories that I hold dear.

M. Cassidy, despite the distance, your unwavering belief in me and your rational advice has been invaluable throughout these last five years.

Edgard, words cannot express the depth of my gratitude for you. Your unwavering support, boundless love, and unshakeable belief in me have been the cornerstone of my success. Thank you for being my rock through the highs and lows of this journey. Your presence fills every day with joy and purpose, and I am endlessly grateful to have you by my side.

Finally, to my family—Mami, Papi, Gaby, Abuela, and Abuelo—your boundless positivity and encouragement have been my greatest motivation. I am eternally grateful for your love and support, which have brought me to where I am today. I thank God for allowing me to have you all by my side, because without you, none of these would have been possible.

Dedication

Le dedico esta tesis a mis padres, Carolyn y José, por impulsarme a ser mejor persona cada día.

Table of Contents

CHAPTER 1: INTRODUCTION	1
1.1 Motivation.....	1
1.2. History and Fate of Per and Polyfluoroalkyl Substances.....	2
1.3 Challenges of Separation Technologies for PFAS Capture, Release, and Destruction	4
1.4 Electrosorption.....	6
1.5 Electrochemically-Mediated Degradation Techniques.....	6
1.6 Thesis Organization	7
1.7 List of Publications	9
CHAPTER 2: MOLECULAR TUNING OF REDOX-COPOLYMERS FOR SELECTIVE ELECTROCHEMICAL REMEDIATION*	11
2.1 Overview	11
2.2 Introduction.....	12
2.3 Methods.....	16
2.3.1 Preparation of <i>P(TMAx-co-TMPMA1-x)-CNT</i> electrodes	19
2.3.2 Material characterization	19
2.4 Results and Discussion	20
2.4.1 Evaluation of redox-electrosorption	20
2.4.2 Redox-mediated regeneration.....	23
2.4.3 Kinetics and stability.....	24
2.4.4 Real water matrices	27
2.4.5 Integration of reactive separation	29
2.4.6 Energy analysis.....	32
CHAPTER 3: ELECTROCHEMICALLY-MEDIATED REMEDIATION OF GENX USING REDOX-COPOLYMERS*	34
3.1 Overview.....	34
3.2 Introduction.....	35
3.3 Methods.....	39
3.3.1 Materials	39
3.3.2 Synthesis of poly(4-methacryloyloxy-2,2,6,6-tetramethylpiperidin-1-oxyl-co-4-methacryloyloxy-2,2,6,6-tetramethylpiperidine) (<i>PTMA-co-PTMPMA</i>).....	39
3.3.3 Flow by-cell assembly.....	40
3.3.4 Sputter coating of a Ti electrode with Pt	41
3.3.5 Analytical methods for PFAS and fluoride detection	41
3.3.6 Electrode preparation and characterization	42
3.3.7 Electrochemical experiments	42
3.3.8 Electrochemical flow cell.....	43
3.4 Results and Discussion	43
3.4.1 <i>PTMA-co-PTMPMA</i> electrode fabrication and characterization	43
3.4.2 Electrosorption of GenX	43
3.4.3 Electroseparation in various water matrices and pH effect	48
3.4.4 Electrode regeneration and an asymmetric release-destruction system	50
CHAPTER 4: INVESTIGATING THE ELECTROCHEMICALLY-DRIVEN CAPTURE AND RELEASE OF LONG-CHAIN PFAS BY REDOX-METALLOPOLYMER SORBENTS*	54
4.1 Overview	54

4.2 Introduction.....	55
4.3 Methods.....	58
4.3.1 Polymer synthesis and characterization	58
4.3.2 Electrode preparation and electrochemical characterization	60
4.3.3 Material characterization and analytical methodology	61
4.4 Results and Discussion	63
4.4.1 Synthesis and characterization of redox-polymers	63
4.4.2 Electrochemically-driven sorption and release of PFOA.....	66
4.4.3 PFAS separation performance and electrochemical stability	69
4.4.4 Kinetics and equilibrium uptake investigation	71
4.4.5 Sorption of PFOA with PMAECOPF ₆ electrosorbents in different water matrices	72
4.4.6 Energy consumption analysis	73
CHAPTER 5: UP-CONCENTRATION AND CONTINUOUS FLOW MEASUREMENTS FOR LEGACY PFAS USING REDOX-MEDIATED ELECTROSORPTION	76
5.1 Overview.....	76
5.2 Introduction.....	77
5.3 Methods.....	82
5.4 Results and Discussion	83
5.4.1 Kinetics and reaction order	83
5.4.2 Energy and optimal up-concentration ratios	85
5.4.3 Flow cell approaches	88
CHAPTER 6: CONCLUSIONS AND FUTURE DIRECTIONS	90
6.1 Overview	90
6.2 Summary of Work.....	90
6.3 Development of an Electrocatalytic Approach for Enhanced Fenton-like Reactions	93
6.4 Long Term Perspective of PFAS Directions	95
REFERENCES	101
Appendix A: Chapter 2 Supplementary Figures and Tables	115
A.1 Adsorption studies and solution analysis	115
A.2 Performance evaluation	117
A.3 Characterization results	120
Appendix B: Chapter 3 Supplementary Figures and Tables.....	126
B.1 Methods	126
B.1.1 LC/MS parameters.....	127
B.2 Characterization techniques.....	128
B.2.1 Scanning electron microscopy (SEM) images.	128
B.2.2 Electron paramagnetic resonance behavior of PTMA-co-TMPMA/MWCNT electrodes	129
B.2.3 XPS analysis	130
B.2.4 Contact angle.....	131
B.3 Adsorption isotherms.....	131
B.4 Kinetic study	132
B.5 Electrochemical experiments.....	135
B.5.1 Chronopotentiometry screening	135
B.5.2 Control experiment.....	136

<i>B.5.3 Energy comparison for chronoamperometry screening versus chronopotentiometry screening</i>	137
<i>B.5.4 Electrochemical measurements</i>	139
<i>B.6 Other experimentations</i>	140
<i>B.6.1 Possible fragmentation</i>	141
Appendix C: Chapter 4 Supplementary Figures and Tables	145
<i>C.1 Polymer characterizations</i>	145
<i>C.2 Other characterization</i>	147
<i>C.3 Electrosorption and electrodesorption screenings and other experiments</i>	150
<i>C.4 Kinetic models</i>	153
<i>C.5 Environmental relevant concentrations</i>	155

CHAPTER 1: INTRODUCTION

1.1 Motivation

Anthropogenic organic pollutants, such as Per- and polyfluoroalkyl substances (PFAS), have been significantly impacting the environment since their development in the early 1950s¹. PFAS are pervasive in our environment, entering ecosystems through consumer products and directly affecting water sources, posing serious health risks to humans and other organisms. These pollutants have been linked to immunological deficiencies, cancer, diabetes, hypertension, and other diseases, emphasizing the urgent need for stringent water remediation methodologies¹.

The challenge with PFAS lies in their ultra-diluted presence, making traditional water separation techniques ineffective in targeting these molecules. To address this, new selective and easily adaptable techniques must be developed. Electrosorption, a method already utilized for water desalination and capturing heavy metals, presents a promising avenue for PFAS removal². By integrating electrosorption into water remediation processes, we can create a novel and effective technique to enhance water quality and protect public health.

This thesis aims to investigate various applications of electrosorption for the capture, release, upconcentration, and destruction of multiple PFAS contaminants. The research will begin by enhancing electrosorption using TEMPO-containing copolymers, examining how electrostatic interactions impact the adsorption and release capacities of PFAS within redox-polymer systems. Subsequently, the study will explore the development of a continuous flow system, integrating upconcentration and advanced oxidative processes to efficiently capture, release, and destruct PFAS contaminants in sequence. Lastly, the thesis will propose a novel idea for future advanced oxidative processes (AOPs) tailored for micropollutant degradation, in combination with

electrocatalysis, to further enhance water quality improvement. Through these investigations, the research aims to advance understanding and practical applications of electrosorption technologies for comprehensive PFAS remediation and water quality enhancement.

1.2. History and Fate of Per and Polyfluoroalkyl Substances

In recent times, there has been a growing trend towards banning the production and use of PFAS in consumer goods. This shift is driven by the widespread contamination of water sources worldwide with these persistent environmental pollutants, often referred to as ‘forever chemicals.’ PFAS, a group of more than 9,000 synthetic compounds, exhibit hydrophobic-oleophobic carbon chains, where hydrogen atoms can be partially (polyfluoroalkyl) or completely (perfluoroalkyl) replaced by fluorine atoms^{1, 3}. These compounds fall into two main categories: perfluoro carboxylic acids (PFCAs) and perfluoroalkane sulfonic acids (PFSAs), distinguished by their end group functionalities. Their unique properties, including thermal stability, chemical resistance, and surfactant behavior, make them attractive for various industrial applications, such as coatings, adhesives, nonstick cookware, and firefighting foams (AFFFs). AFFFs contribute significantly to PFAS contamination in drinking water and groundwater. The extensive use of PFAS, combined with their resistance to degradation, has resulted in their widespread presence in the environment, wildlife, and human bodies. Studies have detected PFAS in human blood, plasma, and urine, with humans having measurable levels of these compounds^{4, 5}. Epidemiological and toxicity studies have linked perfluorinated compounds to adverse health effects, including cancer, elevated cholesterol, preeclampsia, and reduced vaccine effectiveness in children⁶.

Perfluorooctanoic acid (PFOA), a prominent member of the PFAS (per- and polyfluoroalkyl substances) family, finds widespread use in industrial applications like non-stick

coatings and water-repellent textiles. However, due to health concerns associated with PFOA exposure, the U.S. Environmental Protection Agency (EPA) has taken regulatory steps to mitigate its environmental effects. In 2016, the EPA issued a Lifetime Health Advisory (LHA) for both PFOA and perfluorooctane sulfonate (PFOS) in drinking water. The advisory set a combined limit of 70 parts per trillion (ppt) for these compounds, aiming to protect public health, especially vulnerable populations like pregnant women and infants⁷. Yet, enforcing this 70 ppt limit presents significant challenges in detecting and monitoring PFAS contaminants. Standard water testing methods struggle to accurately identify PFAS at such low concentrations, necessitating specialized equipment and techniques⁸. Furthermore, variations in water sources and sample matrices complicate precise measurement and analysis. These challenges underscore the need for ongoing research and innovation in water testing technologies. Developing more sensitive and reliable analytical methods is crucial to ensure compliance with EPA guidelines and safeguard public health against the adverse effects of PFAS exposure.

In response to these findings, manufacturers gradually phased out the production of specific PFAS, including perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS), during the early 2000s. This action led to the establishment of global regulations governing these compounds. However, despite these regulatory efforts, PFAS persistently appear in various environmental contexts, such as groundwater, surface water, soil, and aquifers near locations associated with firefighting, military installations, and wastewater treatment plants. While regulations have set advisory limits for PFAS in drinking water, concentrations exceeding these limits are frequently detected in water sources worldwide⁷.

In response to concerns surrounding bioaccumulation, regulations have spurred the development of chemical substitutes that share similar properties with legacy PFAS (per- and polyfluoroalkyl substances) but exhibit higher volatility and greater mobility. The fate and movement of PFAS are significantly influenced by their amphiphilic nature, which is determined by the length of their fluorinated chain. As a consequence of regulations specifically targeting long-chain PFAS, manufacturers have transitioned toward shorter-chain alternatives. However, the persistence of certain short-chain PFAS compounds raises apprehensions regarding their environmental impact. This underscores the critical need for comprehensive assessment and effective regulation of these compounds to strike a balance between functionality and environmental safety.

1.3 Challenges of Separation Technologies for PFAS Capture, Release, and Destruction

Because of their long-lasting presence in the environment, various techniques have been explored to separate PFAS. These methods encompass membrane technologies like reverse osmosis, nano and ultrafiltration, as well as solvent extraction and adsorption. Nevertheless, many traditional treatment approaches, such as biodegradation, reverse osmosis, and coagulation, often prove ineffective in removing perfluorinated substances from water. They typically demand significant energy input and may necessitate the use of organic solvents or regeneration chemicals, leading to additional waste generation. Therefore, there is a critical imperative to research and develop sustainable and energy-efficient processes for separating and treating PFAS-contaminated water.

Efforts to develop effective PFAS remediation techniques for water have surged in interest. There has been extensive exploration into combining conventional methods, such as integrating activated carbon (AC) adsorbents with nanofiltration. Other techniques like ion exchange resins

(IERS) and reverse osmosis (RO) membranes have also gained attention and demonstrated effective PFAS removal at low concentrations. However, these methods come with several limitations. Membrane fouling can pose a challenge, leading to increased costs in RO processes. Despite its widespread use in adsorption, activated carbon often requires extended equilibration times and chemically-intensive treatments to release and regenerate the adsorbents. Moreover, activated carbon tends to preferentially adsorb higher molecular weight compounds over lower molecular weight ones. Consequently, in treating mixed PFAS streams, achieving complete removal of shorter-chain PFAS using AC adsorption becomes challenging due to the preferential adsorption of longer-chain PFAS and their precursors.

To tackle PFAS removal, advanced oxidation processes (AOPs) have emerged as a standout method that's been applied to deal with various new-age organic pollutants. In these processes, catalysts are used to create hydroxyl radicals ($\text{OH}\cdot$) that break down the contaminants. AOPs can involve ozone (O_3), hydrogen peroxide (H_2O_2), metal oxide catalysts, and even light. Light-based AOPs, especially, have been heavily studied as a promising way to break down PFAS due to the impressive efficiency of photocatalytic materials.

Electrochemical techniques and processes using electrocatalysis show great promise for purifying water by removing pollutants, offering a modular alternative to traditional methods that use chemicals or heat. For example, electrosorption-based methods efficiently remove various pollutants, including perfluorinated compounds, through electrochemical means. Electrochemical advanced oxidation processes (EAOPs), such as electro-Fenton processes and photoelectrocatalysis, provide innovative pathways to break down contaminants without the need for chemicals used in typical AOPs^{7, 9, 10}. These electrochemical methods also offer additional

advantages, such as integration with renewable energy sources for off-grid applications, and reduced chemical costs due to regeneration driven by electrical fields.

1.4 Electrosorption

Electrochemical adsorption, or electrosorption, involves the attachment of dissolved substances to a polarized electrode surface under the influence of an electric field². The potential difference between electrodes causes ions to separate from the solution and adhere to the charged electrode surface, forming an electric double layer. Reversing or removing the potential releases the ions back into the solution, regenerating the electrodes without requiring additional chemicals or physical processes. Electrosorption-based methods show strong selectivity for various pollutants like heavy metals and organic anions². This technique relies on the applied voltage and electric field to enhance the efficiency and specificity of pollutant removal, offering advantages such as simplicity, low energy consumption, and minimal waste generation compared to conventional methods. However, electrosorption has only recently been explored for PFAS remediation, with most studies focusing on long-chain PFAS such as PFOA and PFOS due to their historical use and recent manufacturing bans¹¹. Further research is needed to optimize electrosorption for removing a wider range of PFAS compounds, including shorter-chain variants and emerging contaminants.

1.5 Electrochemically-Mediated Degradation Techniques

Electrochemical methods for degrading contaminants in water have gained significant traction, especially in the realm of perfluorinated substances (PFAS), over the past decade. Among these techniques, electrochemical defluorination stands out as a prominently researched approach, involving the generation of free radicals that catalyze defluorination reactions. This method offers

modularity, scalability, and environmental friendliness, often eliminating the need for external chemical additives.

Within electrochemically-mediated degradation methods, two primary categories are electrochemical advanced oxidation processes (EAOPs) and advanced reduction processes (ARPs). EAOPs, in particular, have been widely explored for PFAS degradation due to their efficacy^{7, 9-12}. These processes involve generating powerful oxidizing species like hydroxyl radicals ($\bullet\text{OH}$) at the electrode surface, which effectively oxidize and break down PFAS molecules¹¹⁻¹⁴.

One distinctive EAOP technique involves the use of boron-doped diamond (BDD) electrodes. Boron-doped diamond electrodes exhibit excellent electrochemical properties, including high stability, chemical inertness, and a wide potential window¹⁵. When used in advanced oxidation processes, BDD electrodes can generate hydroxyl radicals ($\bullet\text{OH}$) through the electrochemical decomposition of water molecules, which can then efficiently degrade PFAS compounds. The unique properties of BDD electrodes make them particularly promising for sustainable and effective PFAS remediation, offering potential applications in both laboratory-scale studies and large-scale water treatment systems¹⁴. Ongoing research aims to optimize the use of BDD electrodes and explore their full potential in addressing PFAS contamination in water resources.

1.6 Thesis Organization

The comprehensive thesis explores innovative approaches for the selective separation and efficient mineralization of per- and polyfluorinated alkyl substances (PFAS) in water remediation. The research addresses the urgent need to remediate PFAS due to their persistence and low

environmental concentrations, which pose significant ecological challenges. Each chapter of the thesis presents novel methods and technologies aimed at advancing PFAS removal and destruction.

Chapter 2 focuses on the development of a copolymer, P(TMA_x-co-TMPMA_{1-x}), designed to selectively capture and release PFAS, specifically perfluorooctanoic acid (PFOA), through electrochemically-controlled processes. The copolymer's unique composition of amine functional groups and redox-active nitroxyl radicals enables efficient PFAS adsorption and regeneration. Integration with a boron-doped diamond electrode facilitates tandem separation and mineralization of PFOA, demonstrating enhanced energy efficiency for water purification.

In Chapter 3, the research investigates the electrochemical adsorption of GenX, a substitute for legacy PFAS, using a redox copolymer, PTMA-co-PTMPMA. This copolymer exhibits high selectivity towards anionic PFAS due to its amine functional groups and enables electrochemical control over adsorption and desorption processes. The study demonstrates effective removal of GenX across various water matrices and pH ranges, transitioning from batch to flow-by cell systems. Additionally, the copolymer-based electrodes coupled with boron-doped diamond counter electrodes achieve close to 100% defluorination efficiency.

Chapter 4 explores the use of redox-active metallopolymer for efficient PFAS removal and regeneration through electrosorption. Metallopolymer containing ferrocene and cobaltocenium units are synthesized and evaluated for their performance in capturing and releasing perfluorooctanoic acid (PFOA). The research reveals correlations between the redox potentials of the metallopolymer and their affinity towards PFAS, demonstrating promising uptake and regeneration efficiencies under electrochemical conditions.

In Chapter 5, innovative PFAS removal and destruction techniques are explored, including up-concentration combined with advanced oxidative processes using boron-doped diamond

electrodes. The use of PTMA-containing polymers for effective capture and release of PFAS is demonstrated, along with the energetic benefits of up-concentration for water treatment processes. This chapter provides insights into addressing the limitations of current PFAS remediation techniques and contributes to achieving comprehensive PFAS removal and destruction for safeguarding public health and the environment.

Chapter 6 summarizes the key findings and conclusions drawn from the research presented in the thesis. It highlights the significance of the developed methodologies for PFAS remediation and suggests future directions for scaling up and real-world implementation of these innovative technologies.

Overall, this thesis advances the field of PFAS remediation by introducing novel copolymer and metallopolymers-based approaches for selective PFAS separation, electrochemical adsorption, and destruction, demonstrating promising applications for sustainable water purification and environmental protection.

1.7 List of Publications

Published

1. K. Kim[†], **P. Baldaguez Medina**[†], J. Elbert, E. Kawiya, R. D. Cusick, Y. Men, X. Su.
Molecular tuning of redox-copolymers for selective electrochemical remediation.
Advanced Functional Materials, 2020, 2004635.
2. **P. Baldaguez Medina**, S. Cotty, K. Kim, J. Elbert, X. Su. Electrochemical Capture and Release of GenX via Redox Copolymers Environmental Science: Water Research and Technology, 2021, 7, 2231-2240.

3. F. Cifuentes-Urtubey[†], **P. Baldaguez Medina**[†], N. Mamaril. Peer Mentorship in a Virtual University Setting: A Hispanic Perspective on How Mentorship Broadens Participation in Advanced Degrees. ASEE Conference proceeding paper, 2023.
4. A. Román Santiago, **P. Baldaguez Medina**, X. Su. Electrochemical Remediation of Perfluoroalkyl Substances in Water. *Electrochimica Acta*, 2021, 139635.
5. N.B. Üner, **P. Baldaguez Medina**, J. L. Dinari, X. Su, R. Mohan Sankaran. Rate, Efficiency, and Mechanisms of Electrochemical Perfluorooctanoic Acid Degradation with Boron-Doped Diamond and Plasma Electrodes. *Langmuir*, 2022, 38, 29, 8975–8986.
6. **P. Baldaguez Medina**, V. Ardila Contreras, F. Hartmann, D. Schmitt, A. Klimek, J. Elbert, M. Gallei, X. Su. Investigating the Electrochemically-Driven Capture and Release of PFAS by Redox-Metallopolymer Sorbents. *ACS Appl. Mater. Interfaces* 2023, 15, 18, 22112–22122.

In Preparation

7. **P. Baldaguez Medina**, D. Raymond, D. E. Chao, J. Elbert, X. Su. Heterogeneous-Redox Catalysts for Electro Fenton Processes. In preparation.
8. **P. Baldaguez Medina**, S. Cotty, S. Peyres, D. E. Chao, R.M. Sankaran, X. Su. Up-Concentration and Continuous Flow Measurements for Legacy PFAS Using Redox-Mediated Electrosorption. In preparation.

CHAPTER 2: MOLECULAR TUNING OF REDOX-COPOLYMERS FOR SELECTIVE ELECTROCHEMICAL REMEDIATION*

2.1 Overview

The selective separation and efficient mineralization of per- and polyfluorinated alkyl substances (PFASs) is of great importance due to its extremely low environmental concentrations and serious ecological persistence. Current PFAS removal technologies show low selectivity, and require energy-intensive processes for remediation and mineralization. Here, we present the development of copolymer of poly(4-methacryloyloxy-2,2,6,6-tetramethylpiperidin-1-oxyl) (PTMA) and poly(4-methacryloyloxy-2,2,6,6-tetramethylpiperidine) (PTMPMA), denoted as (P(TMA_x-co-TMPMA_{1-x})). The amine functional groups provide high affinity for anionic PFAS, while the redox-active nitroxyl radical groups promote the electrochemically-controlled capture and release of PFOA. Controlling the ratio of amines to nitroxyl radicals provides a way of tuning redox-activity, hydrophobicity, and PFAS affinity to synergistically enhance adsorption and regeneration. P(TMA_x-co-TMPMA_{1-x}) removes PFOA with high uptake capacity (>2.54 mmol PFOA/g adsorbent (>1000 mg/g)), with the highest separation factor of 500, and demonstrates high removal efficiencies in various water matrices and wide applicability toward various PFAS compounds. Integration with a boron-doped diamond electrode allowed for the tandem separation and degradation of PFOA within the same electrochemical cell, with improved energy efficiency for PFOA mineralization. This study demonstrates for the first time

*This Chapter was adapted with permission from: K.Kim[†], P. Baldaguez Medina[†] et al. *Adv. Func. Mat.*, 2020, 2004635.

the effectiveness of synergistic ion-exchange and redox active polymers for PFAS removal, and its integration with electrochemical advanced oxidation process for next-generation water purification processes.

2.2 Introduction

Poly- and perfluoro alkyl substances (PFAS) are toxic anthropogenic compounds that can be found in air, water, soil, and almost any household device.¹⁶⁻¹⁸ More than 5,000 types of PFASs exist, and the widespread use of these substances has provoked an increase of polluted water worldwide, especially in industrialized zones.^{19, 20} These toxic compounds are persistent in the environment, as well as in the human and animal body, due to the extremely stable carbon-fluorine bond. Prolonged exposure increased the risk of cancer, immunodeficiency in children, food allergies, and diabetes during gestation to both the child and the mother.¹⁹⁻²⁴ All these health risks have led to enhanced regulatory attention to the concentration of PFASs in water, with the U.S. Environmental Protection Agency (EPA) recommending a limit of 70 ppt of PFOA and PFOS in water, to reduce adverse health effects during the lifetime of exposure.²⁵

Several techniques for PFAS separations have been considered, including adsorption, ion-exchange, filtration, and reverse osmosis.²⁶⁻²⁹ However, most of these conventional procedures suffer from high material/operational cost and costly regeneration which requires the use of strong acid/base or organic solvents.^{30, 31} Even more, the selective separation of PFAS is challenging because of orders-of-magnitude lower concentration of PFASs (ng L^{-1} to hundreds of $\mu\text{g L}^{-1}$) compared to background constituents in contaminated

waters.^{31, 32} Therefore, it is imperative to find new methods that could target these minority components with high selectivity and capacity, and easy recyclability.

Electrosorption have garnered the attention for adsorbing heavy metals and organic anthropogenic substances from water, due to their modularity, scalability, and low environmental footprint.³²⁻³⁶ Electrochemical adsorption of PFAS on MWCNT has been attempted previously, but the regeneration was not electrochemically-mediated and relied on washing the adsorbent physically at elevated temperatures (60 or 90 °C).^{37, 38} Also, low selectivity toward PFOA in the presence of background electrolyte (e.g. < 10 mM Na₂SO₄) has limited the total uptake capacity of non-functionalized electrosorption,^{37, 38} which is disadvantageous considering most PFAS-contaminated water sources are composed of orders-of-magnitudes excess salts (ng L⁻¹ to hundreds of µg L⁻¹). Therefore, the design of functional adsorbents with molecular selectivity is vital for addressing these limitations.

Recent studies have demonstrated that redox-tunable interfaces are an attractive platform for selective removal of pollutants, including heavy metal oxyanions, uncharged organic pollutants and organic anions.^{36, 39-41} Molecular design of the redox-active interfaces have the capability of tuning the binding affinity towards capturing organic micropollutants.⁴¹ In addition, redox-materials have been studied as catalytic interfaces for degradation of organic contaminants,⁴² opening the door to achieving the integration of separation and reaction step.^{35, 36}

These tandem electrochemical approaches have been investigated not only in energy-storage applications, but also water purification devices for maximizing energy efficiency.^{35, 40, 43} Here, we aim to leverage molecularly designed polymer interfaces to achieve energy-efficient selective separation of PFAS through electrochemical control and enable the integration of separation and remediation within a single electrochemical device.

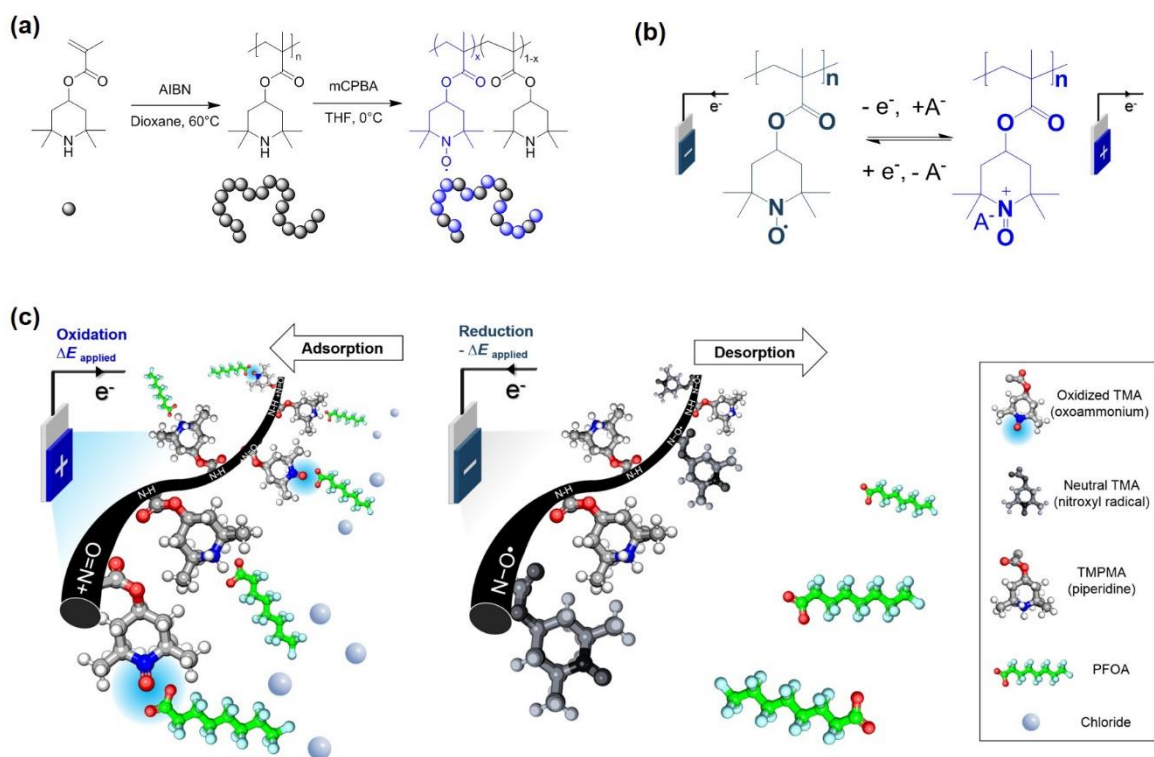


Figure 2.1. (a) Synthesis route of P(TMA_x-co-TMPMA_{1-x}). (b) Redox reaction of redox-active TMA unit in P(TMA_x-co-TMPMA_{1-x}) (A⁻ denotes a generic anion). (c) A schematic illustration showing electrochemically-controlled capture and release of PFOA by P(TMA_x-co-TMPMA_{1-x}). During adsorption, N-H sites of piperidine in TMPMA and redox-active oxoammonium in oxidized TMA units work in a synergistic way for enhanced electrostatic attraction of PFOA. During regeneration, redox-mediated charge repulsion enhanced by nitroxyl/oxoammonium couple facilitates electrochemically-controlled release. The ratio between TMA and TMPMA also tunes hydrophobicity, to achieve an optimal degree for PFOA binding and reversible release.

In this chapter, we developed polymer-functionalized electrodes bearing amine (N-H) functionalities to provide high affinity for anionic PFAS compounds, and at the same time, having appropriate loading of a stimuli-responsive redox couple of nitroxide radicals

(N–O•) and oxoammonium cation (+N=O) for electrically-controlled capture and release of PFAS. For this, we synthesized synergistic ion-exchange and redox-active polymers, which are copolymers of poly(4-methacryloyloxy-2,2,6,6-tetramethylpiperidin-1-oxyl) (PTMA) and poly(4-methacryloyloxy-2,2,6,6-tetramethylpiperidine) (PTMPMA), namely, P(TMA_x-co-TMPMA_{1-x}), with the tunability of redox-activity, affinity for PFAS, and hydrophobicity (**Figure 2.1a**). Amine functionalities are known to play as attractive binding sites for anionic PFAS via electrostatic interaction with carboxylate or sulfonate head groups on the anionic PFAS.^{31, 44-47} The co-existing N-H and N–O• functionalities synergistically combine the affinity of N-H sites with the electrostatic enhancement of the redox-active group, N–O• (**Figure 2.1b**), promoting the electrochemically-controlled capture and release of PFAS molecules, without the need for chemical regenerants and/or harsh operational requirements (**Figure 2.1c**). We examined the adsorption and regeneration capacity of P(TMA_x-co-TMPMA_{1-x}) with various radical contents (x) for their applications onto electrically-controlled PFAS capture and release. Furthermore, we propose the first integration of polymer-functionalized electrode with a boron-doped diamond (BDD) electrode⁴⁸ to achieve separation and defluorination of PFAS within the same electrochemical device. In our proof-of-concept study, we show that the coupled regeneration of P(TMA_x-co-TMPMA_{1-x}) in the asymmetric configuration with BDD allows for a modular and selective reactive separation concept, with significantly reduced energy consumption via the tuning of redox potentials.

2.3 Methods

P(TMA_x-co-TMPMA_{1-x}) (with x indicating the ratio of TMA in the copolymer) was synthesized by partial oxidation of PTMPMA with m-chloroperbenzoic acid (**Figure 2.1a**).⁴⁹ After synthesis, a number of analytical techniques were used to confirm the

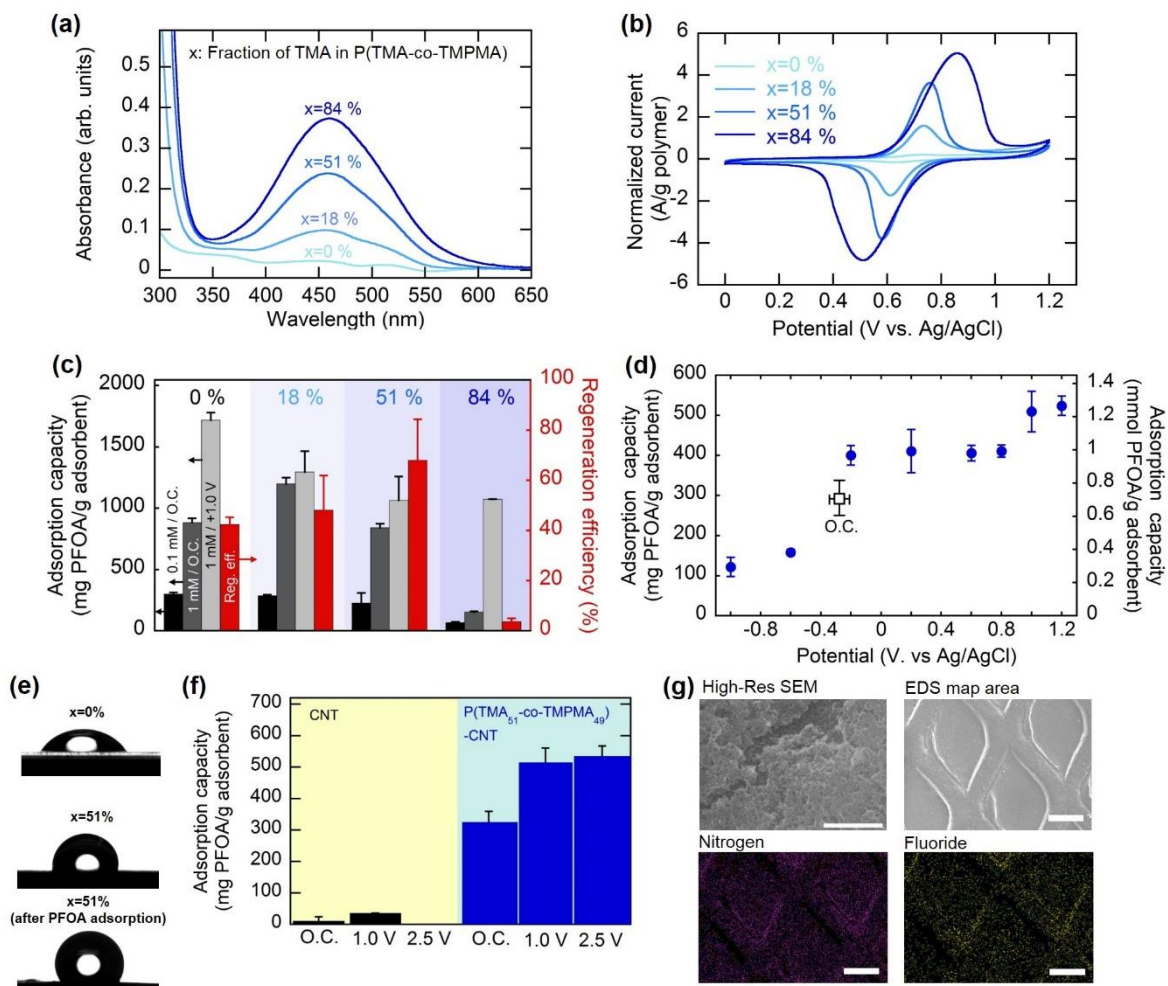


Figure 2.2. (a) UV-vis spectra of P(TMA_x-co-TMPMA_{1-x}) copolymers in chloroform (concentration: 8 mg mL⁻¹). (b) Cyclic voltammograms of P(TMA_x-co-TMPMA_{1-x})-CNT electrodes in 0.1 M NaClO₄ (scan rate: 10 mV s⁻¹). (c) PFOA uptake capacity and regeneration efficiency of P(TMA_x-co-TMPMA_{1-x})-CNT electrodes (adsorption: in 20 mM NaCl + 0.1 mM (black) or 1 mM PFOA (dark gray and gray) at open circuit (black, dark gray) and +1.0 V (gray)

Figure 2.2. (cont.) for 0.5 h; and desorption (red) in 20 mM NaCl at -0.5 V for 0.5 h. Before desorption, adsorption was carried out at +1.0 V for 0.5 h in 1 mM PFOA + 20 mM NaCl (gray bars)). In (a)-(c), x denotes the fraction of TMA in P(TMA-co-TMPMA). (d) PFOA uptake capacity of the P(TMA₅₁-co-TMPMA₄₉)-CNT electrodes at various polarization conditions in 0.1 mM PFOA + 20 mM NaCl for 0.5 h. (e) Images of water droplet on the surface of P(TMA_x-co-TMPMA_{1-x})-coated electrodes in contact angle measurement (contact angles were 70°, 94°, and 126° for 0%, 51%, and 51% after adsorption, respectively). (f) Comparison of PFOA uptake capacity of CNT and P(TMA₅₁-co-TMPMA₄₉)-CNT electrodes in 0.1 mM PFOA + 20 mM NaCl for 0.5 h. (g) Scanning electron microscopy (SEM) of P(TMA₅₁-co-TMPMA₄₉)-CNT electrodes, and EDS mapping of nitrogen and adsorbed fluoride. Scale bar for high-resolution SEM is 2 μ m, and scale bar for EDS and N/F mapping is 200 μ m.

degree of oxidation within the copolymer. The presence of stable N-O• radicals was investigated using ultraviolet-visible (UV-vis) analysis, where typical adsorption at 460 nm is associated with the n- π^* transition of N-O• radicals.⁵⁰ With the increase in the degree of oxidation, a corresponding increase in the concentration of N-O• radicals was observed in the UV-vis spectra (**Figure 2.2a**). Quantification of radical yields based on TEMPO standards (**Figure A.2**) revealed 0, 18, 51, 84 % conversion of TMPMA to TMA. The same trend in radical densities were also monitored via electron paramagnetic resonance (EPR) (**Figure A.3**). EPR characterization of all P(TMA_x-co-TMPMA_{1-x}) samples showed broad singlets, which is in accordance with previous literature.⁵⁰ The signal intensity associated with the radical spin density increases with higher degree of oxidation. The oxidation of N-H functionalities to N-O• radicals was further confirmed via Fourier-transform infrared

spectroscopy (FT-IR) (**Figure A.4**). The FT-IR signals revealed that N-O• in P(TMA_x-co-TMPMA_{1-x}) starts to appear upon oxidation as evidenced by the appearance of N-O• peak at 1467 cm⁻¹.⁴⁹ At the same time, P(TMA₈₄-co-TMPMA₁₆), with the highest radical content, didn't exhibit discernable peak of amine N-H stretch in the range of 3400-3100 cm⁻¹.⁵¹ X-ray photoelectron spectroscopy (XPS) also indicated the conversion of N-H functionalities to N-O• radicals (**Figure A.6**). The peak at the lower binding energy of 398.9-399.7 eV is assigned to N-H groups, and the other peak at about 401.3-401.5 eV is the characteristic peak of N-O• radicals.^{49, 52} When the relative concentration of each component representing N-H and N-O• is compared, the same trend of increasing N-O• content could be observed with higher degree of oxidation. The N-O• contents obtained from XPS exhibited lower values compared to UV-vis-based quantification of N-O•, and this can be ascribed to the distribution of more polar N-H group on the surface caused during the precipitation of polymers in methanol or water. A higher content of redox-active N-O• radical unit with higher x in P(TMA_x-co-TMPMA_{1-x}) was observed using electrochemical characterization of cyclic voltammetry (CV) (**Figure 2.2b**). The reversible peaks could be ascribed to the one-electron redox reaction between N-O• and +N=O, also as shown in **Figure 2.1b**.⁵⁰ As the oxidation degree increased, the normalized current also increased, indicating the larger number of reversible redox couples of N-O• and +N=O exist in P(TMA_x-co-TMPMA_{1-x}) with higher x. The peak separation became more severe with higher oxidation degree, probably due to increased hydrophobicity from the replacement of more hydrophilic N-H with less hydrophilic N-O•, thus limiting ion accessibility. All these spectroscopic and electrochemical characterizations confirm the controllable

composition of N–O• and N-H loadings during the synthesis of P(TMA_x-co-TMPMA_{1-x}) copolymer.

2.3.1 Preparation of P(TMA_x-co-TMPMA_{1-x})-CNT electrodes

The base substrates were prepared by cutting stainless steel cloth (McMaster-Carr, stainless steel wire cloth, 325×325, wire diameter: 0.0014 inch) into a dimension of 1 cm × 2 cm, followed by soldering them with copper wire. 80 mg of CNT and 80 mg of P(TMA_x-co-TMPMA_{1-x}) powder were dispersed in 20 mL of acetone by sonicating for 1 h in icy water. For the coating of P(TMA_x-co-TMPMA_{1-x})-CNT, the base substrates were dip-coated into the ink solution of P(TMA_x-co-TMPMA_{1-x})-CNT, with 3 sec of contact for each dip, and then drying at room temperature for 30 sec between each dipping. 35 Electrochemical active area immersed in electrolyte was 1 cm² (1 cm × 1 cm). The final loadings were controlled to be close to 0.6 mg per electrode. Before use, every electrode was activated by carrying out cyclic voltammetry in 0.1 M NaClO₄ in the range of 0 – 1.2 V (vs. Ag/AgCl) at a scan rate of 10 mV s⁻¹ for 4 cycles.

2.3.2 Material characterization

NMR spectra were recorded on Varian Unity Inova 400 MHz spectrometer equipped with a Nalorac QUAD probe. UV-vis absorbance was obtained first by preparing 8mg mL⁻¹ solutions of P(TMA_x-co-TMPMA_{1-x}) dissolved in chloroform and measuring with UV-vis spectrophotometer (Cary 60, Agilent). Contact angle analysis were carried out with a Ramé-Hart Model 250 Standard Goniometer. DROPimage Advanced software was used for drop shape analyzer. Fourier transform infrared spectroscopy (FT-IR) was measured on the Thermo Nicolet Nexus 670 Fourier transform infrared spectrophotometer. The surface images and elemental mapping images (EDS) of

P(TMA_x-co-TMPMA_{1-x})-CNT electrodes were obtained using a scanning electron microscope (SEM; Hitachi S-4700) operated at an accelerating voltage of 10 kV, equipped with energy dispersive X-ray spectroscopy (EDS; iXRF) with the accelerating voltage of 15 kV. The chemical states of nitrogen and fluoride on the electrodes were characterized using X-ray photoelectron spectroscopy (XPS; Kratos Axis ULTRA) with monochromatic Al K α X-ray source (210 W). The XPS results were analyzed using CASA XPS software (UIUC license). The spectra were calibrated with the C 1s peak (284.8 eV). The spectra were fitted into their components following subtraction of a Shirley background from the region of interest. Electron paramagnetic resonance (EPR) spectroscopy was used to confirm the radical behavior of P(TMA_x-co-TMPMA_{1-x}). The solid analysis was performed in a 3 mm diameter quartz EPR tube and the sample was diluted with high-purity (99.999%) KNO₃ in a 1:9 ratio. The Bruker EMXPlus spectrometer was used with an X-band frequency of 9.8 GHz. The frequency was produced by a Bruker ER4119HS high sensitivity resonator.

2.4 Results and Discussion

2.4.1 Evaluation of redox-electrosorption

P(TMA_x-co-TMPMA_{1-x}) copolymers were blended with CNT as a supporting material to form a homogeneous electrode by dip-coating method.³⁵ The P(TMA_x-co-TMPMA_{1-x})-CNT electrode showed homogenous and nanoporous morphology (**Figure 2.2g**). The removal of PFOA by P(TMA_x-co-TMPMA_{1-x})-CNT electrodes with different x were evaluated using initial PFOA concentration of 0.1 and 1 mM, where the heterogeneous molar ratio of PFOA to total nitrogen species (sum of N-H and N-O $\bullet$) in P(TMA_x-co-TMPMA_{1-x}), PFOA/total N, is 0.5:1 and 5:1, respectively (**Figure 2c**). First, the highest

adsorption uptake in the absence of electricity input (at open circuit) was obtained with less-oxidized polymers; for example, non-oxidized polymer ($x=0\%$) showed the best uptake at 0.1 mM and $x=18\%$ at 1 mM. The trend of decreasing PFOA removal from 18% radical content indicates that the piperidine groups are essential for high PFOA binding when electricity is not applied. At the initial PFOA concentration of 1 mM (dark gray bars in **Figure 2.2c**), the molar ratio of adsorbed PFOA to amine functional groups in $P(\text{TMA}_x\text{-co-TMPMA}_{1-x})$ (PFOA/N-H) was 0.48:1 at $x=0\%$, but increased to close to 1:1 at $x=18$ and 51%, indicating almost full utilization of N-H functionalities as the primary binding sites of PFOA.⁴⁴ Only half utilization (0.48:1) at $x=0\%$ could be ascribed to hydrophilic nature of the piperidine groups (**Figure 2.2e**). Incorporating N-O• radicals increases the hydrophobicity so as to achieve full utilization of N-H functionalities.

Interestingly, applying more positive potential (compared to the potential at open circuit) could improve the adsorption of PFOA onto the electrode. For example, when the applied potential onto $P(\text{TMA}_{51}\text{-co-TMPMA}_{49})$ was finely controlled in 0.1 mM PFOA + 20mM NaCl, positive correlation between applied potential and uptake of PFOA was observed (**Figure 2.2d**). In the same electrolyte condition (0.1 mM PFOA + 20mM NaCl), the potential at open circuit was stabilized at -0.28 ± 0.04 V, and applied potentials lower (higher) than that exhibited poorer (better) uptake compared to open circuit adsorption (**Figure 2.2d**). In **Figure 2.2c**, when x was varied, applying positive bias of +1.0 V (vs. Ag/AgCl) enhances the PFOA uptake compared to open circuit, showing >1000 mg PFOA/g adsorbent for all cases at 1 mM PFOA, with higher uptake being observed with lower x . In particular, the molar ratio of adsorbed PFOA to N-H (PFOA/N-H) in $P(\text{TMA}_{84}\text{-co-TMPMA}_{16})$ during the electrosorption at +1.0 V was 3.85:1, indicating PFOA binding

not only onto N-H, but also redox-active +N=O sites via electrostatic attraction (see the anion doping in **Figure 2.1b**). Our result indicates the critical synergistic interplay between N-H affinity sites and redox-promoted electrostatic interaction for selective PFOA binding. It is worth noting that having only hydrophobic interaction (e.g. CNT at open circuit) or electrostatic interaction without surface functionalization (e.g. CNT at +1.0 and 2.5 V) could not lead to significant uptake (**Figure 2.2f**), demonstrating that surface functionalization is responsible for significant uptake.

After adsorption, the increase in PFOA on the copolymer film was evident through EDS mapping (**Figure 2.2g**). The contact angle analysis also confirmed the formation of significantly increased hydrophobic layer after the adsorption of PFOA (**Figure 2e**). XPS surface analysis showed the uptake of PFOA, as clearly shown in both survey and high-resolution scans (**Figure A.7 and A.8**).

The surface functionalization with P(TMA_x-co-TMPMA_{1-x})-CNT enables molecular selectivity for PFOA uptake in the presence of background anions. For example, at x=51%, in the presence of 200-fold excess of NaCl (0.1 mM PFOA + 20 mM NaCl), a molar comparison revealed the PFOA⁻ to Cl⁻ ratio to be 2.5 at open circuit, equivalent to a separation factor of 500 (**Figure 2.3a**, see Section 2.5.3 in the Supporting Information for calculation details). With the positive potential at +1.0 V, the PFOA⁻ to Cl⁻ ratio was decreased to 0.76, but still the separation factor was 152, indicating strong interaction between PFOA and the copolymer. Applying more positive potential resulted in more competitive attraction of chloride, thereby leading to decreasing trend in Coulombic efficiency for PFOA adsorption (**Figure A.9**) and also in separation factor (37.4 at +2.5 V). This indicates that a certain potential window (<+1.2 V vs. Ag/AgCl) is recommended to

achieve high molecular selectivity (separation factor > 100) as well as to minimize electrical energy consumption, as will be discussed later, suggesting the practical range of operational potential (e.g. +0.6 to +1.2 V vs. Ag/AgCl).

2.4.2 Redox-mediated regeneration

Here, we investigated the benefit from having a suitable degree of redox-active N–O• functional groups. Redox-active species have received great attention because of behaving as high charge storage materials,^{39, 53} and more recently, have been shown to efficiently couple charge storage with electrochemically-switched capture and release of charged pollutants.^{35, 36} As shown in XPS analysis (**Figure A.6**), one-electron oxidation of N–O• radicals forms +N=O,⁵⁴ and its fully reversible redox process (**Figure 2.2b**) accompanies the uptake or expulsion of doped anionic species for charge neutrality (**Figure 2.1b**). In this study, we investigated the effect of the oxidation degree on the regeneration efficiency by first charging at +1.0 V vs Ag/AgCl during adsorption, and then applying -0.5 V vs Ag/AgCl to release the adsorbed anionic PFOA molecules. As depicted in **Figure 2.2c**, the regeneration efficiency (defined as the ratio of PFOA recovered to adsorbed) improved as the radical yield was increased from x=0 to 51%. This result indicates that anion release induced by redox-mediated charge repulsion (as shown in **Figure 2.1b**) is more efficient than non-faradaic, double-layer discharging based on simple polarization of a conductive surface. For x=51%, the regeneration efficiency was enhanced by applying a more negative bias, exhibiting >80% regeneration efficiency at -1.5 V (**Figure A.10**). It was interesting to note that P(TMA₈₄-co-TMPMA₁₆), despite having the highest oxidation degree, showed the poorest regeneration. This could be ascribed to the background hydrophobic interaction

between PFOA and neutral, hydrophobic PTMA layer, evidenced by contact angle analysis which indicated more hydrophobic features with higher N–O• contents (**Figure 2.2e**). Our results confirmed that compositional control of the copolymer, with delicately tuned N-H content, redox-activity, and hydrophobicity, enables not only significant uptake of PFOA but also efficient electrochemically-mediated release of adsorbed PFAS molecules. Our design approach is shown to exert both structural and electrochemical control, thus enabling the reuse of adsorbent without the need for chemical regenerants and/or harsh operational environments.

2.4.3 Kinetics and stability

Based on the highest regeneration efficiency with $x=51\%$, P(TMA₅₁-co-TMPMA₄₉) was used for the further experiments (kinetics, isotherm, and cycling). Adsorption kinetics were studied at open circuit and +1.0 V. As seen in **Figure 2.3b**, 81% of removal was observed within 1 h by applying +1.0 V. The kinetics in the first 3 h at +1.0 V outperformed open circuit, and this is in accordance with our previous finding about the contribution of electrostatic interaction to accelerating PFOA binding (**Figure 2.2c and d**). However, the maximum obtainable uptake after reaching equilibrium (> 10 h) was slightly higher at open circuit compared to positive bias. It is hypothesized that electrostatic interaction plays a positive role of accelerating initial kinetics, but prolonged polarization for a long time induced competitive adsorption of chloride, as previously reflected in the separation factor and Coulombic efficiency analysis (**Figure 2.3a and Figure A.9**). An equilibrium isotherm at open circuit shows that a maximum capacity of up to 970 mg PFOA/g adsorbent can be

achieved (**Figure 2.3c**), which is comparable or higher than reported loadings for various adsorbents for PFOA.^{26, 47, 55-60}

A cycling test was conducted with the P(TMA₅₁-co-TMPMA₄₉)-CNT electrode being charged at +1.0 V, in the presence of 0.1 mM PFOA and 20 mM NaCl for 0.5 h, and then discharged at -1.0 V into clean electrolyte for 1 h. **Figure 2.3d** shows that the regeneration efficiency was maintained at >90 % for a number of cycles per step starting at cycle 2. The incomplete regeneration at the initial release cycle 1 can be ascribed to possible irreversible adsorption due to hydrophobic interactions between the discharged (neutral) polymer and PFOA. Even so, the steady working capacity of the functionalized polymer electrode was preserved at close to 200 mg PFOA/g adsorbent for a number of cycles. This proves the advantage of our P(TMA_x-co-TMPMA_{1-x})-CNT electrodes which are fully electrochemically-controlled and thus not requiring the addition of chemical regenerants for releasing captured PFOA molecules.

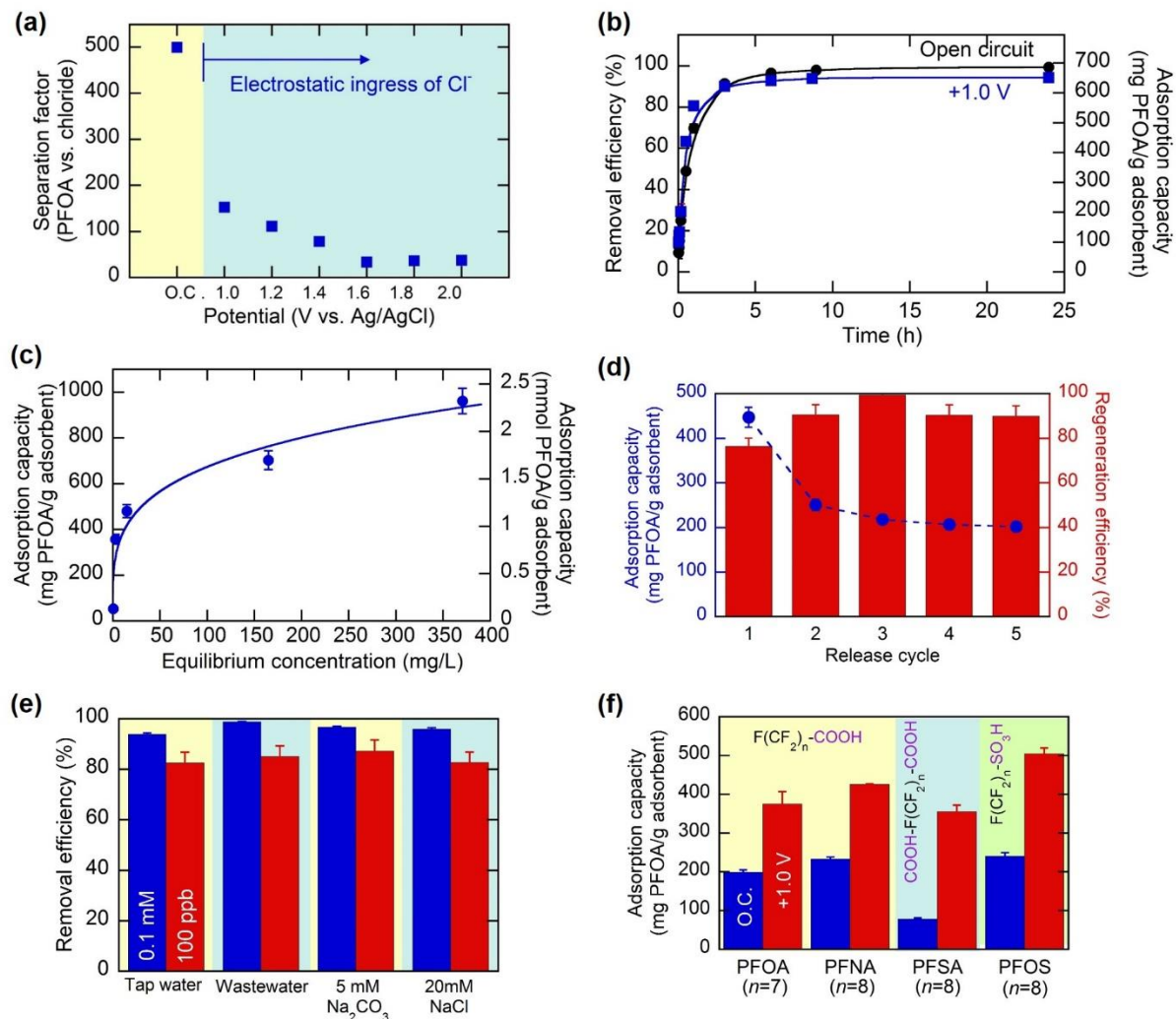


Figure 2.3. (a) Separation factors of PFOA⁻ vs. chloride on P(TMA₅₁-co-TMPMA₄₉)-CNT electrodes after adsorption in 0.1 mM PFOA + 20 mM NaCl for 1 h at open circuit, and different positive potentials vs Ag/AgCl. (b) Adsorption kinetics of PFOA by P(TMA₅₁-co-TMPMA₄₉)-CNT electrode at open circuit and +1.0 V (in 0.1 mM PFOA + 20 mM NaCl). (c) Equilibrium isotherm of P(TMA₅₁-co-TMPMA₄₉)-CNT electrode at open circuit for a range of PFOA concentrations in 20 mM NaCl (blue line represents Freundlich isotherm). (d) PFOA uptake capacity (blue dots) and regeneration efficiency (red bars) of P(TMA₅₁-co-TMPMA₄₉)-CNT electrode over 5 cycles (adsorption: 0.1 mM PFOA + 20 mM NaCl at +1.0 V for 0.5 h; desorption: in 20 mM NaCl at -1.0 V for 1 h). (e) Removal of PFOA in different water matrices

Figure 2.3. (cont.) spiked with 0.1 mM or 100 ppb (0.242 μM). +1.0 V was applied for 3 h. (f) Uptake capacity of different PFAS compounds with P(TMA₅₁-co-TMPMA₄₉)-CNT electrode at open circuit and +1.0 V (adsorption: 0.1 mM PFAS compounds + 20 mM NaCl for 0.5 h).

2.4.4 Real water matrices

To evaluate relevant environmental conditions, the removal of PFOA was tested under different water matrices, including 20 mM NaCl, tap water, 5 mM Na₂CO₃, and municipal secondary wastewater effluent solution (obtained from Urbana-Champaign Sanitary District) (**Figure 2.3e**). In all water matrices, >93% removal efficiency was achieved within 3 h of electrosorption when spiked with 0.1 mM PFOA, and >82.5% at the initial PFOA concentration of 100 ppb (0.242 μM). We also tested the performance of P(TMA₅₁-co-TMPMA₄₉)-functionalized electrodes for the removal of several PFAS compounds with different chemical structures, including perfluorocarboxylic acids ($\text{C}_n\text{F}_{2n+1}\text{COO}^-$), per- and polyfluoro dicarboxylic acids ($^- \text{OOC}-\text{C}_n\text{F}_{2n}-\text{COO}^-$), and perfluoroalkanesulfonic acids ($\text{C}_n\text{F}_{2n+1}\text{SO}_3^-$) (**Figure 2.3f**). For a given chain length ($n=8$), the open circuit adsorption of different PFAS compounds seemed to be mainly affected by hydrophobic interaction; for example, PFSA (perfluorosebacic acid), having double $-\text{COO}^-$ head groups and lacking primary C-F bond, is less hydrophobic and thus shows the poorest uptake. For all cases, however, applying +1.0 V of positive potential led to greatly improved uptake, and PFSA has the highest increase with the positive potential. This shows the importance of electrostatic interaction as a dominant mechanism which balances the affinity interaction. All these results support the wide applicability of our

functionalized polymer electrode to address real-world contamination under relevant conditions and a diversity of chemical structures.

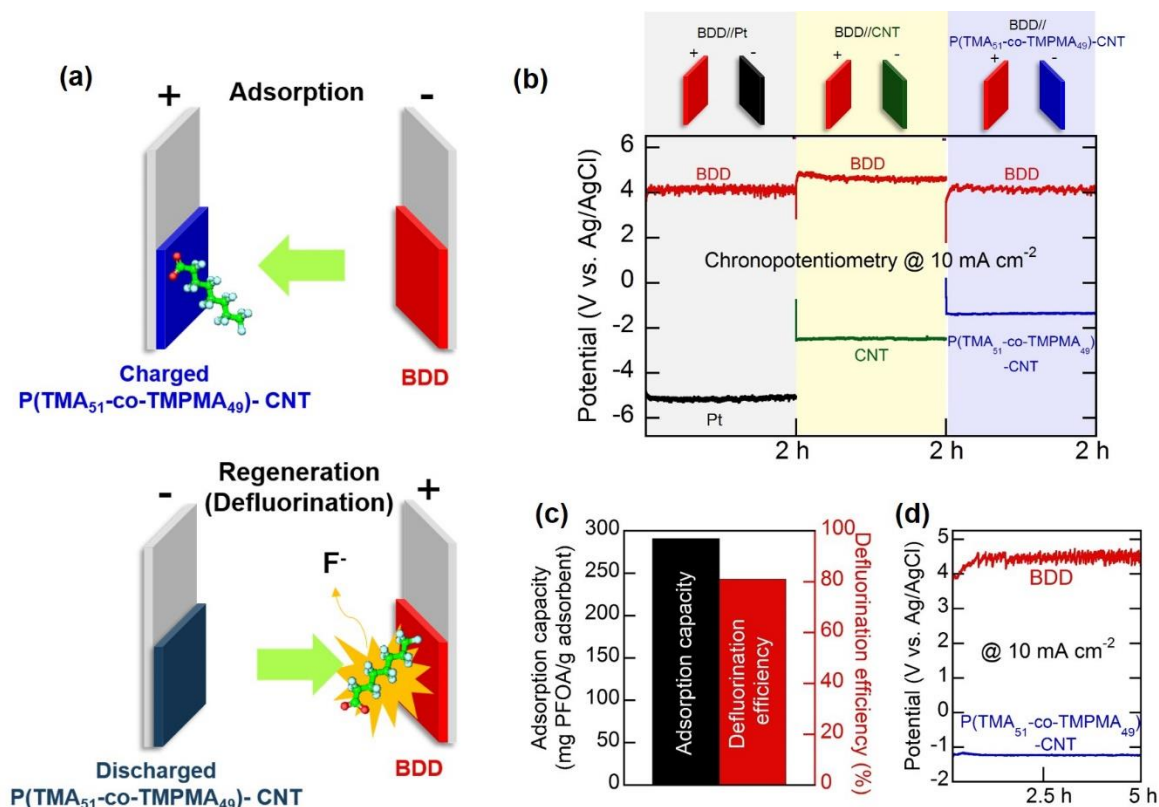


Figure 2.4. (a) Schematic illustrations showing selective uptake of PFOA by P(TMA_x-co-TMPMA_{1-x})-CNT during adsorption and degradation of released PFOA by BDD electrode during regeneration. (b) Simultaneous tracking of anode (BDD) and counter electrode potentials during chronopotentiometry at 10 mA cm⁻² in 0.1 mM PFOA + 20 mM NaCl for 2 h using different counter electrodes of Pt, CNT, and P(TMA₅₁-co-TMPMA₄₉)-CNT. (c) and (d) represent the operation of the asymmetric P(TMA₅₁-co-TMPMA₄₉)-CNT//BDD system for one cycle of adsorption and desorption: (c) PFOA uptake capacity during the adsorption and defluorination efficiency during the regeneration in the asymmetric P(TMA₅₁-co-TMPMA₄₉)-CNT//BDD configuration (adsorption: in 0.1 mM PFOA + 20 mM NaCl for 0.5 h). (d) Tracking of anode

Figure 2.4. (cont.) (BDD) and cathode (P(TMA₅₁-co-TMPMA₄₉)-CNT) potentials during the regeneration (desorption) of P(TMA₅₁-co-TMPMA₄₉)-CNT in 20 mM NaCl at 10 mA cm⁻² for 5 h.

2.4.5 Integration of reactive separation

While our approach suggests a promising way of electrically-controlled adsorption and desorption of PFAS with tunable surface functionalization, the fate of the enriched PFAS waste after separation process must be considered.^{61, 62} Here, we propose a unique approach to achieve tandem separation and degradation of PFOA within the same electrochemical unit, by leveraging an asymmetric electrochemical design that combines the P(TMA_x-co-TMPMA_{1-x})-functionalized CNT electrode with a boron-doped diamond (BDD) electrode. As shown in **Figure 2.4a**, in the asymmetric design of P(TMA_x-co-TMPMA_{1-x})-CNT//BDD, PFOA is first captured by P(TMA_x-co-TMPMA_{1-x}), whereas during release, BDD electrode catalyzes defluorination of released PFOA. BDD anode has proven its promising ability to degrade PFAS and various organic contaminants in wide applications for electrochemical advanced oxidation, showing desirable features of commercial availability, high stability, low adsorption capacity, and high overpotential for oxygen evolution (**Figure A.1**).⁶³⁻⁶⁶ In this study, we explore the performance of P(TMA_x-co-TMPMA_{1-x})-CNT as a suitable counter electrode when coupled with BDD as the working anode, and the overall effect in lowering electrical energy consumption for mineralization. Chronopotentiometric tests on the BDD anode were carried out at 10 mA cm⁻² with various counter electrodes of platinum, CNT, and P(TMA₅₁-co-TMPMA₄₉)-CNT in 0.1 mM PFOA + 20 mM NaCl (**Figure 2.4b**). Simultaneous tracking of the potential at both working

(BDD) and counter electrodes during charging were carried out against a reference Ag/AgCl. The analysis showed that conductive, non-redox counter electrodes (platinum and CNT) reached significantly negative overpotentials; while the redox-active P(TMA₅₁-co-TMPMA₄₉)-CNT on the other hand remains at potentials no lower than -1.4 V (**Figure 2.4b**). This observation indicates that our P(TMA₅₁-co-TMPMA₄₉) provides an energy-efficient option as a counter electrode during electrochemical degradation, enabling much lower voltage windows for BDD-based electrochemical oxidation processes. On the conductive counter electrodes, water decomposition is a major cathodic reaction with a large overpotential, dissipating energy unless evolved H₂ is recovered.^{35, 40} By coupling the P(TMA₅₁-co-TMPMA₄₉)-CNT with BDD, we can efficiently store electrons through N-O•/+N=O electrochemistry, whose redox is directly connected to electrochemically-controlled PFOA capture and release.

A viable implementation of tandem separation and degradation of PFOA in one device (**Figure 2.4a**) was experimentally realized in this asymmetric configuration of P(TMA₅₁-co-TMPMA₄₉)-CNT//BDD, first by adsorbing in 0.1 mM PFOA + 20 mM NaCl for 0.5 h, followed by applying constant current density of 10 mA cm⁻² with reversed polarity for 5 h in clean 20 mM NaCl to release and degrade PFOA. The adsorption capacity was 291 mg PFOA/g adsorbent (**Figure 2.4c**), and applying constant current density of 10 mA cm⁻² with reversed polarity rendered the potential of P(TMA₅₁-co-TMPMA₄₉)-CNT to be -1.2 V (**Figure 2.4d**), which was sufficient to achieve a high regeneration (**Figure A.10**). At the same time, the working potential of BDD anode was maintained at about +4.5 V, a potential range capable of spurring the degradation of PFOA.⁶³ From LC/MS analysis, no PFOA was found in the desorption electrolyte, implying complete degradation of released PFOA. The

final concentration of fluoride was quantified using ion chromatography, and the normalized fluoride recovery out of adsorbed amount (291 mg PFOA/g adsorbent) was found to be 81% after 5 h electrolysis (**Figure 2.4c**), which is comparable or higher than the defluorination ratio (i.e., $C^{F^-}_{\text{produced}}/C^{F^-}_{\text{in PFOA, initial}}$) reported for various electrochemical PFOA degradation.⁶⁶⁻⁷³ Its corresponding F index (i.e., $C^{F^-}_{\text{produced}}/C^{\text{PFOA degraded}}$) was 12.1, implying fluoride recovery of 12.1 out of 15 per PFOA molecule degraded. To the best of our knowledge, our proof-of-concept study is the first realization of the coupling of a redox-active polymer with BDD electrode, providing an efficient remediation pathway for degrading enriched PFAS compounds from separation stream within a single unit operation.

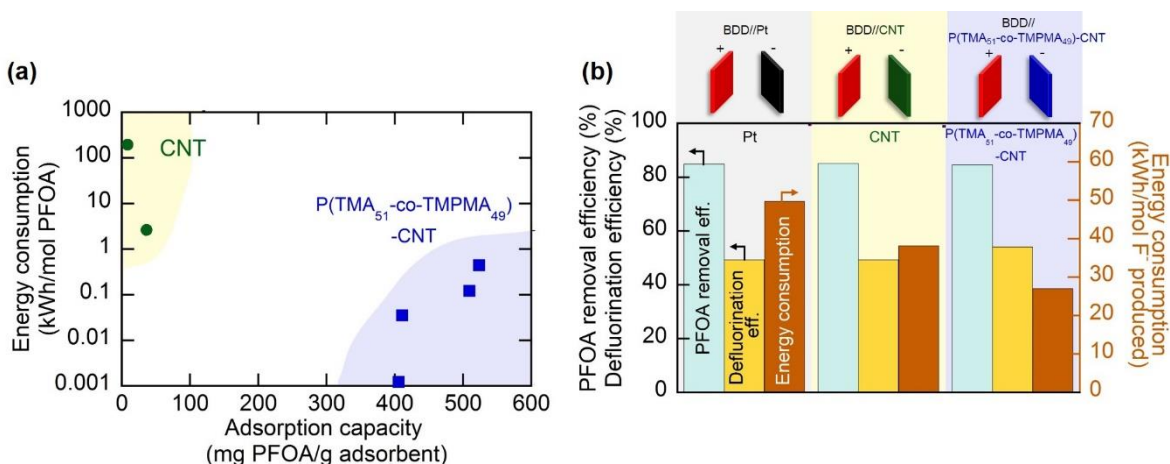


Figure 2.5. (a) Energy consumption during the electroseparation of PFOA by CNT and by P(TMA_x-co-TMPMA_{1-x})-CNT. (b) PFOA removal (sky blue bar), defluorination efficiency (orange bar), and energy consumption (brown bar) during chronopotentiometry at 10 mA cm⁻² in 0.1 mM PFOA + 20 mM NaCl for 2 h using BDD as a working electrode and different counter electrodes of Pt, CNT, and P(TMA₅₁-co-TMPMA₄₉)-CNT.

2.4.6 Energy analysis

Finally, the energy consumption for separation and defluorination was estimated, to highlight the intrinsic performance advantages of our tunable polymer-functionalized interfaces over regular non-Faradaic electrosorption systems. First, we can achieve remarkable energy-efficiency improvement in the electroseparation process. Several experimental tests revealed applying P(TMA_x-co-TMPMA_{1-x})-CNT enabled a significantly improved separation factor during electrosorption, leading to high adsorption capacity and at the same time lowering the amount of energy input in the separation process to < 0.44 kWh/mol PFOA (**Figure 2.5a**). On the other hand, control experiments of PFOA electrosorption based on CNT was estimated to use > 2.67 kWh/mol PFOA for electroseparation (in one data point, the energy consumption turned out to be even 196 kWh/mol PFOA), due to low selectivity and poor affinity of non-functionalized surface (**Figure 2.5a**). Furthermore, the polymer-functionalized interfaces, when coupled with BDD anode, provide a chance to lower the electrical energy consumption via tuning of the redox potentials. In chronopotentiometric operations for 2 h with three different counter electrodes of platinum, CNT, and P(TMA₅₁-co-TMPMA₄₉)-CNT, all the configurations exhibited the same or similar PFOA removal and defluorination performance under the same current density, but a much lower mineralization energy was required with our redox-active polymer counter compared to conductive ones (**Figure 2.6b**).

In our operation of P(TMA₅₁-co-TMPMA₄₉)-CNT//BDD configuration for a cycle of PFOA adsorption and regeneration (**Figure 2.4a**), the mineralization energy estimated from the defluorination performance (**Figure 2.4c**) and voltage and current (**Figure 2.4d**) was found to be 62.3 kWh/mol F⁻ for 5 h. This is among the lowest reported in the literature

(electrochemical (10-1500 kWh/mol F⁻), microwave (4200 kWh/mol F⁻), UV (450-2000 kWh/mol F⁻), and ultrasonic (250-4200 kWh/mol F⁻)),^{68, 74, 75} especially due to high defluorination efficiency as well as the tuning of redox-potential using P(TMA₅₁-co-TMPMA₄₉)-CNT electrode. Our consideration in the energy aspect demonstrates the possibility of using P(TMA_x-co-TMPMA_{1-x})-CNT as not only a cost-effective electrochemically-mediated adsorbent, but also a sustainable counter electrode enabling energy-efficient, tandem degradation of PFOA, all of which provide desirable options for next-generation, energy-integrated water purification devices.

CHAPTER 3: ELECTROCHEMICALLY-MEDIATED REMEDICATION OF GENX USING REDOX-COPOLYMERS*

3.1 Overview

Per- and polyfluorinated alkyl substances (PFASs) are toxic and persistent contaminants that have been continuously detected in groundwater and drinking water around the globe. Hexafluoropropylene oxide dimer (tradename GenX) has been used to substitute legacy PFAS, such as PFOA, but its widespread use is causing high detectable levels in aquifers. In chapter 3, we developed a system that uses a redox copolymer, poly(4-methacryloyloxy-2,2,6,6-tetramethylpiperidin-1-oxyl-co-4-methacryloyloxy-2,2,6,6-tetramethylpiperidine) (PTMA-co-PTMPMA), capable of selectively and electrochemically adsorbing GenX. The implementation of amine functional groups promotes the affinity towards anionic PFASs, and the redox-active nitroxide radicals provide electrochemical control towards adsorption and desorption. Faster kinetics and higher uptake (>475 mg/g adsorbent) were obtained when applying a potential. The copolymer electrodes effectively remove GenX with high uptake and exhibit applicability over a wide pH range and in various environmental water matrices. Moreover, we translated a batch-type system into a flow-by cell system capable of successfully adsorbing and desorbing GenX. Finally, prolonged exposure of GenX under reduction potentials at the redox-electrodes was found to generate smaller PFAS fragments. Thus, for fully defluorinating GenX, we couple the copolymer-based working electrodes with a counter electrode of reactive boron-doped diamond

*This Chapter was Reproduced from *Environ. Sci.: Water Res. Technol.*, 2021,7, 2231-2240 with permission from the Royal Society of Chemistry.

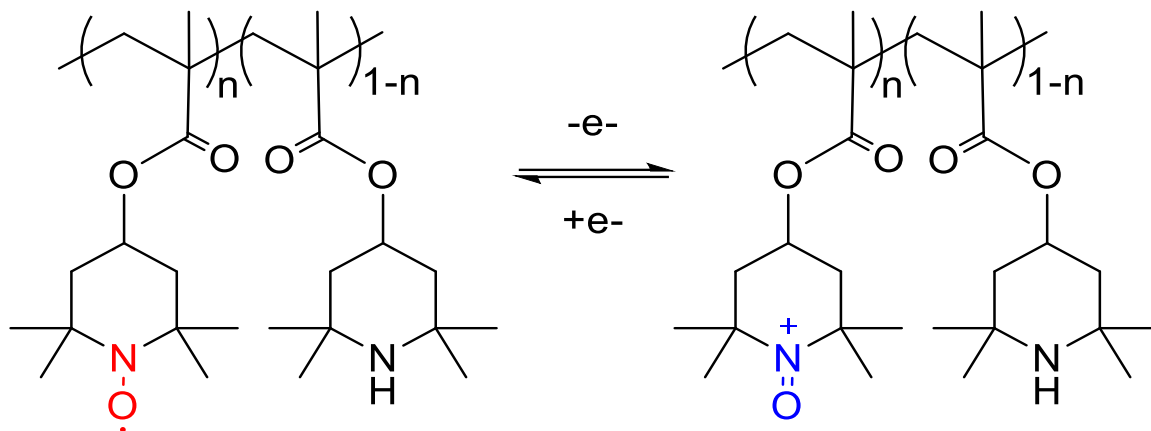


Figure 3.1. Redox-active PTMA-co-PTMPMA copolymer utilized to increase adsorption uptake via electrochemical input. The nitroxide radical group when oxidized becomes an oxoammonium cation that inhibits electrostatic interactions, while the N-H secondary amine counterpart (PTMPMA) enhances adsorption based on amine interactions.

(BDD) to provide a tandem method for integrating separation and defluorination within the same device, demonstrating close to 100% defluorination efficiency. Here, we demonstrate the potential of tunable redox platforms for the reactive separation of fluorotelomers and point to future directions for scaleup and real-world implementation.

3.2 Introduction

PFAS have been detected in aquatic and drinking water at levels that surpass the EPA and European Commission standards⁷⁶⁻⁸⁰. Veneto, Italy, has been one of the places where the abundant concentration of PFAS has been found in drinking water, where concentration levels ranged from 319-1,475 ng/L⁷⁸. While in the United States, surface water has been found to contain levels of PFAS of more than 2000 ng/L and in surface water foams at up to 97000 ng/L^{81, 82}. Also, in groundwater, these compounds have been found at levels of up to 5,200 ng/L⁸³. In addition,

numerous studies have shown their presence in human blood serum and wildlife, which is indicative of the importance of setting water boundaries to prevent further exposure.⁸⁴⁻⁸⁶

Most studies on PFAS adsorption and destruction have targeted PFOA and PFOS as these two compounds were detected more frequently and at much higher concentrations than other PFAS in water monitoring experiments,⁸⁷ as well as being the initial PFAS developed since the early 1940s.⁸⁸ With the more stringent regulation for PFOA and PFOS,⁸⁹ there has been an increase in the use of short-chain PFAS. Therefore, hexafluoropropylene oxide dimer acid (HFPO-DA, also known as GenX) has seen increased use as a direct substitute of PFOA,⁹⁰ and is utilized in larger quantities to match the performance of the longer chain precursors.⁹¹ While GenX could potentially have lower bioaccumulative properties based on their volatility and C-F distribution, it has concerningly been detected in water, with these short-chain compounds as well as degradation byproducts still persisting in the environment.⁹²

The molecular properties of GenX present several challenges for separation processes and environmental remediation. The shorter aliphatic backbone of GenX, along with the middle ether bond, makes it more hydrophilic when compared with the longer chain PFAS. Also, their shorter molecular structure provides higher mobility in the environment, increasing their chances of being found in drinking water and other streams.^{93,94} GenX also exhibits high water solubility and a pKa of 2.84, which provides the molecule with a negative charge over a wide pH range.⁹⁵ Previous studies have targeted GenX for water remediation using conventional treatment techniques such as adsorption, ion exchange, filtration, and reverse osmosis, but better capture and defluorination efficiency must follow.^{96,97} The evidence has shown that for some adsorption materials and other techniques, short-chain PFAS still lack better regeneration efficiencies.^{96,98} In addition, some of

the previous removal methods require the input of organic solvents, which increases the operating cost of the process as well as chemical footprint, while lacking efficient regeneration.⁹⁹

Thus, an electrochemical route for separation and remediation of PFAS can provide an attractive platform that is environmentally friendly by avoiding the intensive use of energy/chemicals. Recently, electrochemical pathways have been explored for the efficient removal and remediation of emerging contaminants in water by leveraging molecularly-tailored interfaces for selective electrosorption.^{35, 100, 101} In particular, our previous study has leveraged redox copolymers for the selective binding and integrated defluorination of long-chain PFAS.¹⁰¹ It revealed that three main interactions – hydrophobicity, amine interactions, and electrostatic interactions – synergistically capture/release legacy PFAS without the use of chemical regenerant.

However, redox electrosorbents have not yet been studied, either in performance or interactions, for shorter chain PFAS – which is a critical gap for the performance of these redox-systems. Here, we selected a copolymer that combines 4-methacryloyloxy-2,2,6,6-tetramethylpiperidin-1-oxyl (TMA) and 4-methacryloyloxy-2,2,6,6-tetramethylpiperidine (TMPMA) repeating units, explicitly PTMA-co-PTMPMA (**Figure 3.1**), proven to be effective in adsorbing long-chain PFAS in our previous study.¹⁰¹ Amine functionalities have been regarded as a superior binding site with affinity for negatively charged PFAS,^{31, 102} and the secondary amine functionality (N-H) of the piperidine unit possesses the high pKa value (pKa=11.28),¹⁰³ providing protonated and thus positively charged binding sites toward negatively charged GenX in a wide range of pHs, which is optimal for environmental needs. At the same time, the redox couple of nitroxide radical/oxoammonium (N-O●/N=O⁺), allows for additional enhancement in the electrostatic interactions with the anionic carboxylate group of

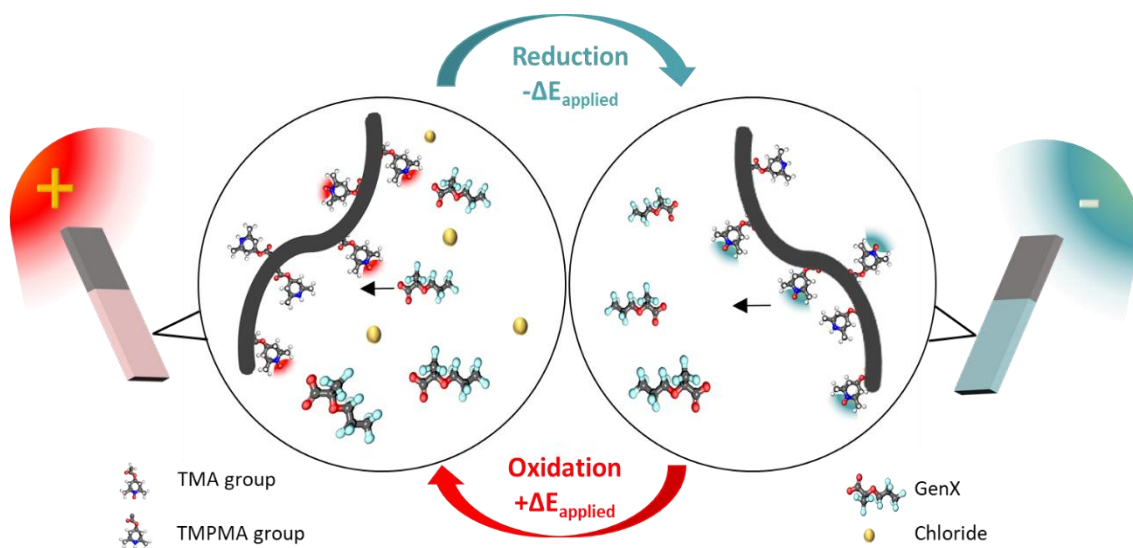


Figure 3.2. A representative scheme of redox-active electrode of PTMA-co-TMPMA for the electrochemical adsorption and desorption of GenX, in the presence of competing anion species. Anodic potential promotes the selective electrosorption of anionic PFAS, while a reductive potential will release the bound molecules.

GenX and serve as a reversible, electrochemically-mediated switch for the adsorption and regeneration.

In this work, we investigate the potential of PTMA-co-PTMPMA as an electrosorbent for short-chain PFAS, specifically GenX. The system adsorbs GenX when an oxidative potential is applied and released at a reductive potential (**Figure 3.2**). Through parametric studies of adsorption/release, we prove the importance of synergistic electrostatic/hydrophobic interaction and the application of our electrosorbent to real environmental conditions. Also, the capability of redox electrodes obtained in an analytical batch scale was translated in an up-scaled flow cell system, showing the capability of redox electrodes of adsorbing/desorbing GenX under flow. Finally, to further explore the destruction of separated GenX, we examine the possibility of

reductive degradation of GenX by the copolymer, and also, we establish an asymmetric redox-copolymer//boron-doped diamonds (BDD) configuration, where the BDD counter electrode is shown to be effective for defluorination for GenX. Thus, in this chapter, it will be explored for the first time the feasibility of redox copolymers for electrosorption of short chain PFAS as well as incorporate it into an electrochemical flow cell system.

3.3 Methods

3.3.1 Materials

Undecafluoro-2-methyl-3-oxahexanoic acid (GenX) (97%) was obtained from Matrix Scientific. All other chemicals were obtained from Sigma Aldrich, VWR, Fisher Scientific, or TCI, and they were used as received. Acetonitrile and ammonium acetate for LC/MS analysis were LC grade. Water for LC/MS and ion chromatography (IC) analysis was obtained from an ELGA Purelab flex 1 system >18M Ω . The stock solution for each PFAS compound was prepared in DI water at a concentration of 10 mM. These solutions were stored in the fridge (4°C), and the storage time was no longer than six months.

3.3.2 Synthesis of poly(4-methacryloyloxy-2,2,6,6-tetramethylpiperidin-1-oxyl-co-4-methacryloyloxy-2,2,6,6-tetramethylpiperidine) (PTMA-co-PTMPMA)

Synthesis for PTMA-co-PTMPMA was described in previous work from our group.¹⁰⁴ Radical content obtained was 51%. This result was obtained by UV-vis measurements with TEMPO used as a reference.¹⁰¹ and SEC data obtained from GPC resulted in M_n of 84.7 kg/mol and M_w of 290.0 kg/mol.¹⁰¹

3.3.3 Flow by-cell assembly

The flow cell assembled is composed of a top flowing (TF) acrylic base, TF electrode backing gasket, PTMA-co-PTMPMA/MWCNT electrode, 1/16" middle gasket, 4x4 cm plastic mesh, Ti electrode, which could be switch to a Pt coated/Ti electrode, bottom flowing (BF) backing electrode backing gasket, and BF acrylic base. The flow cell was tightened with 8 M3 nuts and bolts in an aleatory fashion (1,5,2,6,3,7,4,8) to provide stability and prevent leaking by adjusting to a proper seal. This seal was rapidly tested by passing an initial solution of the solvent without applying any potential and measuring the volume in versus the volume out for one minute.

The PTMA-co-PTMPMA/MWCNT electrode had an active area of 4 cm x 4 cm. A non-conductive tape was placed around the corners of the Ti or Pt coated/Ti plate to obtain a precise coating area of 4 cm x 4 cm. The polymer solution was then dropped cast, and a total volume of 800 uL was injected onto the surface. The solution was dried rapidly in air, and to ensure dryness we applied forced air onto the surface to enhance the drying. Before experimentation, the electrode was pretreated by activating it with cyclic voltammetry in 0.1 M NaClO₄ in the range of 0 – 1.2 V (vs. Ag/AgCl) at a scan rate of 10 mV/s for three cycles to then fully reduce for 3 minutes at 0.0 V.

To start the experimentation, the stock solution, composed of 0.1 mM Genx and 20 mM NaCl or 0.1 mM PFOA and 20 mM NaCl, is placed on a magnetic stirring plate. A suction side tube, connected to the Longer peristaltic pump, is inserted in the stock solution, and the discharge side tube is connected to the bottom flowing inlet of the flow cell. On the other side of the flow cell, a tube is attached to the output flowing outlet of the flow to collect samples. The electrolyte flowed from the bottom of the Ti side to flow out from the top on the PTMA-co-

PTMPMA/MWCNT side. The flow rate of the peristaltic pump is calculated and set to be 1.0 mL/min.

During the experiment, the sample collection was set for one sample collection every five minutes of the experimental run. In addition, a 5 ml stock solution is taken directly before and directly after the experiment. The samples were then diluted and analyze for LC/MS.

3.3.4 Sputter coating of a Ti electrode with Pt

For the flow cell experimental analysis on energy two electrodes were compared. One that contained bare Ti and a Pt/Ti electrode. The Pt coated Ti electrode was sputter coated (3 x 3 in.) through magnetron sputtering (AJA ORION 3 sputter system with ST20 ORION magnetron sputter gun). The base pressure was 2.5×10^{-6} Torr, and argon was used at a process pressure of 3.4 mTorr. Sputtering took place at room temperature, with direct current and 80 W power, ~15 rpm sample rotation, 1 minute pre-sputtering. The recorded sputtering rate was 9.6-10.4 Å/s. The Pt thickness measured by the instrument's quartz crystal microbalance was 251.0 nm.

3.3.5 Analytical methods for PFAS and fluoride detection

A Waters Synapt G2Si with Waters Acquity H-class UPLC LC/MS system was used to detect PFAS concentration in an aqueous solution. All parameters utilized for the LC/MS analysis can be found in the supplementary materials section of this work. For detecting fluoride content, a Thermo Fisher Dionex 2100 ion chromatography system was utilized. The analytical parameters used have been described elsewhere.¹⁰¹ For every analytical run, a new set of calibration curves were assessed for both LC/MS and IC.

3.3.6 Electrode preparation and characterization

The polymer-coated electrodes of PTMA-co-PTMPMA/multiwalled carbon nanotubes (MWCNT) were prepared using a dip-coating technique, which is described in detail in the supplementary information section (Section S3.5.2). The PTMA-co-PTMPMA have been previously synthesized, and this product is composed of 51 mol % TMA and 49 % TMPMA.¹⁰¹ This copolymer is known for its optimal triple interactions with long-chain PFAS and dispersion with MWCNT that serve as an excellent binder to improve the surface area and conductivity. The ink solution ratio was composed of 1:1 PTMA-Co-PTMPMA: MWCNT and was applied onto the stainless-steel mesh electrode via dip-coating technique and dried with air. The loading mass was maintained at 0.5 mg in an active surface area of 2 cm².

3.3.7 Electrochemical experiments

Electrochemical experiments were carried out in a potentiostat (SP-200 Potentiostat, Biologic, and Squidstat Plus, Admiral Instruments). For batch experiments, a BASi VC-S voltammetry electrochemical cell in a three-electrode configuration was selected. Ag/AgCl was used as the reference electrode, and Pt was used as the counter electrode for all adsorption experiments. Batch experiments were performed in 5 mL solutions unless specified. The typical working time was 30 minutes, and the electrolyte solution utilized was 20 mM NaCl; this should be the same unless indicated. All the electrochemical analysis calculations were performed using the total mass of the polymer, and MWCNT was added based on the results obtained in **Figure B.11**.

3.3.8 Electrochemical flow cell

For flow cell experimentation, an in-house designed flow-by cell device was utilized in a two-electrode configuration with 16 cm² area (4cm x 4cm) electrodes. The working electrodes were coated with PTMA-co-PTMPMA/MWCNT solution using a drop-casting technique. Either a bare Titanium or Platinum sputter-coated (thickness of 251.0 nm) with counter electrode were used. All the experiments were performed under chronopotentiometry by applying 2 mA for adsorption and -2 mA for desorption with a GenX flow rate of 1 ml/min from a Longer Instruments peristaltic pump.

3.4 Results and Discussion

3.4.1 PTMA-co-PTMPMA electrode fabrication and characterization

PTMA-co-PTMPMA was synthesized by oxidation of PTMPMA with MCPBA, as described previously.¹⁰¹ The content of nitroxide radicals was 51 mol % and was determined by ultraviolet-visible spectroscopy at 460 nm absorption wavelength.¹⁰¹ In addition, the presence of nitroxide and amine functionalities on the electrode was confirmed by X-ray photoelectron spectroscopy (XPS) (**Figure B.4**). The peak distribution is designated as follows: the lower binding energy peak (398 eV) corresponds to the N-H functional group, while the N-O● peak can be found at 402 eV. The cyclic voltammogram, **Figure 3a**, indicates oxidation of the N-O● to N=O⁺ occurring at 0.83 V vs. Ag/AgCl, while reduction is depicted at 0.53 V vs. Ag/AgCl. Also, the hydrophobic behaviour of our PTMA-co-PTMPMA is expected to be beneficial for GenX uptake (**Figure B.5**).

3.4.2 Electrosorption of GenX

Before each electrochemical experimentation, we carried out a simple pre-treatment step to provide an electrode where most of the active sites pre-experimentation to be fully unoccupied for higher uptake. For pre-treatment, cyclic voltammetry was carried out from 0.0 to 1.2 V vs Ag/AgCl on a 0.1 M NaClO₄ solution (**Figure 3.3a**). Then, the electrode was reduced in the same solution by chronoamperometry with a 0.0 V vs. Ag/AgCl for 3 minutes. Not following this procedure resulted in lesser adsorption uptake, as observed in **Figure B.1**. Based on those results (**Figure B.1**), we hypothesized that by fully reducing the electrode, the adsorption sites that promote higher hydrophobic interactions and electrostatic attractions can be activated simultaneously when applying an anodic potential and consequently increase the kinetics for the adsorption reaction. Electrochemical separation of GenX at different potentials was studied, showing the highest uptake capacity observed at 0.8 V vs. Ag/AgCl (**Figure 3.3b**). At potential higher than 0.83 V vs. Ag/AgCl, which is the oxidation peak of PTMA-co-PTMPMA at 0.83 V vs. Ag/AgCl (**Figure 3.3a**), the uptake capacity decreases due to competing adsorption of chloride attracted to the copolymer when applying increasing high potentials. Further experiments were carried out based on an energy calculation (**Figure B.12a**) at 0.8 V vs. Ag/AgCl. Moreover, when comparing adsorption under electric potential with open circuit adsorption, it is noticeable that applying a charge to the system enhances the adsorption uptake capacity by more than 50 mg/g when compared to 0.8 V (**Figure 3.3b**). These findings prove the importance of additional electrostatic attractions of the oxoammonium cations in oxidized PTMA-co-PTMPMA towards short-chain GenX PFAS. Equilibrium isotherm study reveals that at different concentrations, our system was able to obtain an uptake capacity of up to 497 mg/g adsorbent when applying 0.8 V vs. Ag/AgCl for 30 minutes (**Figure 3.3c**). The isotherm result was fitted using the Langmuir and Freundlich

models. The Langmuir model portrays a better fit based on the correlation coefficient ($R^2=0.997$ for Langmuir vs. $R^2=0.934$ for Freundlich) (**Figure B.6** and **Table B.3**).

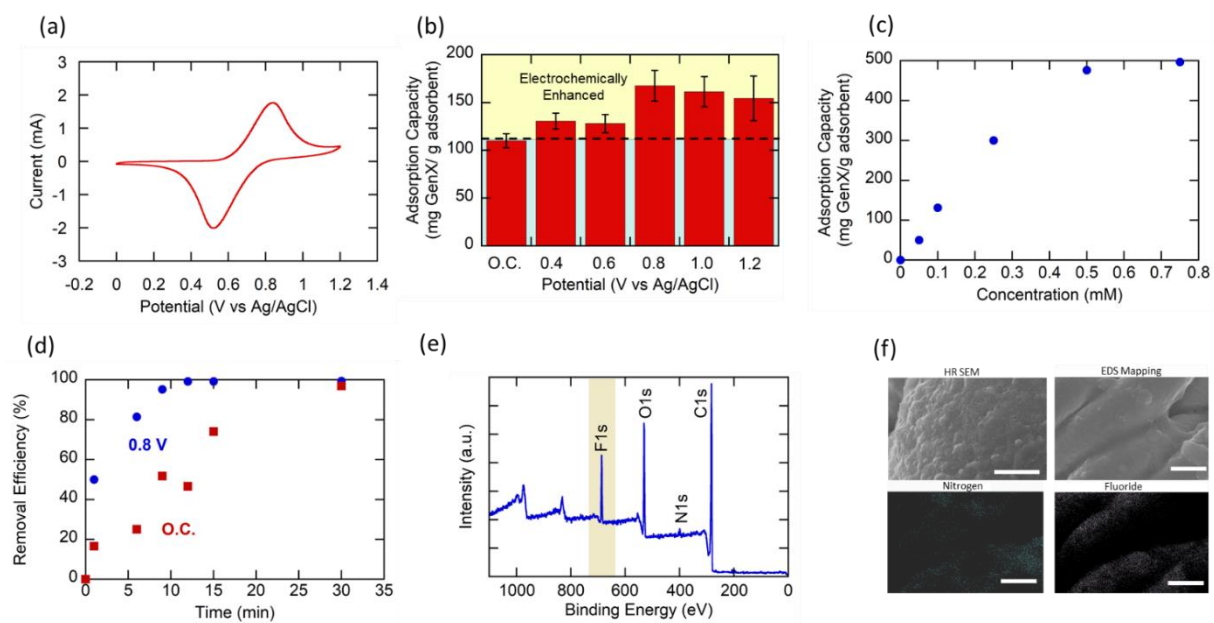


Figure 3.3. Characterization of the PTMA-co-PTMPMA. (a) Cyclic voltammogram of PTMA-co-PTMPMA in 0.1 M NaClO₄, Scan rate of 10 mV/s in a range from 0.0 to 1.2 V vs. Ag/AgCl. (b) Electrochemical uptake of PTMA-co-PTMPMA at different potentials. The experiments were performed under 0.1 mM GenX and 20 mM NaCl for 30 minutes applying continuous stirring of 300 rpm. Error bars correspond to three consecutive experiments. (c) GenX equilibrium isotherm for PTMA-co-PTMPMA with 0.8 V vs. Ag/AgCl for different GenX concentrations in 20 mM NaCl. (d) Comparison of adsorption kinetics of PTMA-co-PTMPMA at open circuit versus 0.8 V vs. Ag/AgCl. The experiment was performed with 0.1 mM GenX and 20 mM NaCl. (e) XPS survey of an electrode after being adsorbed under 0.1 mM GenX and 20 mM NaCl. Fluoride peak of F1s shows high intensity proving adsorption of the PFAS compound (f) Scanning electron microscopy (SEM) figures of a PTMA-co-PTMPMA electrode after 12 hours of

Figure 3.3. (cont.) electrosorption at 0.8 V vs. Ag/AgCl. Energy-dispersive X-ray spectroscopy (EDS) mapping proves fluoride adsorption. The scale bar for the high-resolution image is 5 μm , SEM and EDS mapping on N/F are all 20 μm .

Electrosorption kinetics were explored for open circuit (O.C.) and at 0.8 V vs Ag/AgCl in 2.5 mL of 0.1 mM GenX and 20 mM NaCl (**Figure 3.3d**). Interestingly, electrostatic enhancement promoted >95% of GenX removal in just 9 minutes, while for O.C., the reaction reached >95% removal after 30 minutes. To further investigate the system's kinetics, linear fitting using the pseudo-first-order and pseudo-second-order kinetics model were used. The results show that for the kinetics experiment of 0.8 V, the best model that fits based on the correlation coefficient is the pseudo-second-order kinetics model and its adsorption rate constant was $0.00894 \text{ g} \cdot \text{mg}^{-1} \text{ min}^{-1}$ (**Figure B.7** and **Table B.4**). In contrast, kinetics results for open circuit experiments show better fitting with the pseudo-first-order kinetic model according to the correlation coefficient. The rate constant for the open circuit kinetics experiment based on the pseudo-first-order models was 0.00268 min^{-1} (**Figure B.8** and **Table B.5**). Considering our results when applying potential, we could say that our rate constants are comparable to other studies and surpass the rate of some materials such as ion exchange resins.⁹⁸

XPS analysis performed on an adsorbed PTMA-co-PTMPMA/MWCNT electrode after applying a 0.8 V potential under 0.1 mM GenX and 20 mM NaCl indicates a ratio of 9.85 between F^- and Cl^- , which is equal to 0.89 GenX/ Cl^- ratio. The separation factor was calculated using **Equation 1**, and the results show a separation factor of 178 for GenX, indicating high selectivity of our redox polymer toward GenX.

$$\text{Separation Factor}_{\text{GenX}^-/\text{Cl}^-} = \frac{\frac{q_{\text{F}^-}}{q_{\text{Cl}^-}}}{11 * C_{\text{GenX}^-_0}/C_{\text{Cl}^-_0}}$$

(Eq. 3.1)

Where $C_{\text{GenX}^-_{eq}}$ and $C_{\text{Cl}^-_{eq}}$ are the initial concentration of their respective species in solution, 0.1 mM for GenX and 20 mM for NaCl, while concentrations q_{F^-} and q_{Cl^-} are the solid phase uptakes obtained from the XPS analysis, 90.78 for F^- and 9.22% for Cl^- . **Figure 3.3e** proves the adsorption of GenX based on the intense fluoride peak generated. Also, **Figure 3.3f** depicts a high-resolution scanning electron image of the surface of a new electrode as well as an EDS mapping of a non-saturated electrode ran for 30 min at 0.8V in 0.1 mM GenX and 20 mM NaCl where fluoride could be detected after 30 minutes of electrosorption.

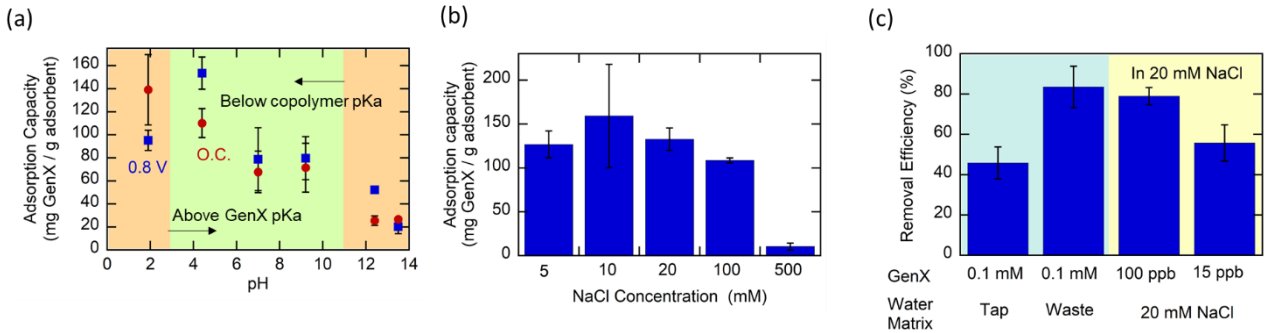


Figure 3.4. (a) Study of adsorption capacity of GenX at different pH. Experiment was performed on 0.1 mM GenX and 20 mM NaCl with 0.8 V for 30 minutes. (b) Adsorption capacity of PTMA-co-PTMPMA with different concentrations of sodium chloride and 0.1 mM GenX under 0.8 V vs. Ag/AgCl (c) Removal efficiency using different water matrices and lower concentrations of GenX in 20 mM NaCl for 3 hours. All error bars correspond to two experiments.

3.4.3 Electroseparation in various water matrices and pH effect

We studied the effect of solution pH on the adsorption of GenX with PTMA-co-PTMPMA. GenX's pKa is 2.84, indicating that it would exist in the anionic form at a higher pH level.⁹⁵ Therefore, at pH 1.9, GenX is neutral, and hydrophobic interaction is hypothesized to be the dominant interaction responsible for the adsorption – note that there is no electrochemically-driven enhancement (**Figure 3.4a**). Then, at pH higher than 4, the adsorption would be mainly ascribed to electrostatic interactions since now GenX exists in anionic form. Therefore, in the pH range of 4 to 9, applying positive potential exhibited better adsorption compared to open circuit. At the high pH region, competition between GenX and hydroxide ions seems to hinder the adsorption of GenX to the polymer film. Also, because the pKa of the piperidine is 11.28,¹⁰³ the polymer becomes deprotonated at a very high pH, and therefore, hydrophobic interaction becomes more responsible for the binding – we see that the adsorption is decreased when applying 0.8 V at pH 13.5, **Figure 3.4a**.

The impact of sodium chloride concentration was studied for 0.1 mM GenX (**Figure 3.4b**). Our findings show almost no change in adsorption capacities from 5 to 100 mM NaCl, while the adsorption in highly saline condition¹⁰⁵ (500 mM NaCl) was poor. The high concentration of competing ions is screening the positive charges on the polymer, thus weakening electrostatic interactions with the GenX species. In addition, different water matrices and low concentrations of GenX were studied to test our system under near environmental conditions (**Figure 3.4c**). The water matrices studied were tap water, municipal secondary wastewater effluent (SWE, from the Urbana-Champaign Sanitary District). The selected concentrations were 100 ppb and 15 ppb of GenX in 20 mM NaCl based on the high levels of PFAS that had been found in surface and groundwater^{81, 82, 106}. Tap water and SWE were spiked with 0.1 mM of GenX, and both achieved

>40% removal efficiency after 3 hours of electrosorption. Meanwhile, ultra-diluted samples showed >55% removal efficiency under the same experimental conditions. Also, we tested the working capacity of our redox-copolymer electrode in separating other short-chain PFAS (**Figure B.15**). Better adsorption was observed for relatively longer-chain PFASs, such as C6 and C7, but C4 PFAS showed a tremendously lower adsorption capacity. This could be ascribed to the lower hydrophobicity of these molecules compared to longer chain PFAS and increasing polarity that can prevent these molecules from pertaining a significant contribution of hydrophobic interactions with the copolymer.

We also translated the result obtained in the batch scale system into an electrochemical flow-by cell system containing a 16 cm² (4cm x 4 cm) working electrode with 8 mg of PTMA-co-PTMPMA coating and equal dimension titanium counter electrode for the adsorption and release of GenX. **Figure 3.5** shows the schematics of our flow cell system, which is described in the methods section and supplementary materials (Section S3.5.1.2). Prior to electrochemical GenX adsorption, 0.1 mM GenX solution was cycled through the flow cell apparatus (1 mL/min) at open circuit for 24 hours to allow system equilibration. Electrochemical GenX adsorption was then carried out via application of a constant +2 mA current for 30 minutes at which 109 mg/g adsorbent was achieved with an energy consumption of 1 kJ/g adsorbent (2 kJ/ g copolymer). The linear uptake profile in **Figure 3.5** indicates that complete saturation of the electrode did not occur within 30 minutes and adsorption equilibrium of GenX is likely to be higher given more time. Following adsorption, the flow cell inlet was changed to a pristine solution containing no GenX and allowed to flush for 10 minutes at open circuit. During the solution change-over, very little GenX was observed to release into the pristine solution, and uptake equilibrated to 100 mg/g, indicating little to no concentration equilibrium-based release mechanism. Once a constant current of -2 mA was

applied, electrode-bound GenX was found to swiftly release into the pristine flowing solution with a regeneration efficiency of 93% achieved after 30 minutes with 1.80 kJ/g adsorbent (3.5 kJ/ g copolymer) energy consumed. The flow cell results clearly showcased the up-scaling capability of the PTMA-co-PTMPMA electrochemical adsorption platform for GenX remediation and the electrochemical nature of GenX adsorption and release where electrode-bound GenX was observed to only release once a reducing current was applied.

3.4.4 Electrode regeneration and an asymmetric release-destruction system

Once a negative potential is applied, the $N=O^+$ sites are reduced to its original radical ($N-O\bullet$) state, advancing the release of the GenX molecule. Different release potentials were tested, ranging from -1.5 V to 0.0 V vs. Ag/AgCl after 1 hour (**Figure B.10**). The results indicated that decreasing potential causes a higher release of GenX. Although, -1 V vs AgAgCl was preferred since it is energetically beneficial. A comparison between GenX release at -1 V vs Ag/AgCl and open circuit is shown in **Figure 3.6a**. The results indicate that applying a reductive potential will enhance desorption compared to open circuit obtaining a release of GenX for more than 80% after one hour of operation (**Figure 3.6a**). Then, cyclability tests of our system for up to 5 cycles were performed. This experiment was done by applying 0.8 V for 30 min using 5 mL of 0.1 mM GenX and 20 mM NaCl for adsorption. For desorption, a -1 V potential was applied, and the system was reduced for 1 hour under 20 mM NaCl. This process was repeated four more times and the results shown in **Figure B.16** indicate that the adsorption capacity of our system was well maintained after five cycles. Interestingly, our system's regeneration efficiency (the amount of GenX recovered during release relative to that adsorbed) decreased considerably, and after four cycles, it was maintained

for up to 20% regeneration efficiency (e.g., GenX released). As such, we hypothesized that a partial degradation of GenX happened during the reductive regeneration (**Figure B.20**).

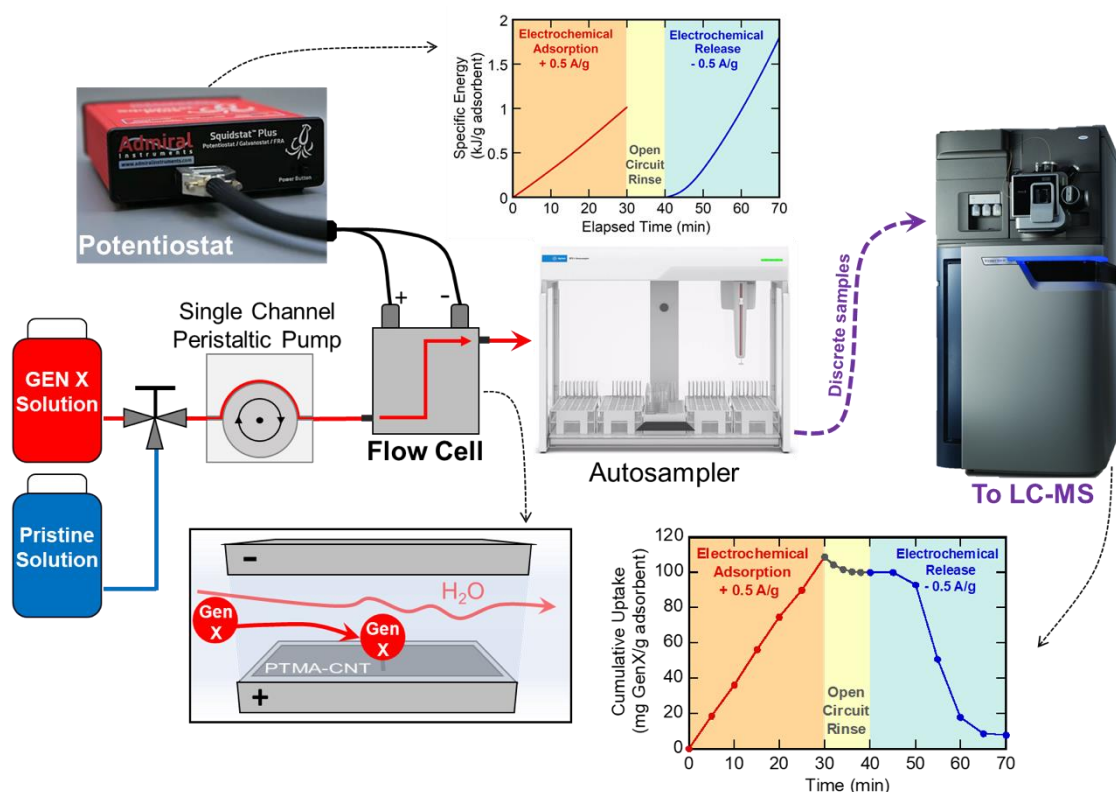


Figure 3.5. Electrochemical flow cell schematic. A 0.1 mM GenX and 20 mM NaCl solution enters the peristaltic pump towards the flow cell. The GenX solution could be switch to a 20 mM NaCl solution (pristine solution). The chronopotentiometric experiments were control with a potentiostat and the resulting samples were collected and analyse with an LCMS. These results show a flow cell experiment of GenX after pre-treating and pre-equilibrating the PTMA-co-PTMPMA electrode. The counter electrode used in this experiment was Ti.

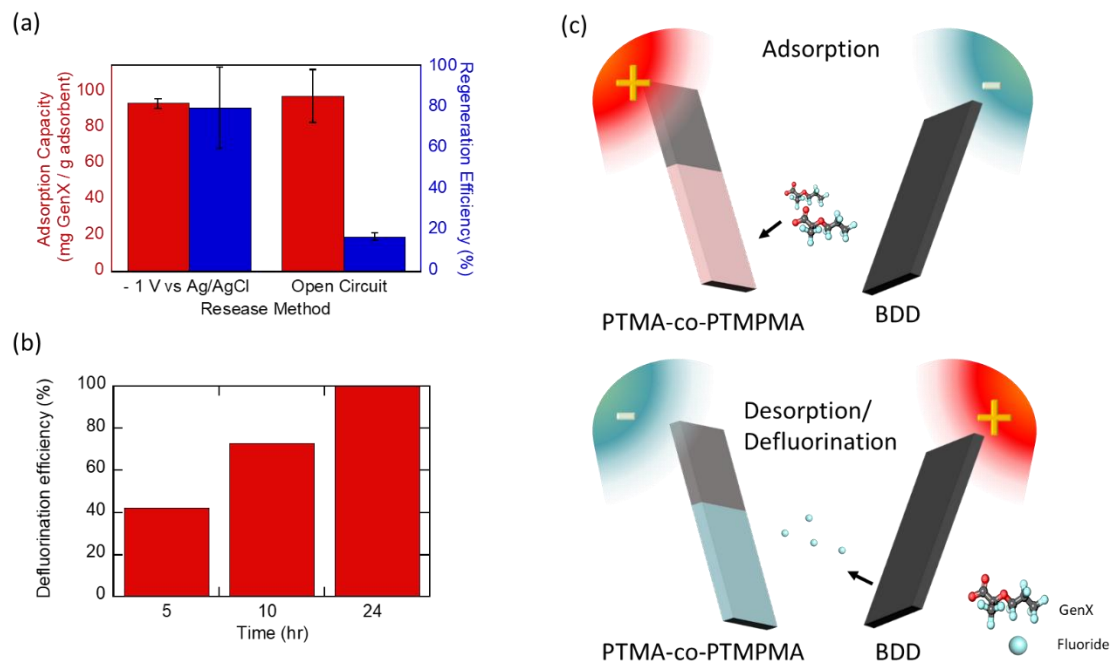


Figure 3.6. (a) Regeneration Efficiency comparison of -1 V vs Ag/AgCl versus open circuit. Adsorption was performed for 30 minutes under 0.8 V vs. Ag/AgCl and 0.1 mM GenX and 20 mM NaCl. (b) Defluorination analysis of BDD by time under 10 mA/cm². The defluorination occurred in a 20 mM NaCl solution after the 0.1 mM GenX was adsorbed. (c) Synergistic adsorption/defluorination technic with PTMA-co-PTMPMA as electrosorbent and BDD as the defluorinating working electrode.

As shown in **Figure B.21-24**, the fragmented species developed starting from the carboxylate group as well as breaking the ether bond. Also, a study on prolonged exposure of 0.024 mM GenX + 20 mM NaCl was performed to observe whether the molecule was degraded by only applying -1 V (**Figure B.22**) for one hour (see chromatogram comparison in **Figure B.22** and HR-MS spectra on **Figure B.23** and **B.24**). Our results indicate that GenX was degraded by applying a reductive potential during the regeneration, causing seemingly low regeneration efficiency. Further analysis

will be carried out in future studies to develop the full kinetic and mechanistic model for GenX breakdown at these redox-electrodes.

Although our system degrades after prolonged exposure to the reduced polymer, it is environmentally safe to fully defluorinated into fluoride rather than degrading into shorter PFAS, with unknown toxicity. The consequences from the formation of these new by-products have not been thoroughly studied but based on their historical profile and similar chemical structure as their former PFAS version, it is highly likely that these C-F compounds would still be recalcitrant.¹⁰⁷ Therefore, we decided to incorporate boron doped diamonds (BDD) to increase the defluorination efficiency and further break down into fluoride and CO₂. Thus, we combined our system with BDD to have a PTMA-co-PTMPMA//BDD configuration for the purpose of integrating separation and defluorination of GenX within a single device. BDD served as an efficient candidate for defluorination since it can generate hydroxyl radicals under high overpotentials that are able to cleave the C-F bond of the PFAS,¹⁰⁸⁻¹¹⁰ while providing chemical and electrochemical stability.¹¹¹ Therefore, we were interested in a system capable of adsorbing GenX and later simultaneously defluorinating when releasing in tandem, as shown in a schematic of our integrated approach (**Figure 3.6c**). We first adsorbed GenX on PTMA-co-PTMPMA for 30 minutes by applying 0.8 V, and then reversed the polarity and desorbed from the PTMA-co-PTMPMA electrode, simultaneously defluorinating with the help of BDD, by applying 10 mA/cm² under continuous stirring (500 rpm). Our results indicate gradual defluorination behaviour with time (**Figure 3.6b**); after 24 h operations at 10 mA cm⁻², our system was able to release adsorbed GenX completely and achieve 100% defluorination efficiency. Future studies will be focused on engineering the electrochemical cell to enhance kinetics and mass transfer.

CHAPTER 4: INVESTIGATING THE ELECTROCHEMICALLY-DRIVEN CAPTURE AND RELEASE OF LONG-CHAIN PFAS BY REDOX-METALLOPOLYMER SORBENTS*

4.1 Overview

The remediation of perfluoroalkyl substances (PFAS) is an urgent challenge due to their prevalence and persistence in the environment. Electrosorption is an emerging approach for contaminant treatment, especially the use of redox-polymers to control binding and release without the additional of external chemical input. However, the design of efficient PFAS redox-electrosorbents face the significant challenge of balancing the high adsorption uptake with maintaining electrochemical regeneration efficiency. To overcome these challenges, we investigate redox-active metallopolymer as a synthetic versatile platform for PFAS removal, and to enhance both electrochemical reversibility and uptake capacity. We select and synthesize a series of metallopolymer bearing ferrocene and cobaltocenium units, spanning a range of redox-potentials, to evaluate their performance for the capture and release of perfluorooctanoic acid (PFOA). Our results demonstrated that PFOA uptake and regeneration efficiency increased with more negative formal potential of the redox-polymers, indicating possible structural correlations with electron density of the metallocenes. Poly(2-(methacryloyloxy)ethyl cobaltocenium-carboxylate hexafluorophosphate) (PMAEC_oPF₆) showed the highest affinity towards PFOA, with an uptake capacity obtained of more than 90 mg PFOA/g-adsorbent at 0.0 V vs Ag/AgCl, and a regeneration efficiency of more than 85% at -0.4 V vs Ag/AgCl. Kinetics

*This Chapter was adapted with permission from: P. Baldaguez Medina et al. ACS Appl. Mater. Interfaces 2023, 15, 18, 22112–22122.

of PFOA release showed that electrochemical bias greatly enhanced the regeneration efficiency when compared to open circuit desorption. Additionally, electrosorption of PFAS from different wastewater matrices and a range of salt concentrations demonstrated the capability of PFAS remediation in complex water sources, even in ppb levels of contaminant. Our work showcases the synthetic tunability of redox-metallopolymers with allows for enhanced electrosorption capacity and regeneration of PFAS.

4.2 Introduction

For PFAS adsorption, the predominant materials are carbon-based technologies,^{112, 113} due to their lower cost. However, carbon-derived sorbents can incur downstream environmental impacts since they often rely on incineration, while state-of-art reusable adsorbents require the need for harsh chemicals for regeneration.¹¹⁴⁻¹¹⁶ At the same time, electrosorption have emerged as a promising approach for PFAS remediation due to their modularity, and regeneration solely by electrochemical control.^{117,118} Electrosorbents mitigate the need for chemical, solvent, or pH input for desorption due to electrochemical control of binding and release, and thus can minimize secondary pollution. Recent applications of electrosorption range from water desalination, metal recovery, reactive separations, and environmental remediation.^{104, 119-123}

However, critical materials advances are still needed for developing more efficient electrosorbents for PFAS, especially to maximize electrochemical regeneration efficiency and achieve higher reversibility. Redox-active materials have been powerful platforms for electrosorption due to their enhanced uptake and tailored molecular selectivity.^{7, 11, 12, 124} Long-chain PFAS electrosorption has been accomplished using radical-based redox-polymers, such as poly 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) methacrylate.^{11, 12} These TEMPO-containing

electrosorbents showed a high PFOA uptake capacity, due to the balance of electrostatic and hydrophobic interactions. However, despite their strong affinity to PFAS, they are limited by relatively low regeneration efficiency, with potentials close or greater than -1.0 V vs Ag/AgCl needed for desorption, and only around ~65% or lower regeneration efficiency after 1 hour of desorption.^{11, 12} Thus, a critical materials challenge is to design more efficient PFAS electrosorbents that maintain high uptake capacity while preserving full regeneration efficiencies.

Redox-metallopolymers present a powerful and versatile synthetic platform for a range of applications, including sensors, batteries, electrocatalysis, and environmental remediation.¹²⁵⁻¹³² Redox-responsiveness has been even harnessed for switching catalytic activity or the tuning of structural colors.^{133, 134} More importantly, these materials have shown promising potential for ion-selective electrochemical separations,^{39, 129, 135} demonstrating controllable charge-transfer interactions for multicomponent separations. Ferrocene or cobaltocene are amongst the most well-studied redox-units due to their high stability and excellent electrochemical properties.¹³⁶⁻¹³⁸ However, metallopolymers have yet to be systematically studied for electrochemical PFAS binding and release.

In this chapter, we leverage the synthetic versatility of redox-metallopolymers and the associated tunability of electrochemical properties, to optimize electrosorption and regeneration performance for PFOA, the model long-chain PFAS. We synthesize and evaluate five redox-metallopolymers across a range of redox-potentials, electronic density, and surface properties, to understand the effect of polymer structure on PFAS electrosorption and release. These metallopolymers are selected based on their accessibility of synthesis, robust electrochemical properties, and varying electronic density and redox-potentials. **Figure 4.1** shows the structure of the selected redox-metallopolymers, poly(2-(methacryloyloxy)ethyl ferrocenecarboxylate)

(PFcMA), polyvinylferrocene (PVF), polyferrocenyl methyl methacrylate (PFMMA), poly(3-ferrocenyl)propyl methacrylamide (PFPMAM), and poly(2-(methacryloyloxy)ethyl cobaltoceniumcarboxylate hexafluorophosphate) (PMAECOPF₆). We explore the electrochemical stability, electrosorption kinetics, and equilibrium uptake of porous electrodes functionalized with metallopolymer, and evaluate their electrosorption performance in various water matrices. Our results demonstrate that while iron-based metallopolymer demonstrate significant electrosorption capacity, cobalt-based metallopolymer display a combination of high capacity and high reversibility for binding. Finally, an energy consumption analysis show that PMAECOPF₆ is the most energy-efficient platform for PFAS capture and release, being a promising candidate for further materials development and scaleup studies.

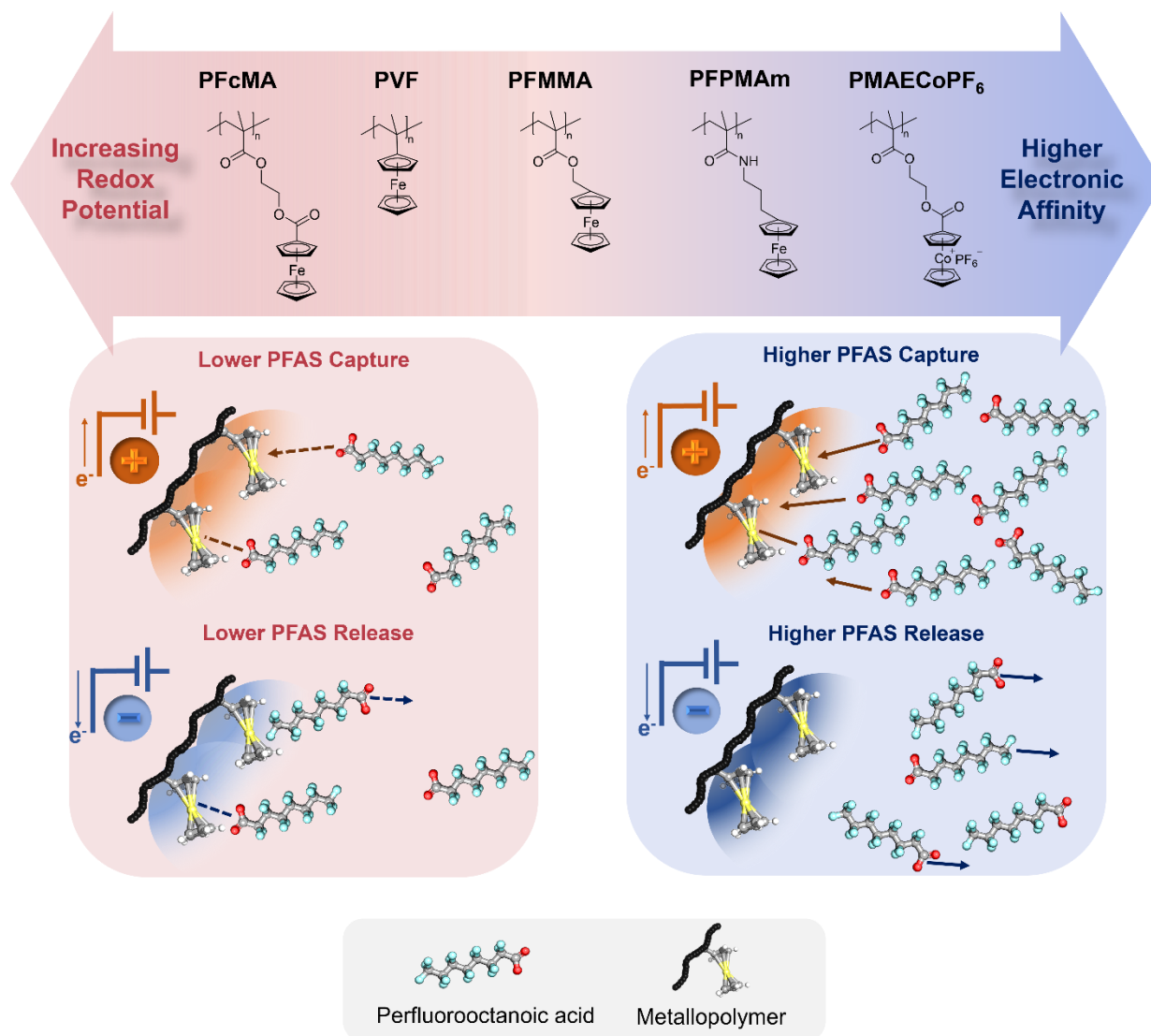


Figure 4.1. Synthesized redox-metallopolymers evaluated for PFAS electrosorption and release, and correlation of structure and electronic properties with electrosorption performance.

4.3 Methods

4.3.1 Polymer synthesis and characterization

All chemicals used for all the experiments were obtained from Sigma Aldrich, VWR, Fisher Scientific, and TCI. No further purification step was performed unless stated otherwise. PVF was

purchased from Polysciences, Inc. LC/MS analysis solvents were LC grade, and the chromatographic method can be found in the supporting section. Deionized water was collected from an in-house ELGA Purelab Flex 1 system >18 M Ω . Wastewater samples were acquired from the Urbana & Champaign Sanitary District. 1,3-Benzenedisulfonyl Azide (1,3-BDSA), FcMA, FPMAm, FMMA, PFMA, and PMAECOPF₆ were synthesized as described elsewhere.^{128, 139-144}

Synthesis of PFPMAm: FPMAm (3.00 g, 9.64 mmol) and AIBN (15.8 mg, 0.096 mmol) were dissolved in 1,4-dioxane (10 mL). The mixture was degassed by bubbling with argon for 15 min and heated to 60 °C for 16 h. The polymer was precipitated in MeOH (100 mL) and filtered. The polymer was dissolved in 20 mL of THF, precipitated again in MeOH, and dried under reduced pressure, yielding 2.45 g (82%) PFPMAm as an orange solid. GPC in DMF/LiBr using PMMA calibration: $M_n = 25.4 \text{ kg mol}^{-1}$, $M_w = 144.5 \text{ kg mol}^{-1}$, $\bar{D} = 5.68$.

Synthesis of PFCMA: FcMA (900 mg, 2.90 mmol) and AIBN (9.5 mg, 0.058 mmol) were dissolved in THF (4 mL). The mixture was degassed by bubbling with argon for 15 min and heated to 70 °C for 16 h. The polymer was precipitated in MeOH (50 mL) and filtered. The polymer was dissolved in 10 mL of THF, precipitated again in MeOH, and dried under reduced pressure, yielding 0.5 g (56%) PFPMAm as an orange solid. GPC in DMF/LiBr using PMMA calibration: $M_n = 9.1 \text{ kg mol}^{-1}$, $M_w = 20.4 \text{ kg mol}^{-1}$, $\bar{D} = 2.24$.

Synthesis of PFMA: This synthesis was done by anionic polymerization, as described elsewhere.¹⁴¹ In an ampule, 500 mg FMMA (1.76 mmol) were dissolved in 50 mL dry THF and mixed with 5 mg LiCl (0.12 mmol). The solution was cooled down to -78 °C. The polymerization was initiated with diphenylhexyl lithium (DPH-Li), which was prepared separately. For this, to 5.2 μL *n*-BuLi (0.008 mmol, 1.6 M in hexane), 2.9 μL DPE (0.016 mmol) was added in THF and stirred at rt for 10 min. The DPH-Li initiator was added quickly to the FMMA solution. The

mixture was stirred at -78 °C for 8 h and terminated with an excess of MeOH. The PFMMA was precipitated in MeOH, filtrated, and dried in vacuum.

Synthesis of PMAECoPF₆: 502.0 mg MAECoPF₆ (1.024 mmol) and 6.7 mg ethyl 2-(phenylcarbonothioylthio)-2-phenylacetate (21 µmol) were dissolved in 1.0 mL dry acetonitrile. After degassing by three freeze-pump-thaw cycles, 2.5 mg AIBN (15 µmol) were added, and the polymerization mixture was heated to 90 °C for 6 h. The polymer was precipitated in dichloromethane. After drying at 40 °C under reduced pressure, 269 mg of the polymer was obtained and analyzed via ¹H-NMR spectroscopy and TGA.

4.3.2 Electrode preparation and electrochemical characterization

For the preparation of the electrodes, an initial ink solution combined multiwalled carbon nanotubes (MWCNT) and a polymer in a suitable solvent, following prior literature methods.^{129,}

¹⁴⁵ In the case of the ferrocene-containing polymers (PFcMA, PVF, PFMMA, and PFPMAm) the solvent used was chloroform. For the PMAECoPF₆ ink solution, we dissolved the polymer and CNT into dimethyl formamide. A 1:1 mass ratio of MWCNT to metallopolymer was used for all the ferrocene-containing polymers while for PMAECoPF₆, the ratio used was of 1:2 MWCNT to PMAECoPF₆, to optimize the dispersion and coating processability. All solutions were prepared at concentrations of 4 mg polymer/mL solvent. Additionally, 10% of 1,3-benzenedisulfonyl azide (1,3-BDSA) as a cross-linker was added to the ink solutions of PFcMA and PMAECoPF₆ to provide higher stability in aqueous solutions. We used a titanium mesh as the current collector cut in 2x1 cm². The ink solution was drop cast into the current collector until obtaining a mass averaging 0.75 mg. Electrochemical studies were performed on an SP-200 (Biologic) or Squidstat Prime (Admiral Instruments) potentiostats. Electron quartz crystal microbalance (EQCM,

Biologic) was used over 100 cycles for stability studies. All the electrochemical systems were assembled in a three-electrode configuration with a VC-2 BASi cell, a platinum wire (0.5 mm diameter) counter electrode, and Ag/AgCl (3M NaCl) as the reference electrode.

4.3.3 Material characterization and analytical methodology

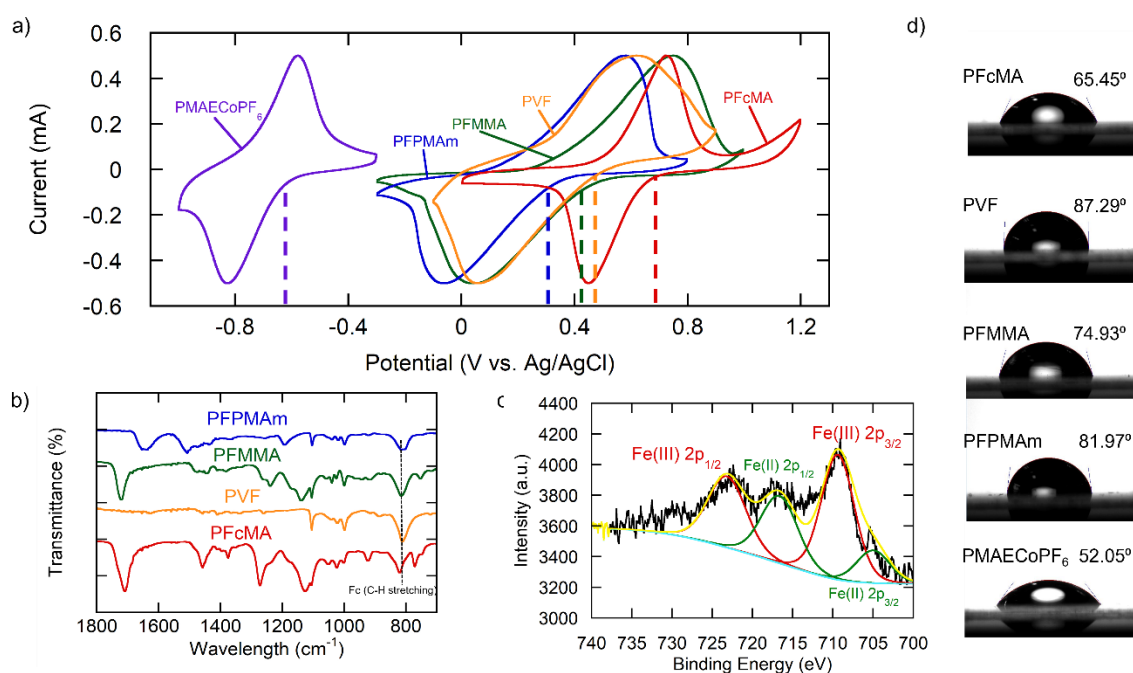


Figure 4.2 (a) Cyclic voltammogram of all the metallopolymers in 100 mM NaClO₄ at a scan rate of 10 mV/s. The dashed lines correspond to the polymer Em. (b) FTIR spectrums of ferrocene-bearing metallocenes from 1800 – 700 cm⁻¹. The straight dashed line corresponds to the ferrocene C-H stretching group at 814 cm⁻¹. (c) High-resolution Fe 2p XPS of PFCMA after activation with 100 mM NaClO₄. (d) Contact angle measurements for all the metallopolymers on a Ti mesh coated with the ink composed of MWCNT dispersed with the polymer.

The concentration of PFOA was measured through liquid chromatography-mass spectrometry (LC/MS, Agilent 1260 Infinity II, Agilent Technologies, USA). An EC-C18 column (2.7 μ m 2.1 mm 50 mm, Agilent POROSHELL 120) was used with mobile phase: A. acetonitrile and B. 5 mM ammonium acetate. Gradient elution was set as follows: 0-6 min, 10% A and 90% B; 6-8 min, 65% A and 35% B; 8-15 min, 100% A and 0% B; 15-17min, 10% A and 90% B. A 1.0 mL/min flow rate was used with a sample injection volume of 1.0 μ L. The column was maintained at 25 °C. Negative electron spray ionization (ESI) mode was used for obtaining the PFOA concentration.

Scanning electron microscopy combined with energy dispersive X-ray spectroscopy (SEM-EDS, ThermoFisher Axia ChemiSEM) was used to obtain the morphology and phase composition of the material. X-ray photoelectron spectroscopy (XPS) was performed by MSE Supplies and was used for the chemical state characterization and reporting the presence of PFOA on the electrodes surface. The analytical mode utilized was a monochromatic Al K_{α} X-ray source, and the analysis was performed using CASA XPS software. NMR spectra were recorded on a Varian Unity Inova 400 MHz spectrometer or a Varian Unity Inova 500 MHz spectrometer, both equipped with a Nalorac QUAD probe. Gel permeation chromatography was measured using a Tosoh EcoSEC 8320 GPC System. Two Tosoh Alpha-M columns were used. 14.5 mM LiBr in DMF was used as the mobile phase. The system was calibrated with a poly(methyl methacrylate) (PMMA) standard for relative molar mass estimations. For gel permeation chromatography (GPC) measurements of PFMMA, an Agilent 1260 Infinity II setup with THF as the eluent at a flow rate of 1 mL min⁻¹ was employed. An SDV column set from polymer standard service (PSS) (SDV 103 Å, SDV 105 Å, SDV 106 Å) and a PSS Security2 RI/UV detector were used. Calibration was carried out using PS standards from PSS. GPC measurements for PFcMA and PFPMAm were performed in a Tosoh EcoSEC 8320 GPC System. The columns used were two Tosoh Alpha-M,

and a mobile phase of 14.5 mM LiBr in DMF was used. The calibration for the analysis was performed with poly(methyl methacrylate) (PMMA) standard for relative molar mass estimations.

The Fourier transform infrared (FTIR) spectrum was obtained using a benchtop Agilent Cary 630 FTIR spectrometer. The data was obtained and processed using the MicroLab PC program. Contact angle experiments were performed in a Rame-Hart 250 Standard Goniometer using DROP Image Advanced for angle analysis. The contact angle experiments were done on top of a glass substrate covered in the respective polymer solution, and the droplet used was of deionized water or with 0.1 mM PFOA + 20 mM NaCl.

4.4 Results and Discussion

4.4.1 Synthesis and characterization of redox-polymers

PFPMAm and PfcMA were synthesized from their corresponding monomers by free radical polymerization, PFMMA was obtained via anionic polymerization, PMAECOPF₆ through RAFT polymerizations, and PVF was purchased from Polysciences, Inc.^{128, 139, 140, 142-144, 146} All polymers were characterized using NMR-spectroscopy and gel permeation chromatography GPC (see Supporting Information section S.4.5.1). **Figure 4.2a** depicts the cyclic voltammograms (CV) of the redox-metallopolymers, PfcMA, PVF, PFMMA, PFPMAm, and PMAECOPF₆, ran at a scan rate of 10 mV/s with 100 mM NaClO₄ as a supporting electrolyte. Each polymer showed a characteristic reversible peak for reduction and oxidation, which for the ferrocenium-containing polymers represents the one-electron transfer between Fc to Fc⁺ (ferrocene to ferrocenium),¹⁴⁷ and for the cobaltocenium-containing metallopolymer, the redox-switch between Cob (Cobaltocene) to Cob⁺(cobaltocenium).¹⁴⁸ Although an additional reduction process for Cob may be possible at

lower potentials, we only study the first reduction to Cob^- due to its more realistic operational conditions within the water splitting window.¹⁴⁹

The selection of the metallopolymers relies on the potential tunability of their structure through the choice of metal center, ligands, polymer backbone, and environmental conditions. The electron configuration and redox potential of the metal center, as well as the electronic properties and steric hindrance of the ligands, can affect the electron transfer kinetics and stability of the metallopolymers. The electrochemical properties of ferrocene can be affected by the electron donating or withdrawing ability of substituents attached to its moiety. A linear correlation has been observed between the formal potentials and the Hammett parameter, which quantifies the electron donating/withdrawing ability of a substituent on an aromatic system.¹⁵⁰ Between all the metallopolymers, the midpoint potential E_m varied depending on the polymer structure, with an increase in electron affinity of the redox-center at lower E_m (**Figure 4.2a**). E_m can also represent the formal potential E^0 ,¹⁵¹ which has been used to correlate the electronic density/affinity of redox materials.^{152, 153} For the case of the studied metallopolymers, the E_m trends followed as $\text{PMAECOPF}_6 < \text{PFPMAM} < \text{PFMMA} < \text{PVF} < \text{PFcMA}$, denoting the cobaltocenium containing polymer as the most electron-rich group. This trend in electron density was also confirmed by measuring the ^1H - NMR peak corresponding to the carbonyl groups at the ferrocene aromatic groups, shown in **Table C.1** ^1H NMR analysis of Fc peak intensity.

Figure 4.2b shows the Fourier Transform (FTIR) spectra of all the ferrocene-containing metallopolymers. The peak at 814 cm^{-1} corresponds to the ferrocene ring C-H stretching vibration.^{129, 154} In the case of PFcMA, the peak is shifted to 818 cm^{-1} . The peak shift indicates a weakening of the C-H bond, compared to the other more electron-rich ferrocene metallopolymers.¹⁵⁵ **Figure 4.2c** depicts the XPS Fe 2p region ranging from 700 to 740 eV of a

PFcMA electrode after oxidized at 0.8 V vs Ag/AgCl for 30 minutes in a 0.1 mM PFOA + 20 mM NaCl solution. We were able to obtain spin orbital energies at 705.3 and 717.4 eV, which belong to the $2p_{3/2}$ and $2p_{1/2}$ unoxidized sites, respectively. In contrast, for oxidized sites, we obtained the $2p_{3/2}$ and $2p_{1/2}$ at 709.2 and 722.5, respectively, correlating to previously observed ferrocenium XPS data.^{129, 156, 157} As seen in **Figure C.5** and **C.6**, where it is observed similar XPS trends for the others ferrocene-containing electrodes.

We also performed contact angle characterization on all the metallopolymer, as shown in **Figure 4.2d**, to obtain information on their interfacial hydrophobicity/hydrophilicity. A glass substrate was coated with 100 μ L of redox polymer solution, composed of 4 mg polymer/mL concentrations. Our results show that all ferrocene-containing polymers have lower wettability when compared to the cobaltocene-containing metallopolymer, which could be due to the higher oxidation degree of cobaltocenium due to its much lower redox-potential.¹³⁷ **Figure C.8** portrays the relationship of the polymer's hydrophobic interaction with the presence of PFOA, with contact angle errors from the measurements in **4.2d** summarized in **Table C.3**. We see that the hydrophobicity decreased for polymers with higher E_m , which could lead to an indirect correlation that higher affinity is correlated to the polymer with the lowest redox potential (PMAECOPF₆). Next, the exact affinity of the polymers to the PFAS under applied bias will be studied in more detail with heterogeneous electrosorption tests.

Additionally, these results indicate that the electrosorption of PFOA by metallopolymer compounds is dependent on several factors, including the hydrophobicity or polarity changes induced by the charging and changing polarity/electron density of the ferrocene or cobaltocenium groups, or even possibly sterics. These properties are altered by the charging and changing polarity/electron density of the ferrocene or cobaltocenium groups, which in turn affect the

interactions between the metallopolymer and PFOA. Specifically, the metallopolymer's charge state is a crucial factor that affects the electrostatic interactions with PFOA molecules, with a positively charged metallopolymer promoting adsorption and a neutral charged metallopolymer promoting desorption. Also, the hydrophobicity or polarity of the metallopolymer can influence the partitioning of PFOA between the bulk solution and the metallopolymer surface, with an increase of hydrophobicity enhancing adsorption and polarity decreasing it. A more detailed mechanistic study on the balance between electrostatic and hydrophobic studies can be further investigated in the future, through computational investigations – an approach which was recently applied to correlate binding between fluorophilic copolymers and a range of short chain PFAS.¹⁵⁸ Going forward, molecular dynamic simulations can assist in elucidating the differential contributions of charge-transfer, hydrophobicity, and sterics.

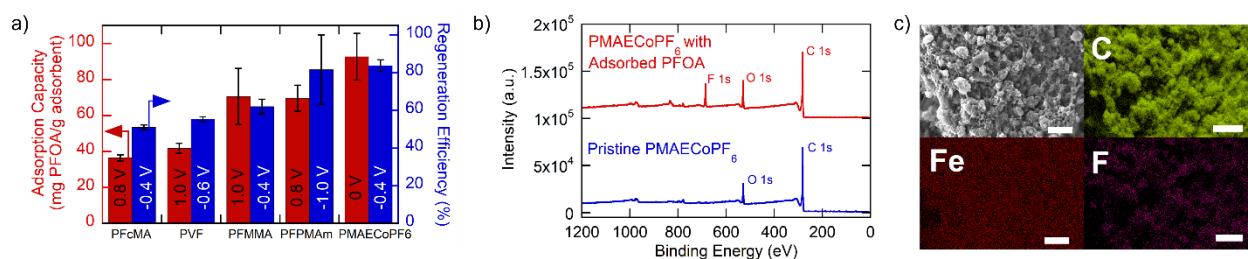


Figure 4.3. (a) Adsorption and regeneration uptake for all the metallopolymers at their optimal potentials. (b) XPS spectra before and after electrosorption of the PMAECOPF₆ electrode. (c) Scanning electron microscopy EDS demonstrating the fluorine uptake on the PFPMAM redox-metallopolymer. Scale bar corresponds to 50 μm.

4.4.2 Electrochemically-driven sorption and release of PFOA

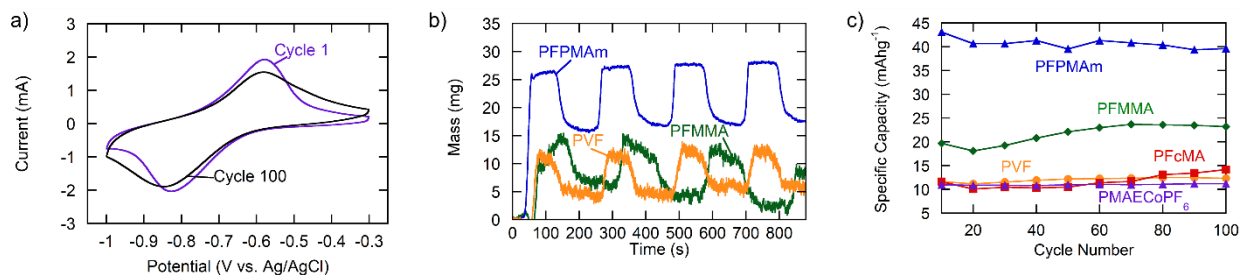


Figure 4.4. (a) Cyclic voltammogram of PMAECOPF₆ electrode after 100 cycles in 100 mM NaClO₄ at a scan rate of 10 mV/s. (b) EQCM Cyclic voltammetry trend uptake for PFPMAm, PFMMA, and PVF comparison. The potential profile for each polymer goes from -0.3 to 0.8 V vs Ag/AgCl for PFPMAm, -0.3 V to 1.0 V for PFMMA, and -0.1 to 0.9 V vs Ag/AgCl for PVF. (c) Specific capacity comparison of the-ferrocene containing metallopolymer.

Figure C.10 portrays the electrosorption of PFOA screened for each metallopolymer at electrochemical potentials ranging from -1 V vs Ag/AgCl to +1 V vs Ag/AgCl. We used a three-electrode cell with a Ti sheet as a current collector, coated with 1 mg/cm² of the polymer-CNT mixture, and a platinum counter electrode. For the initial screening, all electrosorption experiments were performed for 30 minutes under continuous stirring (300 rpm), using 5 mL of a stock solution containing 0.1 mM PFOA in 20 mM NaCl. Based on the screening experiment, the optimal potential to carry out both electrosorption and regeneration efficiency was identified for each redox-polymer. The regeneration efficiency is defined as the percentage of PFOA released from the surface of the electrode after adsorption vs the initial PFOA adsorbed in the electrode.¹² The regeneration experiments were done for 1 hr using 400 rpm in 5 mL of a 20 mM NaCl solution. The electrochemical potentials used per metallopolymer are -0.4 V for PFCMA, -0.6 V for PVF, -0.4 V PFMMA, -1.0 V PFPMAm, and -0.4 V for PMAECOPF₆, all vs. Ag/AgCl.

The optimal electrosorption and electro-regeneration results from these screening tests are summarized in **Figure 4.3a**. We observed a notable trend in PFOA electrosorption uptake ranging from the polymer of lowest electron affinity, PFCMA, having the lowest uptake, while to the polymer with the highest electron affinity, PMAECOPF₆, with higher uptake. Therefore, this trend suggests that a correlation of PFOA uptake with the metallopolymer redox-potential and electron density of the redox-center. At the same time, the regeneration efficiency also displayed similar trends to electrosorption. While we achieved more than 50% regeneration efficiency with all five metallopolymer, PFPMAm and PMAECOPF₆ both showed over 80% regeneration efficiency, which is significantly higher than previously reported radical redox-polymers.¹²

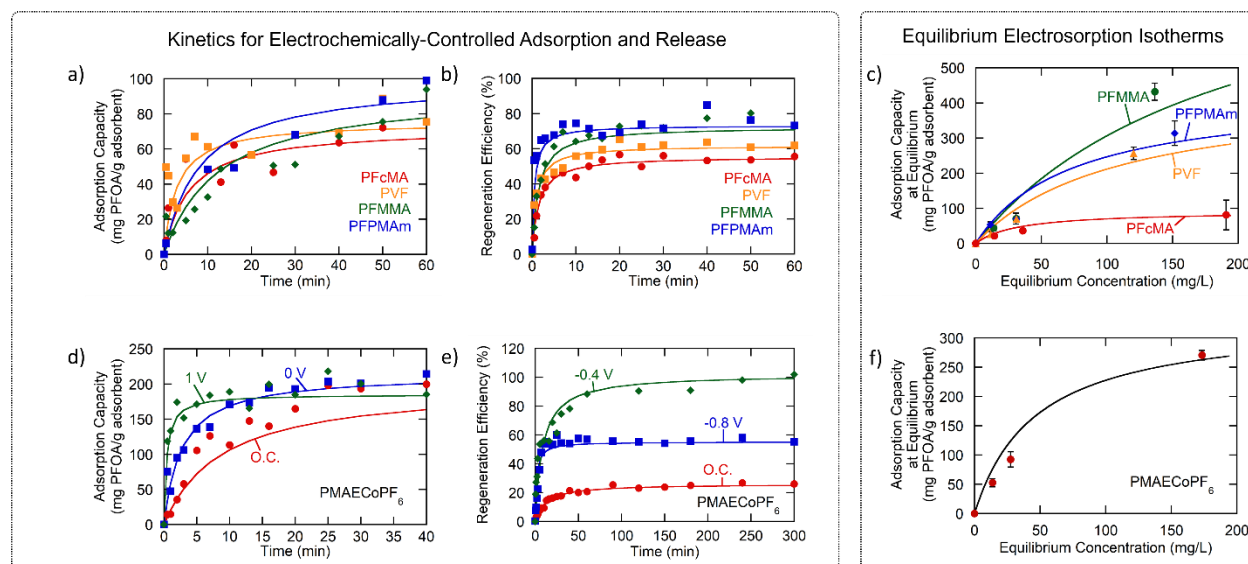


Figure 4.5. All experiments were performed using 0.1 mM PFOA + 20 mM NaCl for adsorption and 20 mM NaCl for desorption. (a) Electrosorption kinetics for the ferrocene metallopolymer, (b) and desorption kinetics for the ferrocene metallopolymer-CNT electrodes. (c) Equilibrium electrosorption isotherms for ferrocene metallopolymer-CNT electrodes. (d) Electrosorption kinetics of PMAECOPF₆-CNT electrodes at different potentials and open circuit (O.C.). (e)

Figure 4.5. (cont.) Electrochemical desorption kinetics of PMAECOPF₆-CNT electrodes at different potentials and O.C. (f) Equilibrium electrosorption isotherms for PMAECOPF₆-CNT electrodes.

We investigated the elemental analysis of the electrodes after electrosorption, and tracked the Fe2p regions by X-ray photoelectron spectroscopy (XPS). **Figure 4.3b** shows the difference between a PMAECOPF₆ electrode before electrosorption (pristine electrode) and after adsorption (adsorbed PMAECOPF₆). An intense F1s peak appears after electrosorption, confirming the uptake of PFOA onto the surface of the electrode, while for the pristine electrode, the F-1s peak can only be observed by obtaining the high-resolution spectra of the same area, which is mainly derived from the PF₆⁻ counter-ion originally present on the cobaltocenium redox-polymer. Interestingly, a high separation factor between fluoride and chloride was observed for all five electrodes using the XPS atomic percentage ratio at a coated electrodes are after 30 minutes adsorption of 0.1 mM PFOA + 20 mM NaCl. Our results showed no observable separation factor trend that could be correlated with the structure of the polymers (**Table C.2**).¹² However, both PFPMAM and PMAECOPF₆ showed a very high separation factor for PFAS over chloride (>10³), significantly higher than previously reported with radical-based polymers.^{11, 12} Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) (**Figure 4.3c**) illustrate the distinct capture of the PFAS through the fluorine content on the electrodes after electrosorption.

4.4.3 PFAS separation performance and electrochemical stability

We investigated the performance of the redox-metallopolymers through multiple cycles by electrosorption and desorption. First, we analyzed the performance of the cobaltocene-containing

metallopolymer by cyclic voltammogram ranging from -1.0 V to -0.3 V vs Ag/AgCl in a 100 mM NaClO₄ solution at a scan rate of 10 mV/s. As shown in **Figure 4.4a**, the shift in oxidation and reduction peaks is minimal, indicating a robust and stable electron-transfer system, with a slight broadening of the peaks observed, in accordance with prior reports of redox-CV.¹⁵⁹

Next, we investigated the electrosorption performance of the electrodes coated with metallopolymers under in the presence of 0.1 mM PFOA. We use electrochemical quartz crystal microbalance (EQCM) measurements as a means of tracking the mass changes of our porous materials.^{160, 161} The mass loading was obtained using the Sauerbrey's equation, which correlates quartz resonance frequency to changes in mass.¹⁶² We observed the uptake and released performance of the PFPMAm, PVF, and PFMMA electrodes after four cycles on 0.1 mM PFOA and 20 Mm NaClO₄. The EQCM gold sensor was coated with 100 μ L ink solution and dried in air. Due to the thermal stability of the sensor, we performed the EQCM experiments on the electrodes that did not contain a crosslinker (PFPMAm, PVF, and PFMMA). **Figure 4.4b** shows that the mass load throughout time after four cycles has been well maintained. Higher uptake is seen with the PFPMAm metallopolymer when compared to all other ferrocene containing metallopolymers, which is in accordance with the electrosorption uptake data from **Figure 4.3a**. No significant change in stability was observed throughout the four cycles.

The specific capacity (mAhg⁻¹) was obtained for all the metallopolymers to evaluate electrochemical performance under multiple adsorption and desorption cycles. We carried out 100 cycles of 5 minutes of adsorption at the polymer's specific optimal potential and 5 minutes of release at the polymer's optimal release potential. The solution used for these cyclability experiments consisted of 0.1 mM PFOA + 20 mM NaCl. Depending on the polymer, the potential applied for electro- sorption and desorption would have been the optimal, as seen in **Figure 4.3a**.

Based on the results obtained in **Figure 4.4c**, we are able to confirm the capacity retention of each electrode in the system where the capacity was observed to be stable throughout the 100 cycles. It is observed that the capacity remains continuous throughout the whole 100 cycles, with some polymers even increasing their capacity after the 100 cycles (PFMMA and PFcMA). This demonstrates that metallocenes possess an advantage in durability and robust materials.

4.4.4 Kinetics and equilibrium uptake investigation

To evaluate the kinetics of PFAS binding to the redox electrode surface, we performed time-dependent electrosorption tests of PFAS on all five redox-polymers. For the electrosorption/desorption experiment, we selected the optimal operating potential for each polymer for electrosorption and release. In addition, various potentials for adsorption and desorption using PMAECoPF₆ were investigated. An initial solution of 0.1 mM PFOA + 20 mM NaCl was used for all the kinetics experiments and desorbed into a solution containing only 20 mM NaCl. We carried out a comparison of the pseudo-first-order kinetic model and the pseudo-second-order (PSO) kinetic model, and based on the fit results found in **Table C.4**, we determined that the PSO model best describes our system's performance. Details on how we calculated the PSO could be observed in section 4 of the SI.

In the case of the ferrocene-metallopolymers, the kinetics trend is shown in **Figure 4.5a** for electrosorption and **Figure 4.5b** for desorption. For the electrosorption experiments, we obtained rate constants ranging of 9.0×10^{-4} (PFMMA), 0.0013 (PFPMAM), 0.0046 PVF, and 0.0025 [mg/g]⁻¹min⁻¹ (PFcMA). On the other hand, for the desorption kinetics on the ferrocene polymers, we obtained kinetics rate constants ranging of 1.2×10^{-3} (PFcMA), 9.0×10^{-3} (PFMMA), 0.0165 (PVF), and 0.0256 [mg/g]⁻¹min⁻¹ (PFPMAM). These desorption rate constants indicate the

fast kinetics when compared to the electrosorption process step, possibly due to the more negative potential relative to their formal potential and point of zero charge.¹⁶³ For the cobaltocenium metallopolymer, PMAECOPF₆, we observed significantly lower kinetics at open circuit (O.C.), with a rate constant of 0.0005 [mg/g]⁻¹min⁻¹. Electrosorption kinetics for PMAECOPF₆ shown in **Figure 4.5d** and **4.5e**. The results demonstrate the ability of the PMAECOPF₆ metallopolymer to rapidly regenerate PFOA, even at moderate voltages, with close to full regeneration efficiency after 1 hr. Furthermore, we performed equilibrium uptake studies which were fitted with the Langmuir isotherms models for all the metallopolymer electrodes, as shown in **Figure 4.5c** and **4.5f**. We were able to achieve equilibrium uptakes up to 350 mg/g using PFMMA, 314 mg/g for PFPMAm, 231 mg/g for PVF, 83 mg/g with the PFCMA, and 270 mg/g the PMAECOPF₆. At the higher PFAS concentrations, the higher adsorption uptake on PFMMA could be attributed to the relatively higher hydrophobicity of the PFMMA polymers.

4.4.5 Sorption of PFOA with PMAECOPF₆ electrosorbents in different water matrices

For the best-performing metallopolymer PMAECOPF₆, we studied its electrosorption performance under different water matrices, including tap water, secondary wastewater effluent (from the Urbana-Champaign Sanitary District), and a range of salt concentrations ranging from 5 mM, 20 mM, 100 mM, and saline conditions of 500 mM.¹⁶⁴ All samples were spiked with 0.1 mM PFOA and ran for 30 min under continuous stirring (300 rpm) at its optimal potential of 0 V. For the tap water samples, the adsorption capacity was 139.82 mg PFOA/ g adsorbent, while for the wastewater effluent samples the average uptake was of 123.40 mg PFOA/ g adsorbent, as seen in **Figure 4.6a**. The reduction in adsorption capacity could be caused by interfering species in the water. **Table C.6** contains detailed information on the water matrix composition. We also

performed experiments at more dilute concentrations at 15 ppb PFOA, as shown in **Table C.7** which shows the results of the ultra-diluted experiment after three hours of operation. We selected these pp-level concentrations to confirm the applicability of our cobaltocene-containing polymer for relatively dilute PFAS contaminations in real world water system.¹⁶⁵⁻¹⁶⁹ For electrosorption of the 15 ppb PFOA samples, we were able to obtain a PFOA removal of more than 50%. Future device optimization and sizing of electrodes is expected to enhance this removal efficiency even further. In general, our findings on different salt concentrations show an increase in the uptake from 5 to 100 mM NaCl. The rise in uptake could be ascribed to the increase in solution conductivity that provides higher currents and charging, thus promoting more electrosorption into the PMAECOPF₆ metallopolymer. Although, for 500 mM, the uptake significantly decreases, which is due to the high concentrations of competing anions, as well as increased ion screening that reduces the electrostatic mechanisms for selectivity at the redox-metallopolymer.

4.4.6 Energy consumption analysis

We calculated the energy consumption (kJ/mol) of the electrosorption and electrodesorption process of our five metallopolymer to evaluate the effectiveness of this system for future translation to wastewater remediation. The energy consumption was calculated based on the electrical energy required to adsorb or desorb a PFOA mol in a 5 mL, and one and a half hour batch process. **Equation 4.1** shows the calculation, where E_w is the potential of the working electrode while E_c is the potential of the counter electrode, i is the circuit current, and n are the moles of PFOA being adsorbed or desorbed, depending on the process step.

$$\text{Energy consumption (kJ/mol)} = \frac{(\int E - E_c) \times i dt)_{\text{adsorption}}}{n_{\text{adsorbed}}} + \frac{(\int (E_w - E_c) \times i dt)_{\text{desorption}}}{n_{\text{desorbed}}} \quad (\text{Eq. 4.1})$$

As seen in **Figure 4.6b**, PVF is the material with most energy being consumed during the electrosorption and electrodesorption process combined, with 62.02 kJ/mol spent. This higher energy is due to the higher voltage applied, 1.0 V vs Ag/AgCl for the 30 min electrosorption experiment, which may also result in lower current efficiencies due to possible water splitting side reactions. Then, PFPMAm, and PFMA, in descending order, consumed 52.60 kJ/mol and 39.07 kJ/mol, respectively. Since the goal is to minimize the energy, when comparing PVF, PFPMAm, and PFMA with PFCMA or PMAECOPF₆, it is notable that these materials are not suitable for further usage since their energy consumption and PFAS uptake are not the most optimal when compared to the later two materials. In the case of PFCMA, we see an energy consumption of 21.8 kJ/mol. Although, when compared with the energy consumption of PMAECOPF₆, 13.9 kJ/mol, PFCMA has a higher energy consumption and was also not as effective in adsorbing PFOA due to its lower uptake. In sum, PMAECOPF₆ is the most effective compound in terms of energy consumption as well as in adsorption/release performance for PFAS capture processes, with 76% lesser energy consumption when compared with PVF, a commercially available metallopolymer.

Prior investigations leveraging redox-copolymers composed of 4-methacryloyloxy-2,2,6,6-tetramethylpiperidin-1-oxyl (TMA) and 4-methacryloyloxy-2,2,6,6-tetramethylpiperidine (TMPMA) as electrosorbents, namely, PTMA for short, had achieved adsorption uptake

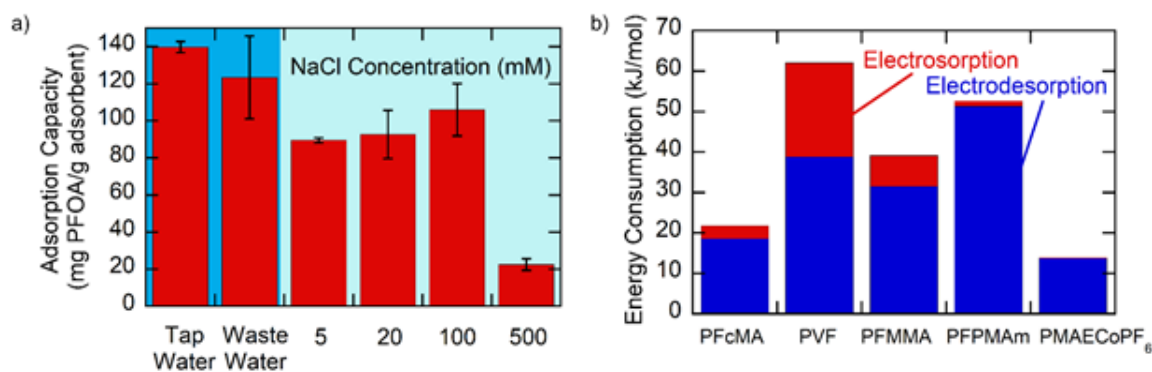


Figure 4.6. (a) PMAECOPF₆ adsorption using different water matrices at 0.0 V vs Ag/AgCl for 30 min. All samples were spiked with 0.1 mM PFOA. (b) Energy consumption analysis of the metallopolymer polymers adsorbed and desorbed at their optimal potentials.

capacities of more than 500 mg/g with 0.1 mM PFOA and 20 mM NaCl for 30 minutes.¹² However, these separations were also accompanied with significantly higher energy consumption (sometimes by more than an order of magnitude).¹² Additionally, our system can regenerate >80% of PFOA while the PTMA system has only been able to obtain up to 65% regeneration. Thus, we conclude that synthetic tunability of metallopolymer can have an important impact on energy efficiency, electrosorption, and reversibility towards long-chain PFAS removal. Going forward, we seek to evaluate the integration of our electrochemical separation systems with PFAS destruction and mineralization technologies, with potential methods to consider including plasma degradation or advanced oxidation methods such as boron-doped diamond electrodes.¹⁷⁰

CHAPTER 5: UP-CONCENTRATION AND CONTINUOUS FLOW MEASUREMENTS FOR LEGACY PFAS USING REDOX-MEDIATED ELECTROSORPTION

5.1 Overview

Per- and polyfluoroalkyl substances (PFAS) are a group of synthetic chemicals used in various industrial and consumer products, including firefighting foam, non-stick cookware, and stain-resistant fabrics. These chemicals are persistent, meaning they do not break down in the environment and can accumulate in the human body, leading to health problems such as cancer and immune system dysfunction. Therefore, removing and destroying PFAS is crucial to protecting public health and the environment. However, current techniques for capturing and releasing PFAS are limited, and advanced oxidative processes alone may not be sufficient for complete remediation. Up-concentration, which involves concentrating PFAS from contaminated water and soil into a smaller volume for more efficient destruction, can be an energetically beneficial method for PFAS remediation. Thus, our research has developed innovative and effective PFAS removal and destruction techniques, including up-concentration, where more than 250 mg/g were captured, obtaining a removal efficiency of more than 90% in a flow-through system. PTMA-containing polymers were used as adsorbents for successful capture and release. Tendentially, an advanced oxidative process bearing boron doped diamonds was implemented. The BDD results after up-concentration, led to a total defluorination of almost 100%. By addressing the limitations of current techniques and providing a viable solution through up-concentration and the utilization of PTMA-containing polymers, this research contributes significantly to the ongoing efforts in achieving comprehensive PFAS remediation, safeguarding both public health and the environment for a sustainable future.

5.2 Introduction

The removal of PFAS from water sources is crucial due to their harmful effects on human health and the environment. Aside from the several adverse health effects, including developmental and reproductive problems, liver damage, and cancer,¹⁷¹ there is a need for developing efficient and cost-effective methods for removing PFAS from contaminated water sources in a continuous fashion.

One promising approach to PFAS removal is using flow systems for up concentration.¹⁷² These systems allow for the selective adsorption and concentration of PFAS from large volumes of water when combined with suitable materials, making them easier to detect and destroy.^{173, 174} The use of flow systems can also reduce the amount of waste generated during the treatment process, making them an environmentally friendly option.^{175, 176} Flow systems can also be used in situ and applied directly to contaminated water sources without sample collection and transportation.^{177, 178}

Using novel adsorbent materials can further enhance the efficiency and effectiveness of flow systems for PFAS removal.¹⁷⁹ Polytempo methacrylate is a recently developed adsorbent material that shows promise for use in electrosorption up concentration systems.^{7, 11, 12} It has a unique structure, which allows for the selective adsorption of PFAS from water.^{11, 12} It has good chemical stability and can be easily regenerated, making it a cost-effective option for large-scale applications. Overall, the use of innovative adsorbent materials such as poly-tempo methacrylate in conjunction with flow systems has the potential to provide an effective and sustainable solution for removing PFAS from water sources.

The use of redox adsorbent materials for the removal of PFAS in water sources has been recently studied in batch scale system, but so far, no efforts of incorporating flow processes with

redox electrosorbents are not very well known.^{11, 12, 179, 180} To overcome these limitations, we propose using the redox polymer PTMA in our electrochemical technology for point-of-source PFAS removal and defluorination. PTMA is an electroactive polymer that has demonstrated high selectivity and electrochemical reversibility, making it an ideal candidate for PFAS removal.^{11, 12} Additionally, chemical functionalization of PTMA allows for the tuning of its molecular chemistry towards multiple types of PFAS. PTMA has been shown to achieve the uptake of up to 500 mg/g of perfluorooctanoic acid and hexafluoropropylene oxide dimer.¹² The hybrid structure of our adsorbent material system consists of a porous framework of multiwalled carbon nanotubes (MWCNTs) and redox-responsive PTMA, which can be easily tuned for optimal selectivity and efficiency towards different target species of PFAS. The use of PTMA will provide a more economical and robust method for PFAS removal, with fewer byproducts and no need for chemical regenerants.

Moreover, the technology proposed in this study has the potential to upconcentrate PFAS from water sources, enabling selective capture of these contaminants. This can have significant benefits for communities that depend on water sources for crop irrigation, where selective capture can be used to promote safer crops and improve economic sustainability.^{181, 182} Additionally, integrating boron-doped diamonds (BDD) with this technology can effectively remediate water sources by transforming PFAS into less harmful byproducts like water and CO₂.¹⁸³

Incorporating boron-doped diamonds (BDD) into PFAS removal systems is also an important area of research.^{7, 11, 184, 185} BDD is a unique material with exceptional electrochemical properties, making it ideal for use in electrochemical systems for PFAS destruction. BDD-based electrochemical systems have been shown to degrade PFAS compounds, producing harmless byproducts effectively.^{11, 12, 184} Furthermore, BDD-based systems have a longer lifespan and lower

operating costs than other electrochemical systems, making them an attractive option for large-scale applications.¹⁸⁶ Incorporating BDD into PFAS removal systems has the potential to provide an efficient, cost-effective, and sustainable solution for the destruction of PFAS from water sources.¹⁸⁶ Continued research and development in this area are crucial for ensuring safe and clean water sources for present and future generations.

The electrode fabrication process is simple, using a dip coating technique that provides a high level of control over the composition, structure, and morphology of the adsorbent materials. To develop a modular electrochemical technology that can efficiently remove PFAS from water sources, functionalization of the redox polymers and screening will be a critical aspect of the proposed project. Our system for PFAS removal comprises an up-concentration system that utilizes innovative adsorbent materials to selectively adsorb and concentrate PFAS, followed by an electrochemical flow system equipped with BDD electrodes that can efficiently destroy the concentrated PFAS, generating harmless byproducts. The proposed system combines the strengths of up-concentration and BDD-based electrochemical methods, providing a sustainable and effective solution for complete PFAS removal from water sources. Additionally, it can be used in situ, minimizing sample collection and transportation, reducing waste, and making it a cost-effective and environmentally friendly option. Ongoing research and development in this area are critical for ensuring clean and safe water sources for present and future generations.

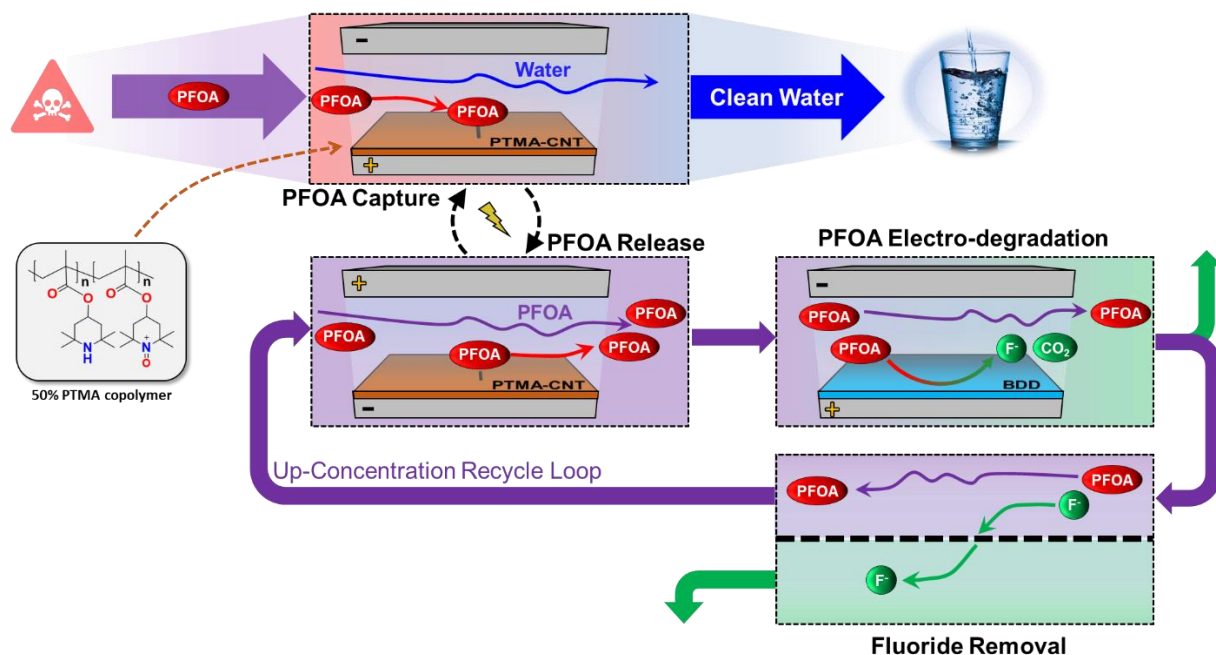


Figure 5.1. Up-concentration/electrodegradation system of PFAS.

The proposed design will commence with a contaminated water stream containing persistent and emerging PFAS contaminants. The water will undergo an electrosorption process where PTMA redox adsorbent will be employed to selectively remove the PFAS species from the water. Subsequently, the contaminated water stream will be separated into two flows using an electrochemical cell. The first flow will consist of clean water that exits the electrosorption cell, while the second flow will comprise the contaminated PFAS remaining on the surface of the electrode. The release of PFAS from the surface of the electrode will be facilitated by switching the applied potential and initiating desorption. The desorbed PFAS species will be collected in a more concentrated solution, which will then be subjected to continuous treatment using boron-doped diamond (BDD) electrocatalytic systems. The BDD electrodes will catalyze the transformation of the concentrated PFAS solution into less harmful compounds such as CO₂ and fluoride through oxidative defluorination. This integrated electrochemical system holds great

potential for the selective removal and remediation of PFAS from contaminated water streams, with the added advantage of minimizing the generation of secondary wastes. This design can be observed in **Figure 5.1**.

To complete the main goals for the project, several procedures will involve (a) construction of electrochemical cell for defluorination of the PFAS contaminants, (b) target multiple PFAS in tandem, (c) incorporate BDD electrocatalytic systems in batch process, and (d) develop and energy analysis. Firstly, the construction of an electrochemical cell for removal and up-concentration of the PFAS contaminants will require the optimization of electrochemical process parameters such as pH and optimal concentration ratio. Additionally, the electrode stability and durability will be evaluated under various operating conditions to ensure the long-term effectiveness of the electrochemical cell. Secondly, targeting multiple PFAS in tandem will involve the selection of appropriate redox polymer materials that can selectively adsorb and defluorinate multiple PFAS contaminants simultaneously. The selectivity and efficiency of the redox polymer materials for various PFAS compounds will be evaluated. Thirdly, incorporation of BDD electrocatalytic systems in batch processes will require the investigation of the electrocatalytic activity of the BDD electrodes towards the defluorination of PFAS contaminants and determining operating conditions for maximum efficiency. The degradation kinetics will be evaluated to determine the optimal operating conditions. Lastly, the development of an energy analysis will require the calculation of the energy consumption and energy efficiency of the electrochemical process for PFAS removal. The overall cost-effectiveness and environmental impact of the electrochemical process for PFAS removal will be evaluated, and the key factors that can affect the economic and environmental sustainability of the process will be identified.

5.3 Methods

We bought all chemicals from commercial suppliers and used them as-is. Unless specified otherwise, we used Nanopure water (with a resistivity of $>18.2 \text{ M}\Omega \text{ cm}$) for all measurements and experiments. The 4-methacryloyloxy-2,2,6,6-tetramethylpiperidin-1-oxyl (TMA) and 4-methacryloyloxy-2,2,6,6-tetramethylpiperidine (TMPMA), shortly denoted as PTMA, was synthesized as specified elsewhere.¹²

To prepare the electrodes, an initial ink solution containing multiwalled carbon nanotubes (MWCNTs) and PTMA in acetone was combined using established methodologies reported in the literature.^{11, 12} The dispersion and coating processibility were optimized by employing a 1:1 mass ratio of MWCNT/PTMA. All solutions were prepared at a concentration of 4 mg polymer per mL of solvent. The current collector for batch experiments consisted of a $2 \times 1 \text{ cm}^2$ stainless steel mesh, whereas for flow cell experiments, a $4 \times 4 \text{ cm}^2$ Ti plate electrode was utilized.

In the batch experiments, the ink solution was dip-coated onto the current collector until an average mass of 0.50 mg was achieved. For the flow cell experiments, the PTMA solution was drop cast, resulting in a final mass of 4 mg of the ink solution. Electrochemical studies were performed using either a SP-200 (Biologic) or a Squidstat Prime (Admiral Instruments) potentiostat. In the batch electrochemical systems, a three-electrode configuration was employed, comprising a VC-2 BASi cell, a platinum wire (0.5 mm diameter) as the counter electrode, and Ag/AgCl (3M NaCl) as the reference electrode. In the flow cell experiments, a two-electrode cell was assembled, with a $4 \times 4 \text{ cm}^2$ Ti plate serving as the counter electrode.

The concentration of PFOA was determined using liquid chromatography–mass spectrometry (LC/MSD, 1200 Series, Agilent Technologies). An EC-C18 column (2.7 μm , 2.1 mm, 50 mm; InfinityLab Poroshell 120) was employed with mobile phase A (acetonitrile) and B

(5 mM ammonium acetate). The gradient elution protocol was set as follows: 0–3 min, 10% A and 90% B; 3–4 min, 65% A and 35% B; 4–5 min, 100% A and 0% B; 5–8.5 min, 100% A and 0% B; 8.5–10 min, 10% A and 90% B. The flow rate was set at 0.4 mL/min with a sample injection volume of 1.0 μ L. The column temperature was maintained at 25 °C. Negative electron spray ionization (ESI) mode was employed to measure the PFOA concentration.

To determine the morphology and phase composition of the material, scanning electron microscopy combined with energy-dispersive X-ray spectroscopy (SEM-EDS, ThermoFisher Axia ChemiSEM) was utilized.

5.4 Results and Discussion

5.4.1 Kinetics and reaction order

Our results show that the concentration of PFOA degradation using 10 mA of current with a BDD electrode corresponds to a first order model fit, which indicates that the degradation of PFOA follows a linear rate law, as seen in the experimental and fitted data shown in **Figure 5.2a**.¹⁸⁷ This means that the rate of degradation is directly proportional to the concentration of PFOA present in the solution.¹⁸⁶ Additionally, almost complete degradation was achieved after 120 min, which further supports the efficacy of using a BDD electrode for PFOA degradation. The first order kinetics in this process is important as it provides valuable information for the design and optimization of the electrochemical system, such as predicting the degradation rate and determining the optimal operating conditions. The ability to accurately model the degradation kinetics can ultimately lead to the development of more efficient and effective electrochemical systems for the removal of PFOA and other persistent pollutants from contaminated water sources.

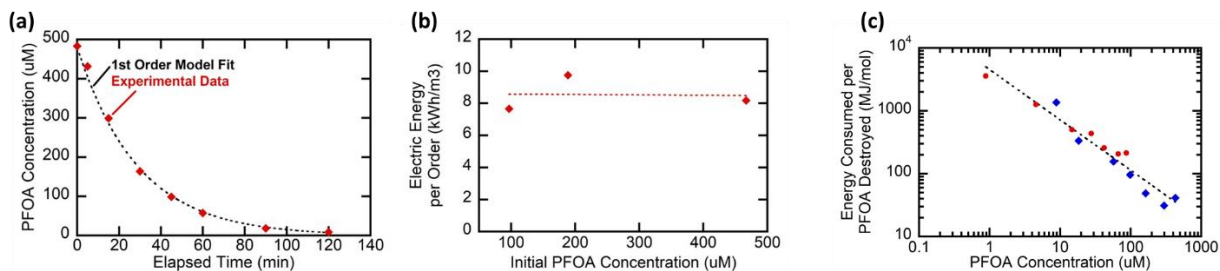


Figure 5.2. BDD kinetics for the electrocatalytic process of PFOA degradation; (a) 1st order model fit vs the experimental data with 0.5 mM PFOA + 20 mM NaCl, (b) Electric energy per order (EEO) for 0.1, 0.2, and 0.5 mM PFOA degradation using BDD, and (c) Energy consumption per PFOA destroyed shows a linear behavior in a log scale for a broad range of concentrations (0.1, 0.2, and 0.5 mM).

Based on our electrochemical system's first-order kinetics, we conducted a kinetics experiment by altering the PFOA concentration. We found that the kinetic order did not alter with concentration changes. The only change observed was a rise in the slope angle with increasing concentration. This behavior is likely due to the concentration's effect on the rate constant (k), which remained constant irrespective of concentration changes. In contrast, the increase in slope angle can be explained by the increase in the number of PFOA molecules available for degradation, resulting in a higher rate of degradation. Our findings suggest that our electrochemical system's performance is consistent and predictable, allowing for better optimization and control of the process for effective degradation of PFOA contaminants.

In addition, we investigated the electric energy per order (EEO) associated with the degradation process using BDD. The outcomes of this investigation are depicted in **Figure 5.2b** for degradation at concentrations of 0.1, 0.2, and 0.5 mM. These results provide compelling evidence that the EEO remains constant across the wide spectrum of concentrations examined.

The constancy of the EEO in BDD degradation can be attributed to the excellent electrochemical properties of BDD, including high conductivity and low energy losses. This ensures consistent energy input regardless of concentration. The generation of reactive species and the stability of the BDD electrode also contribute to the constant EEO. Further investigations may provide more insights.

To investigate the energy consumption per PFOA molecule destroyed during our BDD experiments, we conducted kinetics experiments and analyzed the energy behavior throughout the degradation process, as depicted in **Figure 5.2c**. By employing a logarithmic scale, we observed a linear trend, indicating a relationship between energy consumption and PFOA destruction. However, it is important to note that this linear behavior is only evident when considering the data on a logarithmic scale. Furthermore, our data revealed that lower PFOA concentrations corresponded to higher energy consumption. This observation suggests that upconcentrating systems, which allow for the treatment of more concentrated streams of PFAS, can be beneficial in reducing the energy required by advanced oxidative processes. Concentrating the PFAS stream allows for a more efficient treatment process, potentially lowering the overall energy consumption. These findings highlight the importance of considering the concentration of contaminants when designing treatment strategies for PFAS removal, as it can have a significant impact on energy efficiency. Further research and optimization of up-concentration techniques could lead to more sustainable and energy efficient PFAS treatment processes.

5.4.2 Energy and optimal up-concentration ratios

In our up-concentration experiment, we conducted a series of PFAS to PFAS ratios to enhance the scientific rigor of our study. Specifically, we employed adsorption at a given concentration followed by desorption in a solution with either the same concentration or a higher concentration

of PFOA. The outcomes of these experiments are presented in **Figure 5.3a**, where the electrosorption uptake remained consistently high, exceeding 175 mg/g adsorbent across all three trials. The electrodes used in this process were composed of a PTMA electrode combined with a MWCNT ratio of 1:1, as detailed in the materials and methods section.

For electrodesorption, we successfully desorbed PFOA in solutions containing concentrations of 0.1 mM, 0.2 mM, and 0.5 mM. Each electro-adsorption/desorption combination corresponded to concentration ratios of 1:1, 2:1, and 5:1, respectively. Notably, our findings, as depicted in **Figure 5.3a**, unequivocally demonstrate up-concentration of more than 50% in all three scenarios. During the desorption phase, when subjected to solutions with equal or higher PFOA concentrations, the electrochemical potential applied to the electrode facilitates the release of PFOA from the electrode surface. This process occurs due to the repulsion between similarly charged PFOA molecules and the negatively charged electrode, causing the desorbed PFOA to migrate towards the solution. Furthermore, the increased PFOA concentration in the desorption solution creates a concentration gradient that promotes the diffusion of PFOA away from the electrode, leading to successful desorption.

Based on **Figure 5.3b**, our study found that the concentration ratio significantly impacts the energy consumption during the electrochemical degradation of PFAS. Specifically, we observed that when the concentration ratio is higher (e.g., 5:1 versus 1:1), the energy consumption is lower in terms of degradation. This is since the degradation kinetics are much faster when higher concentrations of PFAS are present, as seen in **Figure 5.2a**. However, regarding adsorption, the energy consumption is higher for samples with higher concentrations, as there are more PFAS molecules to be separated. Therefore, the energy consumption for the overall process will depend on the initial concentration ratio and the specific steps involved. Hence, our results suggest

optimizing the concentration ratio is essential for achieving efficient and cost-effective PFAS treatment.

The concentration ratio plays a crucial role in the up-concentration processes of PFAS contaminants. As seen in **Figure 5.3b**, when the concentration ratio is higher, there is a significant increase in the up-concentration factor, meaning that more concentrated solutions can be obtained from more polluted streams. This is particularly important when dealing with wastewater or other contaminated sources that have relatively low initial concentrations of PFAS, as it allows for more efficient and cost-effective separation and degradation of these contaminants. Moreover, a higher concentration ratio can also reduce the energy consumption required for separation, as there is less water to be treated and processed. Therefore, the concentration ratio is a critical parameter to consider when designing and optimizing electrochemical systems for PFAS removal and up-concentration.

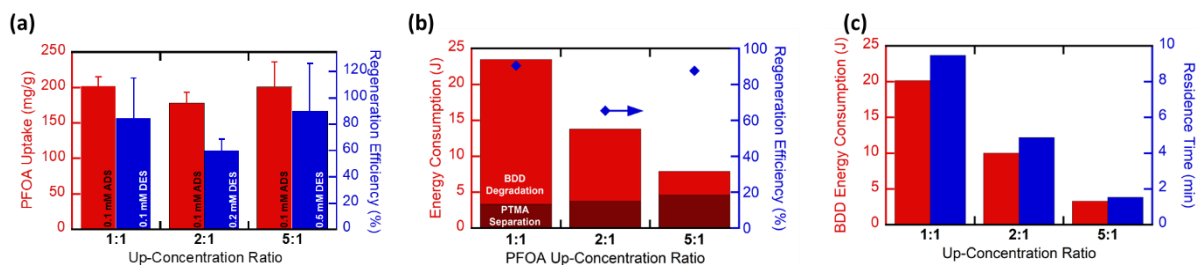


Figure 5.3. Up-concentration ratios (a)Energy consumption analysis and regeneration efficiencies, (b) Adsorption capacities to different ratios and their regeneration efficiencies.

Additionally, **Figure 5.3c** substantiates a direct correlation between energy consumption and residence time. This observation suggests that higher energy input leads to longer residence times within the system. It further implies that a greater PFOA up-concentration ratio corresponds

to an increased concentration of PFOA species available for degradation. Consequently, the concentration of PFOA unequivocally influences the interaction between reactants and the BDD catalysts, thereby impacting the reaction rate, as previously observed in the section where the concentration of PFOA species was found to determine the rate of reaction. The extended residence time resulting from higher energy input enables a more prolonged contact between the PFOA species and the BDD catalyst surface. This prolonged interaction allows for enhanced adsorption, desorption, and subsequent degradation of the PFOA species. As a result, a higher PFOA up-concentration ratio translates into a larger quantity of PFOA species available for degradation, leading to a more efficient removal of the contaminant. The concentration-dependent nature of the interaction between reactants and the BDD catalysts highlights the significance of controlling the PFOA concentration in the system. By manipulating the concentration, the reaction rate can be modulated, thus optimizing the degradation efficiency. Moreover, the concentration-dependent behavior further supports the notion that the concentration of PFOA species plays a pivotal role in governing the overall degradation kinetics.

5.4.3 Flow cell approaches

In the flow cell experiment we conducted, we aimed to investigate the feasibility of using our electrochemical system for up-concentration and regeneration of PFAS contaminants. We used a 10:1 ratio and varied the pH for desorption, as shown in **Figure 5.4a**. Our preliminary results show that the pre-equilibrium uptake was more than 300 mg/g, indicating a high adsorption capacity of our system. Furthermore, once electrochemical adsorption was introduced, further uptake was observed, indicating the potential for the up-concentration of PFAS contaminants. We also observed more than 90% regeneration in a 10 times more concentrated stream, which confirms the applicability of our system for the removal and up-concentration of PFAS contaminants. However,

further optimization and stability research must be performed to ensure the long-term effectiveness of our system. Additionally, exploring other materials and different types of PFAS contaminants could further improve our understanding and the potential applications of our electrochemical system.

Additionally, we performed 1:1 and 2:1 up-concentration ratio flow cell experiments where no pH change was necessary. This indicated that our system is also highly capable of exceeding flow cell desorption without the need for chemical regenerants.

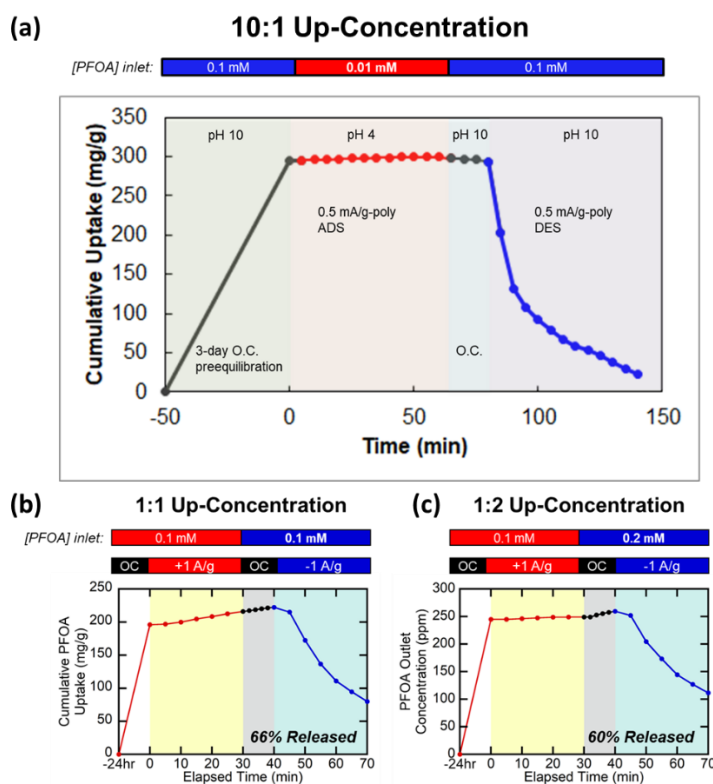


Figure 5.4. Flow-cell experiment for a 10:1 PFOA ratio up-concentration (a) at pH 4 to 10, (b) at pH 4, 1:1 ratio, and (c) at pH 4, 1:2 ratio.

CHAPTER 6: CONCLUSIONS AND FUTURE DIRECTIONS

6.1 Overview

This research has significantly advanced the field of PFAS remediation by introducing novel copolymers and metallopolymers with tailored redox functionalities for efficient PFAS capture, separation, and degradation. The integration of electrochemical techniques, such as BDD electrodes, further enhances the energy efficiency and effectiveness of PFAS removal processes. These findings contribute valuable insights to the ongoing efforts aimed at safeguarding public health and the environment from the persistent threat of PFAS contamination. Future directions should focus on scaling up these technologies for practical implementation and addressing emerging PFAS variants to achieve comprehensive and sustainable PFAS remediation strategies.

6.2 Summary of Work

In conclusion, this thesis has investigated innovative approaches and technologies for addressing the pervasive environmental and health challenges posed by PFAS. PFAS contamination has become a significant concern due to its widespread presence and persistence in various ecosystems and water sources, leading to serious health risks for humans and wildlife. The research presented in this thesis underscores the urgent need for effective remediation strategies to mitigate PFAS-related health hazards and safeguard water quality. Through a comprehensive exploration of electrosorption techniques, redox-active polymers, and integrated treatment approaches, this thesis contributes valuable insights into advancing sustainable methods for PFAS removal and destruction. The findings presented across multiple chapters demonstrate promising avenues for

enhancing water remediation processes, protecting public health, and promoting environmental sustainability in the face of PFAS pollution.

Chapter 1 introduces the pervasive impact of anthropogenic organic pollutants, particularly Per- and polyfluoroalkyl substances (PFAS), on the environment since their development in the 1950s. These pollutants pose serious health risks due to their widespread presence in consumer products and water sources, leading to immunological deficiencies, cancer, and other diseases. The chapter highlights the inadequacy of traditional water separation techniques against ultra-diluted PFAS and advocates for the development of new, selective methods like electrosorption. By integrating electrosorption into water remediation processes, the chapter proposes a promising avenue to enhance water quality and protect public health from PFAS-related health hazards.

Chapter 2 focuses on the development of a redox-active copolymer (P(TMAx-co-TMPMA1-x)) designed for selective PFAS capture and mineralization. The copolymer demonstrates high affinity for PFAS, exhibiting exceptional uptake capacities (>2.54 mmol PFOA/g adsorbent) and separation factors, making it effective across various water matrices. This chapter introduces a novel approach using synergistic ion-exchange and redox-active polymers for efficient PFAS removal. The integration with electrochemical processes further enhances the remediation capabilities, showcasing the potential of redox-based materials for sustainable water treatment.

Chapter 3 investigates the electrochemical adsorption of GenX using a redox copolymer electrode, emphasizing kinetic enhancements and defluorination capabilities. The redox copolymer exhibits rapid kinetics and high uptake for GenX (>475 mg/g adsorbent), demonstrating successful translation from batch to flow-through systems. This research contributes to the development of scalable and efficient methods for selective PFAS removal and defluorination

using redox-based electrodes. The findings underscore the potential of electrochemical techniques in addressing PFAS contamination in various environmental settings.

Chapter 4 explores the use of redox-active metallopolymer to enhance PFAS electrosorption and regeneration efficiency. Metallopolymer with varied redox potentials show improved PFAS uptake and regeneration capabilities, indicating structural correlations with electron density. This chapter showcases the tunability of redox-metallopolymer for efficient PFAS capture and release, providing valuable insights into enhancing electrosorption technologies for comprehensive water remediation.

Chapter 5 emphasizes the importance of up-concentration techniques coupled with advanced oxidative processes for comprehensive PFAS removal. Polymer adsorbents coupled with advanced oxidation processes achieve high removal efficiencies (>90%) and defluorination rates, demonstrating innovative strategies for PFAS remediation. The integration of PTMA-containing polymer in up-concentration processes contributes significantly to sustainable water quality enhancement. This research underscores the urgency of developing and implementing effective remediation strategies to safeguard public health and the environment from the persistent threats posed by PFAS contaminants.

In conclusion, the thesis highlights the critical need for advanced and sustainable technologies to address PFAS contamination effectively. The collective findings from these chapters demonstrate the potential of electrosorption, redox-active polymer, and integrated treatment approaches in tackling PFAS pollution, offering valuable insights and methodologies for achieving comprehensive PFAS remediation. These contributions are essential for protecting public health and the environment from the persistent risks associated with PFAS contaminants.

6.3 Development of an Electrocatalytic Approach for Enhanced Fenton-like Reactions

The Fenton process has long been recognized for its efficacy in generating hydroxyl radicals ($\text{HO}\cdot$) to degrade hazardous organic pollutants. However, its practical application is hindered by the need for acidic conditions and the use of chemical additives like iron salts and hydrogen peroxide, which can lead to equipment corrosion, increased costs, and challenging disposal of ferric sludge. To overcome these limitations, this thesis proposes the development and characterization of an innovative electrocatalyst for promoting Fenton-like reactions under mild conditions without the need for chemical additives.

Our research should focus on the design and synthesis of a redox-copolymer electrocatalyst, termed $\text{P}(\text{xAQ-co-xFPMaM})$, where x represents the percentage of monomers in the material. This electrocatalyst leverages polyanthraquinone (AQ) for hydrogen peroxide (H_2O_2) generation and ferrocene (FPMaM) for facilitating the Fenton process by promoting the oxidation of Fe(II) to Fe(III) . Notably, this electrocatalyst operates effectively under both strong acidic conditions and neutral pH environments, offering versatility and robust performance.

The fundamental innovation of our electrocatalyst lies in its ability to promote the Fenton-like reaction in situ, eliminating the need for exogenous chemical additives. This not only simplifies the process but also mitigates issues related to equipment corrosion and waste disposal associated with traditional Fenton processes. Moreover, the electrocatalyst's compatibility with neutral pH conditions expands its potential applicability in diverse environmental settings.

To validate the efficiency of our electrocatalytic approach, we conducted degradation studies using triclosan (TCS), a persistent and toxic pollutant commonly found in antimicrobial products. Remarkably, so far our electro-Fenton system achieved more than 95% degradation of TCS within just 30 minutes under specific electrochemical conditions (e.g., -0.5 V vs Ag/AgCl).

The degradation pathway led to the formation of oxalic, maleic, and glycolic acids as consumable by-products, highlighting the effectiveness and environmental relevance of our approach (**Figure 6.1**).

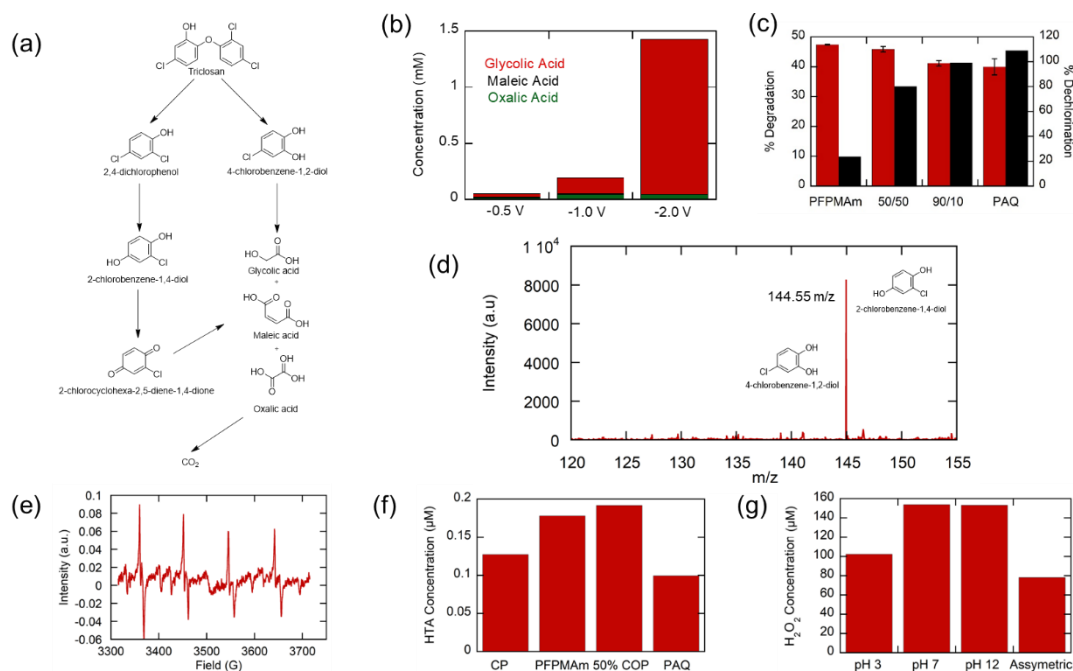


Figure 6.1. By-product formation in the Electro-fenton reaction process. (a) potential degradation pathway. (b) Carboxylic acid formation after electrodegrading for one hour in 0.1 mM TCS + 20 mM NaBr. (c) Different degradation and dichlorination percentages with different electrodes containing FPMAM monomer. (d) Degradation of TCS by-products confirmed through MS/MS after an electrocatalytic process of 30 minutes at -0.5 V vs Ag/AgCl on 0.1 mM TCS +20 mM NaBr. (e) Electron Paramagnetic Resonance results for HO· peaks after an electrocatalytic process of 30 minutes at -0.5 V vs Ag/AgCl on 0.1 mM TCS +20 mM NaBr. (f) HTA concentration proving H₂O₂ formation for different electro-fenton electrodes after an electrocatalytic process of 30 minutes at -0.5 V vs Ag/AgCl on 0.1 mM TCS +20 mM NaBr. (g) H₂O₂ formation after an electrocatalytic process of 30 minutes at -0.5 V vs Ag/AgCl on 0.1 mM TCS +20 mM NaBr at different pH.

In summary, this pioneering electrocatalytic strategy for enhancing Fenton-like reactions, offering a sustainable and efficient alternative to traditional Fenton processes. The demonstrated capabilities of our electrocatalyst in pollutant degradation underscore its potential for broader applications in environmental remediation and wastewater treatment, contributing to advancements in advanced oxidative processes and addressing pressing environmental concerns.

6.4 Long Term Perspective of PFAS Directions

Taking a long-term perspective on the issue of per- and polyfluoroalkyl substances (PFAS) contamination, it is imperative to consider future directions and strategies that can effectively address the persistent challenges posed by these pollutants. PFAS contamination has emerged as a critical environmental and public health concern, given the widespread distribution and persistence of these chemicals in the environment. Looking ahead, several key points and directions can be emphasized to guide ongoing efforts in managing and mitigating the impact of PFAS:

A. Technological Advancements: Continued research and development of advanced technologies are essential for improving PFAS remediation efficacy and sustainability. Innovations in electrosorption, as explored in this thesis, hold great promise for selectively capturing and removing PFAS from water sources. Further advancements in materials science and engineering can lead to the design of more efficient and scalable treatment methods capable of addressing PFAS contamination across diverse environmental settings.

Technological advances in the field of PFAS remediation are crucial for developing efficient and sustainable methods to address contamination. Here are further details on key technological advancements that can shape future approaches to PFAS treatment:

Advanced Adsorbent Materials: One of the forefront areas of research involves the development of advanced adsorbent materials specifically designed for PFAS removal. This includes the synthesis of novel polymers, such as redox-active polymers or functionalized resins, with tailored properties that enhance PFAS adsorption capacity and selectivity. Researchers are exploring the use of nanomaterials, such as graphene-based materials or metal-organic frameworks (MOFs), which offer high surface areas and unique binding affinities for PFAS contaminants. These advanced adsorbents can significantly improve treatment efficiency and reduce the overall cost of PFAS removal processes.

Electrochemical Technologies: Electrochemical methods, including electrosorption, hold great promise for efficient PFAS removal and destruction. Ongoing research focuses on optimizing electrode materials and configurations to enhance the performance of electrochemical reactors. For instance, the use of conductive carbon-based electrodes or metal-doped electrodes can improve electron transfer efficiency and facilitate PFAS oxidation or reduction. Advances in electrochemical cell design and operation parameters can lead to more energy-efficient and scalable technologies for treating PFAS-contaminated water.

Membrane-Based Separation Processes: Membrane filtration technologies, such as reverse osmosis (RO) or nanofiltration (NF), are commonly used for water treatment but face challenges in effectively removing PFAS due to their small molecular size and stability. Recent advancements in membrane materials, including the development of selective PFAS removal membranes or hybrid membrane processes, aim to improve PFAS rejection rates while reducing energy

consumption and fouling issues. Integrating membrane processes with other treatment methods, such as adsorption or advanced oxidation, can enhance overall treatment performance and expand the applicability of membrane technologies for PFAS removal.

Advanced Oxidation Processes (AOPs): AOPs involve the generation of highly reactive hydroxyl radicals to oxidize and degrade PFAS contaminants. Research is focused on developing novel AOPs, such as photochemical or electrochemical oxidation processes, to enhance PFAS destruction rates and minimize the formation of harmful byproducts. By optimizing reaction conditions, catalyst materials, and reactor designs, advanced oxidation technologies can offer effective solutions for treating PFAS in contaminated water and wastewater streams. An example has already been established in Section 6.3 where the incorporation of electro-fenton processes promotes rapid destruction of pharmaceuticals and can harness a new energy effective technology for PFAS degradation. Despite their effectiveness, AOPs for PFAS treatment face several challenges, including the formation of byproducts, high energy consumption, and challenges with cost and scalability. To be more specific, some AOPs may generate toxic intermediates or byproducts during PFAS degradation, requiring careful monitoring and management. Additionally, AOPs can be energy-intensive, necessitating the development of energy-efficient reactor designs and process optimization strategies. Also, implementation of large-scale AOPs for PFAS treatment may involve high capital and operational costs, highlighting the importance of cost-effective treatment approaches. That is why there are multiple avenues for researchers to develop new ways to improve AOPs.

Process Integration and Optimization: Future advancements will emphasize the integration of multiple treatment processes into holistic treatment trains or hybrid systems. This includes combining adsorption, electrochemical treatment, membrane separation, and advanced oxidation

techniques to achieve synergistic effects and improve overall treatment efficiency. Process optimization strategies, such as real-time monitoring, automated control systems, and adaptive treatment algorithms, will be essential for maximizing resource utilization and minimizing environmental impacts during PFAS remediation operations.

In summary, ongoing technological advances in adsorbent materials, electrochemical technologies, membrane-based processes, advanced oxidation, and process integration are driving innovations in PFAS remediation. These advancements hold great potential for developing cost-effective, energy-efficient, and environmentally sustainable solutions to address PFAS contamination and safeguard water resources for future generations. Continued research and collaborative efforts between academia, industry, and regulatory agencies will be critical for translating these advancements into practical applications and addressing the complex challenges posed by PFAS pollution.

B. Integration of Treatment Approaches: Future strategies should focus on integrating multiple treatment approaches, such as electrochemical processes and advanced oxidation, to achieve comprehensive PFAS removal and destruction. The findings from this thesis underscore the potential of combining redox-active polymers with electrochemical methods for efficient PFAS capture and mineralization. This integrated approach can enhance treatment efficacy and promote sustainable water quality management practices. For example, Sequential treatment strategies should be observed. It involves the sequential application of different treatment steps to achieve comprehensive PFAS removal. This may include combining physical separation (e.g., filtration) with chemical treatment (e.g., oxidation) or biological processes (e.g., microbial degradation). Sequential treatment approaches optimize treatment efficiency by targeting different PFAS compounds and addressing specific challenges associated with their removal and degradation.

Then, consideration of process optimization and control systems is also crucial in developing new treatment approaches. Effective integration of treatment approaches requires advanced process optimization and control systems to ensure optimal performance and resource utilization. Real-time monitoring of key parameters, such as PFAS concentrations, treatment efficiency, and energy consumption, allows for adaptive control and adjustment of treatment operations. Process modeling and simulation tools can aid in the design and optimization of integrated treatment systems, optimizing performance while minimizing operational costs and environmental impacts.

C. Scaling Up and Real-World Implementation: Moving forward, efforts should be directed towards scaling up laboratory-developed technologies for real-world implementation. The translation of innovative PFAS remediation techniques from bench-scale studies to pilot-scale and full-scale applications is crucial for addressing contamination in large-scale water systems and contaminated sites. Collaborative partnerships between researchers, industry stakeholders, and policymakers will be essential to facilitate technology transfer and deployment.

Combining electrosorption with novel AOPs represents an innovative approach that can be upscaled for practical implementation in water treatment plants and large-scale water remediation projects. Electrosorption technologies can be integrated into existing water treatment infrastructure, such as filtration systems or electrochemical cells, to selectively concentrate PFAS contaminants from large volumes of water. The concentrated PFAS-laden stream can then be subjected to novel AOPs, such as electro-Fenton reactions or photocatalysis, to efficiently degrade and mineralize the adsorbed PFAS compounds. Upscaling this integrated approach involves optimizing system designs, electrode configurations, and process parameters to accommodate higher flow rates and treatment capacities. Additionally, advancements in electrode materials, catalysts, and reactor technologies are essential for achieving cost-effective and energy-efficient

PFAS remediation at industrial scales. Collaborative efforts between researchers, engineers, regulators, and industry stakeholders are crucial for translating laboratory-scale innovations into scalable and commercially viable technologies for addressing PFAS contamination in water streams and treatment facilities. The upscale of electrosorption combined with novel AOPs holds significant promise for advancing the field of PFAS remediation and ensuring the sustainability of water resources for future generations.

In conclusion, addressing the long-term challenges associated with PFAS contamination requires a concerted effort to advance technological solutions, integrate treatment approaches, strengthen regulatory frameworks, and enhance monitoring and risk assessment practices. The research presented in this thesis contributes to the growing body of knowledge on PFAS remediation and underscores the importance of sustained interdisciplinary collaboration to achieve lasting improvements in water quality and environmental health. By embracing a forward-looking approach and implementing strategic actions, stakeholders can work towards mitigating the impacts of PFAS contamination and safeguarding ecosystems and communities for future generations.

REFERENCES

1. Gaines, L. G. T., Historical and current usage of per- and polyfluoroalkyl substances (PFAS): A literature review. *American Journal of Industrial Medicine* **2023**, 66 (5), 353-378.
2. Chen, R.; Sheehan, T.; Ng, J. L.; Brucks, M.; Su, X., Capacitive deionization and electrosorption for heavy metal removal. *Environmental Science: Water Research & Technology* **2020**, 6 (2), 258-282.
3. Glüge, J.; London, R.; Cousins, I. T.; DeWitt, J.; Goldenman, G.; Herzke, D.; Lohmann, R.; Miller, M.; Ng, C. A.; Patton, S.; Trier, X.; Wang, Z.; Scheringer, M., Information Requirements under the Essential-Use Concept: PFAS Case Studies. *Environmental Science & Technology* **2022**, 56 (10), 6232-6242.
4. Ma, D.; Lu, Y.; Liang, Y.; Ruan, T.; Li, J.; Zhao, C.; Wang, Y.; Jiang, G., A Critical Review on Transplacental Transfer of Per- and Polyfluoroalkyl Substances: Prenatal Exposure Levels, Characteristics, and Mechanisms. *Environmental Science & Technology* **2022**, 56 (10), 6014-6026.
5. Xie, L.-N.; Wang, X.-C.; Su, L.-Q.; Ji, S.-S.; Gu, W.; Barrett, H.; Dong, X.-J.; Zhu, H.-J.; Hou, S.-S.; Li, Z.-H.; Liu, Y.-L.; Zhang, L.; Zhu, Y., The association between per-/polyfluoroalkyl substances in serum and thyroid function parameters: A cross-sectional study on teenagers living near a Chinese fluorochemical industrial plant. *Science of The Total Environment* **2024**, 920, 170985.
6. Chen, J. C.; Baumert, B. O.; Li, Y.; Li, Y.; Pan, S.; Robinson, S.; Rubbo, B.; Costello, E.; He, J.; Hampson, H.; Beglarian, E.; Rock, S.; Goodrich, J. A.; Eckel, S. P.; Aung, M. T.; McConnell, R.; Conti, D. V.; Chatzi, L., Associations of per- and polyfluoroalkyl substances, polychlorinated biphenyls, organochlorine pesticides, and polybrominated diphenyl ethers with oxidative stress markers: A systematic review and meta-analysis. *Environmental Research* **2023**, 239, 117308.
7. Román Santiago, A.; Baldaguez Medina, P.; Su, X., Electrochemical remediation of perfluoroalkyl substances from water. *Electrochimica Acta* **2022**, 403, 139635.
8. Partington, J. M.; Rana, S.; Szabo, D.; Anumol, T.; Clarke, B. O., Comparison of high-resolution mass spectrometry acquisition methods for the simultaneous quantification and identification of per- and polyfluoroalkyl substances (PFAS). *Analytical and Bioanalytical Chemistry* **2024**, 416 (4), 895-912.
9. Ko, J. S.; Le, N. Q.; Schlesinger, D. R.; Zhang, D.; Johnson, J. K.; Xia, Z., Novel niobium-doped titanium oxide towards electrochemical destruction of forever chemicals. *Scientific Reports* **2021**, 11 (1), 18020.
10. Ma, Q.; Gao, J.; Cheng, K.; Young, J.; Zhao, M.-Q.; Ronen, A.; Zhang, W., Electrooxidation of Perfluorocarboxylic Acids by an Interfacially Engineered Magnéli Phase Titanium Oxide (Ti₄O₇) Electrode with MXene. *ACS ES&T Engineering* **2024**.
11. Baldaguez Medina, P.; Cotty, S.; Kim, K.; Elbert, J.; Su, X., Emerging investigator series: electrochemically-mediated remediation of GenX using redox-copolymers. *Environmental Science: Water Research & Technology* **2021**, 7 (12), 2231-2240.
12. Kim, K.; Baldaguez Medina, P.; Elbert, J.; Kayiwa, E.; Cusick, R. D.; Men, Y.; Su, X., Molecular Tuning of Redox-Copolymers for Selective Electrochemical Remediation. *Advanced Functional Materials* **2020**, 30 (52), 2004635.
13. Xia, C.; Qu, S.; Bhattacharjee, L.; Lim, X. E.; Yang, H.; Liu, J., Degradation of perfluoroalkyl substances using UV/Fe⁰ system with and without the presence of oxygen. *Environmental Technology* **2023**, 44 (18), 2725-2736.

14. Barisci, S.; Suri, R., Removal of polyfluorinated telomer alcohol by Advanced Oxidation Processes (AOPs) in different water matrices and evaluation of degradation mechanisms. *Journal of Water Process Engineering* **2021**, 39, 101745.
15. Panizza, M., Boron-Doped Diamond Electrodes. In *Encyclopedia of Interfacial Chemistry*, Wandelt, K., Ed. Elsevier: Oxford, 2018; pp 393-400.
16. Barber, J. L.; Berger, U.; Chaemfa, C.; Huber, S.; Jahnke, A.; Temme, C.; Jones, K. C., Analysis of per- and polyfluorinated alkyl substances in air samples from Northwest Europe. *Journal of Environmental Monitoring* **2007**, 9 (6), 530-541.
17. Hu, X. C.; Andrews, D. Q.; Lindstrom, A. B.; Bruton, T. A.; Schaidler, L. A.; Grandjean, P.; Lohmann, R.; Carignan, C. C.; Blum, A.; Balan, S. A.; Higgins, C. P.; Sunderland, E. M., Detection of Poly- and Perfluoroalkyl Substances (PFASs) in U.S. Drinking Water Linked to Industrial Sites, Military Fire Training Areas, and Wastewater Treatment Plants. *Environ Sci Technol Lett* **2016**, 3 (10), 344-350.
18. Scher, D. P.; Kelly, J. E.; Huset, C. A.; Barry, K. M.; Hoffbeck, R. W.; Yingling, V. L.; Messing, R. B., Occurrence of perfluoroalkyl substances (PFAS) in garden produce at homes with a history of PFAS-contaminated drinking water. *Chemosphere* **2018**, 196, 548-555.
19. Barry, V.; Winkquist, A.; Steenland, K., Perfluorooctanoic acid (PFOA) exposures and incident cancers among adults living near a chemical plant. *Environ Health Perspect* **2013**, 121 (11-12), 1313-8.
20. Vieira, V. M.; Hoffman, K.; Shin, H. M.; Weinberg, J. M.; Webster, T. F.; Fletcher, T., Perfluorooctanoic acid exposure and cancer outcomes in a contaminated community: a geographic analysis. *Environ Health Perspect* **2013**, 121 (3), 318-23.
21. Grandjean, P.; Andersen, E. W.; Budtz-Jorgensen, E.; Nielsen, F.; Molbak, K.; Weihe, P.; Heilmann, C., Serum vaccine antibody concentrations in children exposed to perfluorinated compounds. *JAMA* **2012**, 307 (4), 391-7.
22. Buser, M. C.; Scinicariello, F., Perfluoroalkyl substances and food allergies in adolescents. *Environ Int* **2016**, 88, 74-79.
23. Matilla-Santander, N.; Valvi, D.; Lopez-Espinosa, M. J.; Manzano-Salgado, C. B.; Ballester, F.; Ibarluzea, J.; Santa-Marina, L.; Schettgen, T.; Guxens, M.; Sunyer, J.; Vrijheid, M., Exposure to Perfluoroalkyl Substances and Metabolic Outcomes in Pregnant Women: Evidence from the Spanish INMA Birth Cohorts. *Environ Health Perspect* **2017**, 125 (11), 117004.
24. Zhang, C.; Sundaram, R.; Maisog, J.; Calafat, A. M.; Barr, D. B.; Buck Louis, G. M., A prospective study of prepregnancy serum concentrations of perfluorochemicals and the risk of gestational diabetes. *Fertil Steril* **2015**, 103 (1), 184-9.
25. US Environmental Protection Agency, *FACT SHEET PFOA & PFOS Drinking Water Health Advisories*, EPA 800-F-16-003 **2016**.
26. Gagliano, E.; Sgroi, M.; Falciglia, P. P.; Vagliasindi, F. G. A.; Roccaro, P., Removal of poly- and perfluoroalkyl substances (PFAS) from water by adsorption: Role of PFAS chain length, effect of organic matter and challenges in adsorbent regeneration. *Water Res* **2020**, 171, 115381.
27. Qu, Y.; Jiang, X.; Cagnetta, G.; Liu, L.; Bao, Y.; Li, W.; Wang, Q.; Liang, C.; Huang, J.; Yang, H.; Yu, G., Poly- and perfluoroalkyl substances in a drinking water treatment plant in the Yangtze River Delta of China: Temporal trend, removal and human health risk. *Science of The Total Environment* **2019**, 696, 133949.

28. Lockwood, T. E.; Talebi, M.; Minett, A.; Mills, S.; Doble, P. A.; Bishop, D. P., Micro solid-phase extraction for the analysis of per- and polyfluoroalkyl substances in environmental waters. *Journal of Chromatography A* **2019**, *1604*, 460495.
29. Appleman, T. D.; Higgins, C. P.; Quiñones, O.; Vanderford, B. J.; Kolstad, C.; Zeigler-Holady, J. C.; Dickenson, E. R. V., Treatment of poly- and perfluoroalkyl substances in U.S. full-scale water treatment systems. *Water Research* **2014**, *51*, 246-255.
30. Wei, Z.; Xu, T.; Zhao, D., Treatment of per- and polyfluoroalkyl substances in landfill leachate: status, chemistry and prospects. *Environmental Science: Water Research & Technology* **2019**, *5* (11), 1814-1835.
31. Ateia, M.; Alsbaiee, A.; Karanfil, T.; Dichtel, W., Efficient PFAS Removal by Amine-Functionalized Sorbents: Critical Review of the Current Literature. *Environmental Science & Technology Letters* **2019**, *6* (12), 688-695.
32. Chen, R.; Sheehan, T.; Lian Ng, J.; Brucks, M.; Su, X., Capacitive deionization and electrosorption for heavy metal removal. *Environmental Science: Water Research & Technology* **2019**, *6* (2), 258-282.
33. Ma, C.-Y.; Huang, S.-C.; Chou, P.-H.; Den, W.; Hou, C.-H., Application of a multiwalled carbon nanotube-chitosan composite as an electrode in the electrosorption process for water purification. *Chemosphere* **2016**, *146*, 113-120.
34. Bayram, E.; Ayranci, E., Electrosorption based waste water treatment system using activated carbon cloth electrode: Electrosorption of benzoic acid from a flow-through electrolytic cell. *Separation and Purification Technology* **2012**, *86*, 113-118.
35. Kim, K.; Cotty, S.; Elbert, J.; Chen, R.; Hou, C. H.; Su, X., Asymmetric Redox-Polymer Interfaces for Electrochemical Reactive Separations: Synergistic Capture and Conversion of Arsenic. *Adv Mater* **2020**, *32* (6), e1906877.
36. Su, X.; Kushima, A.; Halliday, C.; Zhou, J.; Li, J.; Hatton, T. A., Electrochemically-mediated selective capture of heavy metal chromium and arsenic oxyanions from water. *Nat Commun* **2018**, *9* (1), 4701.
37. Wang, S.; Li, X.; Zhang, Y.; Quan, X.; Chen, S.; Yu, H.; Zhao, H., Electrochemically enhanced adsorption of PFOA and PFOS on multiwalled carbon nanotubes in continuous flow mode. *Chinese Science Bulletin* **2014**, *59* (23), 2890-2897.
38. Li, X.; Chen, S.; Quan, X.; Zhang, Y., Enhanced Adsorption of PFOA and PFOS on Multiwalled Carbon Nanotubes under Electrochemical Assistance. *Environmental Science & Technology* **2011**, *45* (19), 8498-8505.
39. Su, X.; Kulik, H. J.; Jamison, T. F.; Hatton, T. A., Anion-Selective Redox Electrodes: Electrochemically Mediated Separation with Heterogeneous Organometallic Interfaces. *Advanced Functional Materials* **2016**, *26* (20), 3394-3404.
40. Su, X.; Tan, K.-J.; Elbert, J.; Rüttiger, C.; Gallei, M.; Jamison, T. F.; Hatton, T. A., Asymmetric Faradaic systems for selective electrochemical separations. *Energy & Environmental Science* **2017**, *10* (5), 1272-1283.
41. Mao, X.; Tian, W.; Ren, Y.; Chen, D.; Curtis, S. E.; Buss, M. T.; Rutledge, G. C.; Hatton, T. A., Energetically efficient electrochemically tunable affinity separation using multicomponent polymeric nanostructures for water treatment. *Energy & Environmental Science* **2018**, *11* (10), 2954-2963.
42. Su, X.; Bromberg, L.; Tan, K.-J.; Jamison, T. F.; Padhye, L. P.; Hatton, T. A., Electrochemically Mediated Reduction of Nitrosamines by Hemin-Functionalized Redox Electrodes. *Environmental Science & Technology Letters* **2017**, *4* (4), 161-167.

43. Kim, S.; Piao, G.; Han, D. S.; Shon, H. K.; Park, H., Solar desalination coupled with water remediation and molecular hydrogen production: a novel solar water-energy nexus. *Energy & Environmental Science* **2018**, *11* (2), 344-353.
44. Ji, W.; Xiao, L.; Ling, Y.; Ching, C.; Matsumoto, M.; Bisbey, R. P.; Helbling, D. E.; Dichtel, W. R., Removal of GenX and Perfluorinated Alkyl Substances from Water by Amine-Functionalized Covalent Organic Frameworks. *J Am Chem Soc* **2018**, *140* (40), 12677-12681.
45. Klemes, M. J.; Ling, Y.; Ching, C.; Wu, C.; Xiao, L.; Helbling, D. E.; Dichtel, W. R., Reduction of a Tetrafluoroterephthalonitrile-beta-Cyclodextrin Polymer to Remove Anionic Micropollutants and Perfluorinated Alkyl Substances from Water. *Angew Chem Int Ed Engl* **2019**, *58* (35), 12049-12053.
46. Niu, Z.; Wang, Y.; Lin, H.; Jin, F.; Li, Y.; Niu, J., Electrochemically enhanced removal of perfluorinated compounds (PFCs) from aqueous solution by CNTs-graphene composite electrode. *Chemical Engineering Journal* **2017**, *328*, 228-235.
47. Zhang, D. Q.; Zhang, W. L.; Liang, Y. N., Adsorption of perfluoroalkyl and polyfluoroalkyl substances (PFASs) from aqueous solution - A review. *Sci Total Environ* **2019**, *694*, 133606.
48. Carter, K. E.; Farrell, J., Oxidative Destruction of Perfluorooctane Sulfonate Using Boron-Doped Diamond Film Electrodes. *Environmental Science & Technology* **2008**, *42* (16), 6111-6115.
49. Rostro, L.; Wong, S. H.; Boudouris, B. W., Solid State Electrical Conductivity of Radical Polymers as a Function of Pendant Group Oxidation State. *Macromolecules* **2014**, *47* (11), 3713-3719.
50. Zhang, K.; Hu, Y.; Wang, L.; Fan, J.; Monteiro, M. J.; Jia, Z., The impact of the molecular weight on the electrochemical properties of poly(TEMPO methacrylate). *Polymer Chemistry* **2017**, *8* (11), 1815-1823.
51. Chinelatto, M. A.; Agnelli, J. A. M.; Canevarolo, S. V., Synthesis and Characterization of Copolymers from Hindered Amines and Vinyl Monomers. *Polímeros Ciência e Tecnologia* **2014**, *24* (1), 30-36.
52. Hung, M.-K.; Wang, Y.-H.; Lin, C.-H.; Lin, H.-C.; Lee, J.-T., Synthesis and electrochemical behaviour of nitroxidepolymer brush thin-film electrodes for organic radical batteries. *J. Mater. Chem.* **2012**, *22* (4), 1570-1577.
53. Su, X.; Hatton, T. A., Redox-electrodes for selective electrochemical separations. *Adv Colloid Interface Sci* **2017**, *244*, 6-20.
54. Wang, S.; Li, F.; Easley, A. D.; Lutkenhaus, J. L., Real-time insight into the doping mechanism of redox-active organic radical polymers. *Nat Mater* **2019**, *18* (1), 69-75.
55. Yu, Q.; Zhang, R.; Deng, S.; Huang, J.; Yu, G., Sorption of perfluorooctane sulfonate and perfluorooctanoate on activated carbons and resin: Kinetic and isotherm study. *Water Res* **2009**, *43* (4), 1150-8.
56. Li, X.; Chen, S.; Quan, X.; Zhang, Y., Enhanced adsorption of PFOA and PFOS on multiwalled carbon nanotubes under electrochemical assistance. *Environ Sci Technol* **2011**, *45* (19), 8498-505.
57. Ateia, M.; Attia, M. F.; Maroli, A.; Tharayil, N.; Alexis, F.; Whitehead, D. C.; Karanfil, T., Rapid Removal of Poly- and Perfluorinated Alkyl Substances by Poly(ethylenimine)-Functionalized Cellulose Microcrystals at Environmentally Relevant Conditions. *Environmental Science & Technology Letters* **2018**, *5* (12), 764-769.

58. Du, Z.; Deng, S.; Bei, Y.; Huang, Q.; Wang, B.; Huang, J.; Yu, G., Adsorption behavior and mechanism of perfluorinated compounds on various adsorbents--a review. *J Hazard Mater* **2014**, 274, 443-54.
59. Liu, K.; Zhang, S.; Hu, X.; Zhang, K.; Roy, A.; Yu, G., Understanding the Adsorption of PFOA on MIL-101(Cr)-Based Anionic-Exchange Metal-Organic Frameworks: Comparing DFT Calculations with Aqueous Sorption Experiments. *Environ Sci Technol* **2015**, 49 (14), 8657-65.
60. Deng, S.; Zheng, Y. Q.; Xu, F. J.; Wang, B.; Huang, J.; Yu, G., Highly efficient sorption of perfluorooctane sulfonate and perfluorooctanoate on a quaternized cotton prepared by atom transfer radical polymerization. *Chemical Engineering Journal* **2012**, 193-194, 154-160.
61. Bentel, M. J.; Yu, Y.; Xu, L.; Kwon, H.; Li, Z.; Wong, B. M.; Men, Y.; Liu, J., Degradation of Perfluoroalkyl Ether Carboxylic Acids with Hydrated Electrons: Structure-Reactivity Relationships and Environmental Implications. *Environ Sci Technol* **2020**, 54 (4), 2489-2499.
62. Bentel, M. J.; Yu, Y.; Xu, L.; Li, Z.; Wong, B. M.; Men, Y.; Liu, J., Defluorination of Per- and Polyfluoroalkyl Substances (PFASs) with Hydrated Electrons: Structural Dependence and Implications to PFAS Remediation and Management. *Environ Sci Technol* **2019**, 53 (7), 3718-3728.
63. Zhuo, Q.; Deng, S.; Yang, B.; Huang, J.; Wang, B.; Zhang, T.; Yu, G., Degradation of perfluorinated compounds on a boron-doped diamond electrode. *Electrochimica Acta* **2012**, 77, 17-22.
64. Gomez-Ruiz, B.; Gómez-Lavín, S.; Diban, N.; Boiteux, V.; Colin, A.; Dauchy, X.; Urtiaga, A., Efficient electrochemical degradation of poly- and perfluoroalkyl substances (PFASs) from the effluents of an industrial wastewater treatment plant. *Chemical Engineering Journal* **2017**, 322, 196-204.
65. Juang, Y.; Nurhayati, E.; Huang, C.; Pan, J. R.; Huang, S., A hybrid electrochemical advanced oxidation/microfiltration system using BDD/Ti anode for acid yellow 36 dye wastewater treatment. *Separation and Purification Technology* **2013**, 120, 289-295.
66. Schaefer, C. E.; Andaya, C.; Burant, A.; Condee, C. W.; Urtiaga, A.; Strathmann, T. J.; Higgins, C. P., Electrochemical treatment of perfluorooctanoic acid and perfluorooctane sulfonate: Insights into mechanisms and application to groundwater treatment. *Chemical Engineering Journal* **2017**, 317, 424-432.
67. Zhuo, Q.; Deng, S.; Yang, B.; Huang, J.; Yu, G., Efficient electrochemical oxidation of perfluorooctanoate using a Ti/SnO₂-Sb-Bi anode. *Environ Sci Technol* **2011**, 45 (7), 2973-9.
68. Le, T. X. H.; Haflich, H.; Shah, A. D.; Chaplin, B. P., Energy-Efficient Electrochemical Oxidation of Perfluoroalkyl Substances Using a Ti₄O₇ Reactive Electrochemical Membrane Anode. *Environmental Science & Technology Letters* **2019**, 6 (8), 504-510.
69. Schaefer, C. E.; Andaya, C.; Urtiaga, A.; McKenzie, E. R.; Higgins, C. P., Electrochemical treatment of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) in groundwater impacted by aqueous film forming foams (AFFFs). *J Hazard Mater* **2015**, 295, 170-5.
70. Yang, B.; Jiang, C.; Yu, G.; Zhuo, Q.; Deng, S.; Wu, J.; Zhang, H., Highly efficient electrochemical degradation of perfluorooctanoic acid (PFOA) by F-doped Ti/SnO₂ electrode. *J Hazard Mater* **2015**, 299, 417-24.

71. Ma, Q.; Liu, L.; Cui, W.; Li, R.; Song, T.; Cui, Z., Electrochemical degradation of perfluorooctanoic acid (PFOA) by Yb-doped Ti/SnO₂-Sb/PbO₂ anodes and determination of the optimal conditions. *RSC Advances* **2015**, 5 (103), 84856-84864.
72. Lin, H.; Niu, J.; Ding, S.; Zhang, L., Electrochemical degradation of perfluorooctanoic acid (PFOA) by Ti/SnO₂-Sb, Ti/SnO₂-Sb/PbO₂ and Ti/SnO₂-Sb/MnO₂ anodes. *Water Res* **2012**, 46 (7), 2281-9.
73. Niu, J.; Lin, H.; Xu, J.; Wu, H.; Li, Y., Electrochemical mineralization of perfluorocarboxylic acids (PFCAs) by Ce-doped modified porous nanocrystalline PbO₂ film electrode. *Environ Sci Technol* **2012**, 46 (18), 10191-8.
74. Hu, Y. B.; Lo, S. L.; Li, Y. F.; Lee, Y. C.; Chen, M. J.; Lin, J. C., Autocatalytic degradation of perfluorooctanoic acid in a permanganate-ultrasonic system. *Water Res* **2018**, 140, 148-157.
75. Xu, Z.; Yu, Y.; Liu, H.; Niu, J., Highly efficient and stable Zr-doped nanocrystalline PbO₂ electrode for mineralization of perfluorooctanoic acid in a sequential treatment system. *Sci Total Environ* **2017**, 579, 1600-1607.
76. Hu, X. C.; Andrews, D. Q.; Lindstrom, A. B.; Bruton, T. A.; Schaidler, L. A.; Grandjean, P.; Lohmann, R.; Carignan, C. C.; Blum, A.; Balan, S. A.; Higgins, C. P.; Sunderland, E. M., Detection of Poly- and Perfluoroalkyl Substances (PFASs) in U.S. Drinking Water Linked to Industrial Sites, Military Fire Training Areas, and Wastewater Treatment Plants. *Environmental Science & Technology Letters* **2016**, 3 (10), 344-350.
77. Anderson, R. H.; Long, G. C.; Porter, R. C.; Anderson, J. K., Occurrence of select perfluoroalkyl substances at U.S. Air Force aqueous film-forming foam release sites other than fire-training areas: Field-validation of critical fate and transport properties. *Chemosphere* **2016**, 150, 678-685.
78. Pitter, G.; Da Re, F.; Canova, C.; Barbieri, G.; Zare Jeddi, M.; Daprà, F.; Manea, F.; Zolin, R.; Bettega Anna, M.; Stopazzolo, G.; Vittorii, S.; Zambelli, L.; Martuzzi, M.; Mantoan, D.; Russo, F., Serum Levels of Perfluoroalkyl Substances (PFAS) in Adolescents and Young Adults Exposed to Contaminated Drinking Water in the Veneto Region, Italy: A Cross-Sectional Study Based on a Health Surveillance Program. *Environmental Health Perspectives* **2016**, 124 (2), 027007.
79. Post, G. B., Recent US State and Federal Drinking Water Guidelines for Per- and Polyfluoroalkyl Substances. *Environmental Toxicology and Chemistry* **2021**, 40 (3), 550-563.
80. Goodrow, S. M.; Ruppel, B.; Lippincott, R. L.; Post, G. B.; Procopio, N. A., Investigation of levels of perfluoroalkyl substances in surface water, sediment and fish tissue in New Jersey, USA. *Science of The Total Environment* **2020**, 729, 138839.
81. Bai, X.; Son, Y., Perfluoroalkyl substances (PFAS) in surface water and sediments from two urban watersheds in Nevada, USA. *Science of The Total Environment* **2021**, 751, 141622.
82. Schwichtenberg, T.; Bogdan, D.; Carignan, C. C.; Reardon, P.; Rewerts, J.; Wanzek, T.; Field, J. A., PFAS and Dissolved Organic Carbon Enrichment in Surface Water Foams on a Northern U.S. Freshwater Lake. *Environ Sci Technol* **2020**, 54 (22), 14455-14464.
83. Hepburn, E.; Madden, C.; Szabo, D.; Coggan, T. L.; Clarke, B.; Currell, M., Contamination of groundwater with per- and polyfluoroalkyl substances (PFAS) from legacy landfills in an urban re-development precinct. *Environmental Pollution* **2019**, 248, 101-113.
84. Yeung, L. W. Y.; Mabury, S. A., Are humans exposed to increasing amounts of unidentified organofluorine? *Environmental Chemistry* **2016**, 13 (1), 102-110.

85. Glynn, A.; Berger, U.; Bignert, A.; Ullah, S.; Aune, M.; Lignell, S.; Darnerud, P. O., Perfluorinated Alkyl Acids in Blood Serum from Primiparous Women in Sweden: Serial Sampling during Pregnancy and Nursing, And Temporal Trends 1996–2010. *Environ Sci Technol* **2012**, 46 (16), 9071-9079.
86. Pike, K. A.; Edmiston, P. L.; Morrison, J. J.; Faust, J. A., Correlation Analysis of Perfluoroalkyl Substances in Regional U.S. Precipitation Events. *Water Research* **2021**, 190, 116685.
87. Quiñones, O.; Snyder, S. A., Occurrence of Perfluoroalkyl Carboxylates and Sulfonates in Drinking Water Utilities and Related Waters from the United States. *Environ Sci Technol* **2009**, 43 (24), 9089-9095.
88. Lindstrom, A. B.; Strynar, M. J.; Libelo, E. L., Polyfluorinated Compounds: Past, Present, and Future. *Environ Sci Technol* **2011**, 45 (19), 7954-7961.
89. Lifetime Health Advisories and Health Effects Support Documents for Perfluorooctanoic Acid and Perfluorooctane Sulfonate. <https://www.epa.gov/ground-water-and-drinking-water/supporting-documents-drinking-water-health-advisories-pfoa-and-pfos>.
90. Sun, M.; Arevalo, E.; Strynar, M.; Lindstrom, A.; Richardson, M.; Kearns, B.; Pickett, A.; Smith, C.; Knappe, D. R. U., Legacy and Emerging Perfluoroalkyl Substances Are Important Drinking Water Contaminants in the Cape Fear River Watershed of North Carolina. *Environmental Science & Technology Letters* **2016**, 3 (12), 415-419.
91. Ateia, M.; Maroli, A.; Tharayil, N.; Karanfil, T., The overlooked short- and ultrashort-chain poly- and perfluorinated substances: A review. *Chemosphere* **2019**, 220, 866-882.
92. Brendel, S.; Fetter, É.; Staude, C.; Vierke, L.; Biegel-Engler, A., Short-chain perfluoroalkyl acids: environmental concerns and a regulatory strategy under REACH. *Environmental Sciences Europe* **2018**, 30 (1), 9.
93. J, K.; Jensen, A.; M, W., *Short-chain Polyfluoroalkyl Substances (PFAS). A literature review of information on human health effects and environmental fate and effect aspects of short-chain PFAS*. 2015.
94. Zhou, Z.; Liang, Y.; Shi, Y.; Xu, L.; Cai, Y., Occurrence and Transport of Perfluoroalkyl Acids (PFAAs), Including Short-Chain PFAAs in Tangxun Lake, China. *Environ Sci Technol* **2013**, 47 (16), 9249-9257.
95. Gannon, S. A.; Fasano, W. J.; Mawn, M. P.; Nabb, D. L.; Buck, R. C.; Buxton, L. W.; Jepson, G. W.; Frame, S. R., Absorption, distribution, metabolism, excretion, and kinetics of 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoic acid ammonium salt following a single dose in rat, mouse, and cynomolgus monkey. *Toxicology* **2016**, 340, 1-9.
96. Li, F.; Duan, J.; Tian, S.; Ji, H.; Zhu, Y.; Wei, Z.; Zhao, D., Short-chain per- and polyfluoroalkyl substances in aquatic systems: Occurrence, impacts and treatment. *Chemical Engineering Journal* **2020**, 380, 122506.
97. Harfmann, J. L.; Tito, K.; Kieber, R. J.; Avery, G. B.; Mead, R. N.; Shimizu, M. S.; Skrabal, S. A., Sorption of Hexafluoropropylene Oxide Dimer Acid to Sediments: Biogeochemical Implications and Analytical Considerations. *ACS Earth and Space Chemistry* **2021**, 5 (3), 580-587.
98. Wang, W.; Maimaiti, A.; Shi, H.; Wu, R.; Wang, R.; Li, Z.; Qi, D.; Yu, G.; Deng, S., Adsorption behavior and mechanism of emerging perfluoro-2-propoxypropanoic acid (GenX) on activated carbons and resins. *Chemical Engineering Journal* **2019**, 364, 132-138.

99. Guo, D.; Shi, Q.; He, B.; Yuan, X., Different solvents for the regeneration of the exhausted activated carbon used in the treatment of coking wastewater. *Journal of Hazardous Materials* **2011**, 186 (2), 1788-1793.
100. Kim, Y.; Kim, K.; Eom, H. H.; Su, X.; Lee, J. W., Electrochemically-assisted removal of cadmium ions by redox active Cu-based metal-organic framework. *Chemical Engineering Journal* **2021**, 421, 129765.
101. Kim, K.; Baldaguez Medina, P.; Elbert, J.; Kayiwa, E.; Cusick, R. D.; Men, Y.; Su, X., Molecular Tuning of Redox-Copolymers for Selective Electrochemical Remediation. *Advanced Functional Materials* **2020**, 2004635.
102. Ji, W.; Xiao, L.; Ling, Y.; Ching, C.; Matsumoto, M.; Bisbey, R. P.; Helbling, D. E.; Dichtel, W. R., Removal of GenX and Perfluorinated Alkyl Substances from Water by Amine-Functionalized Covalent Organic Frameworks. *Journal of the American Chemical Society* **2018**, 140 (40), 12677-12681.
103. Zhukova, I. Y.; Papina, E. N.; Tyaglivaya, I. N., Prospects of Wasteless Technologies of Selective Alcohols Oxidation. *IOP Conference Series: Earth and Environmental Science* **2020**, 459, 032011.
104. Kim, K.; Cotty, S.; Elbert, J.; Chen, R.; Hou, C.-H.; Su, X., Asymmetric Redox-Polymer Interfaces for Electrochemical Reactive Separations: Synergistic Capture and Conversion of Arsenic. *Advanced Materials* **2020**, 32 (6), 1906877.
105. Survey, U. S. G. Saline Water and Salinity. https://www.usgs.gov/special-topic/water-science-school/science/saline-water-and-salinity?qt-science_center_objects=0#qt-science_center_objects.
106. Hoffman, K.; Webster Thomas, F.; Bartell Scott, M.; Weisskopf Marc, G.; Fletcher, T.; Vieira Verónica, M., Private Drinking Water Wells as a Source of Exposure to Perfluorooctanoic Acid (PFOA) in Communities Surrounding a Fluoropolymer Production Facility. *Environmental Health Perspectives* **2011**, 119 (1), 92-97.
107. Horst, J.; McDonough, J.; Ross, I.; Houtz, E., Understanding and Managing the Potential By-Products of PFAS Destruction. *Groundwater Monitoring & Remediation* **2020**, 40 (2), 17-27.
108. Pierpaoli, M.; Szopińska, M.; Wilk, B. K.; Sobaszek, M.; Łuczkiwicz, A.; Bogdanowicz, R.; Fudala-Książek, S., Electrochemical oxidation of PFOA and PFOS in landfill leachates at low and highly boron-doped diamond electrodes. *Journal of Hazardous Materials* **2021**, 403, 123606.
109. Soriano, Á.; Gorri, D.; Biegler, L. T.; Urtiaga, A., An optimization model for the treatment of perfluorocarboxylic acids considering membrane preconcentration and BDD electrooxidation. *Water Research* **2019**, 164, 114954.
110. Lin, H.; Niu, J.; Xu, J.; Huang, H.; Li, D.; Yue, Z.; Feng, C., Highly Efficient and Mild Electrochemical Mineralization of Long-Chain Perfluorocarboxylic Acids (C9–C10) by Ti/SnO₂–Sb–Ce, Ti/SnO₂–Sb/Ce–PbO₂, and Ti/BDD Electrodes. *Environ Sci Technol* **2013**, 47 (22), 13039-13046.
111. Panizza, M., Importance of Electrode Material in the Electrochemical Treatment of Wastewater Containing Organic Pollutants. In *Electrochemistry for the Environment*, Comninellis, C.; Chen, G., Eds. Springer New York: New York, NY, 2010; pp 25-54.
112. Chen, R.; Huang, X.; Li, G.; Yu, Y.; Shi, B., Performance of in-service granular activated carbon for perfluoroalkyl substances removal under changing water quality conditions. *Science of the Total Environment* **2022**, 848.

113. Son, H.; Kim, T.; Yoom, H. S.; Zhao, D.; An, B., The Adsorption Selectivity of Short and Long Per- and Polyfluoroalkyl Substances (PFASs) from Surface Water Using Powder-Activated Carbon. *Water (Switzerland)* **2020**, *12* (11), 3287.
114. Militao, I. M.; Roddick, F. A.; Bergamasco, R.; Fan, L., Removing PFAS from aquatic systems using natural and renewable material-based adsorbents: A review. *Journal of Environmental Chemical Engineering* **2021**, *9* (4), 105271.
115. Pauletto, P. S.; Bandosz, T. J., Activated carbon versus metal-organic frameworks: A review of their PFAS adsorption performance. *Journal of Hazardous Materials* **2022**, *425*, 127810.
116. Leung, S. C. E.; Shukla, P.; Chen, D.; Eftekhari, E.; An, H.; Zare, F.; Ghasemi, N.; Zhang, D.; Nguyen, N.-T.; Li, Q., Emerging technologies for PFOS/PFOA degradation and removal: A review. *Science of The Total Environment* **2022**, *827*, 153669.
117. Alkhadra, M. A.; Su, X.; Suss, M. E.; Tian, H.; Guyes, E. N.; Shocron, A. N.; Conforti, K. M.; de Souza, J. P.; Kim, N.; Tedesco, M.; Khoiruddin, K.; Wenten, I. G.; Santiago, J. G.; Hatton, T. A.; Bazant, M. Z., Electrochemical Methods for Water Purification, Ion Separations, and Energy Conversion. *Chemical Reviews* **2022**, *122* (16), 13547-13635.
118. Srimuk, P.; Su, X.; Yoon, J.; Aurbach, D.; Presser, V., Charge-transfer materials for electrochemical water desalination, ion separation and the recovery of elements. *Nature Reviews Materials* **2020**, *5* (7), 517-538.
119. Kumar, A.; Kim, Y.; Su, X.; Fukuda, H.; Naidu, G.; Du, F.; Vigneswaran, S.; Drioli, E.; Hatton, T. A.; Lienhard, J. H., Advances and challenges in metal ion separation from water. *Trends in Chemistry* **2021**, *3* (10), 819-831.
120. Kim, N.; Jeon, J.; Chen, R.; Su, X., Electrochemical separation of organic acids and proteins for food and biomanufacturing. *Chemical Engineering Research and Design* **2022**, *178*, 267-288.
121. Kim, K.; Raymond, D.; Candeago, R.; Su, X., Selective cobalt and nickel electrodeposition for lithium-ion battery recycling through integrated electrolyte and interface control. *Nature Communications* **2021**, *12* (1), 6554.
122. Kim, K.; Candeago, R.; Rim, G.; Raymond, D.; Park, A.-H. A.; Su, X., Electrochemical approaches for selective recovery of critical elements in hydrometallurgical processes of complex feedstocks. *iScience* **2021**, *24* (5), 102374.
123. Kim, N.; Jeon, J.; Elbert, J.; Kim, C.; Su, X., Redox-mediated electrochemical desalination for waste valorization in dairy production. *Chemical Engineering Journal* **2022**, *428*, 131082.
124. Su, X., Electrochemical interfaces for chemical and biomolecular separations. *Current Opinion in Colloid & Interface Science* **2020**, *46*, 77-93.
125. Eloi, J.-C.; Chabanne, L.; Whittell, G. R.; Manners, I., Metallopolymers with emerging applications. *Materials Today* **2008**, *11* (4), 28-36.
126. Hübner, H.; Candeago, R.; Schmitt, D.; Schießer, A.; Xiong, B.; Gallei, M.; Su, X., Synthesis and covalent immobilization of redox-active metallopolymers for organic phase electrochemistry. *Polymer* **2022**, *244*, 124656.
127. Xiang, J.; Ho, C.-L.; Wong, W.-Y., Metallopolymers for energy production, storage and conservation. *Polymer Chemistry* **2015**, *6* (39), 6905-6930.
128. Vapnik, H.; Elbert, J.; Su, X., Redox-copolymers for the recovery of rare earth elements by electrochemically regenerated ion-exchange. *Journal of Materials Chemistry A* **2021**, *9* (35), 20068-20077.

129. Chen, R.; Feng, J.; Jeon, J.; Sheehan, T.; Rüttiger, C.; Gallei, M.; Shukla, D.; Su, X., Structure and Potential-Dependent Selectivity in Redox-Metallopolymers: Electrochemically Mediated Multicomponent Metal Separations. *Advanced Functional Materials* **2021**, *31* (15), 2009307.
130. Huang, Y.; Feng, W.; Zhou, Z.; Zheng, H.; Zhao, Y.; Yan, H.; Lü, X., Tetraphenylethylene-based Eu³⁺-metallopolymers with aggregation-enhanced white emission for self-calibrating temperature sensing and white light-emitting diodes (WLEDs). *Journal of Materials Chemistry C* **2022**, *10* (19), 7586-7593.
131. Liu, S.; Zhang, K.; Lu, J.; Zhang, J.; Yip, H.-L.; Huang, F.; Cao, Y., High-Efficiency Polymer Solar Cells via the Incorporation of an Amino-Functionalized Conjugated Metallopolymer as a Cathode Interlayer. *Journal of the American Chemical Society* **2013**, *135* (41), 15326-15329.
132. Verma, A.; Chaudhary, P.; Tripathi, R. K.; Singh, A.; Yadav, B. C., State of the Art Metallopolymer Based Functional Nanomaterial for Photodetector and Solar Cell Application. *Journal of Inorganic and Organometallic Polymers and Materials* **2022**, 2807–2826.
133. Elbert, J.; Mersini, J.; Vilbrandt, N.; Lederle, C.; Kraska, M.; Gallei, M.; Stühn, B.; Plenio, H.; Rehahn, M., Reversible Activity Modulation of Surface-Attached Grubbs Second Generation Type Catalysts Using Redox-Responsive Polymers. *Macromolecules* **2013**, *46* (11), 4255-4267.
134. Winter, T.; Su, X.; Hatton, T. A.; Gallei, M., Ferrocene-Containing Inverse Opals by Melt-Shear Organization of Core/Shell Particles. *Macromolecular Rapid Communications* **2018**, *39* (22), 1800428.
135. Cotty, S.; Jeon, J.; Elbert, J.; Jeyaraj, V. S.; Mironenko, A. V.; Su, X., Electrochemical recycling of homogeneous catalysts. *Science Advances* **2022**, *8* (42), eade3094.
136. Gallei, M.; Rüttiger, C., Recent Trends in Metallopolymer Design: Redox-Controlled Surfaces, Porous Membranes, and Switchable Optical Materials Using Ferrocene-Containing Polymers. *Chemistry – A European Journal* **2018**, *24* (40), 10006-10021.
137. Elbert, J.; Gallei, M.; Rüttiger, C.; Brunsen, A.; Didzoleit, H.; Stühn, B.; Rehahn, M., Ferrocene Polymers for Switchable Surface Wettability. *Organometallics* **2013**, *32* (20), 5873-5878.
138. Abbott, N. L. W., G. M, Potential-Dependent Wetting of Aqueous Solutions on Self-Assembled Monolayers Formed from 15-(Ferrocenylcarbonyl)pentadecanethiol on Gold. *Langmuir* **1994**, *10*, 1493-1497.
139. Baker, D. A.; East, G. C.; Mukhopadhyay, S. K., Synthesis and characterization of some disulfonyl azides as potential crosslinking agents for textile fibers. *Journal of Applied Polymer Science* **2001**, *79* (6), 1092-1100.
140. Kim, B. Y.; Ratcliff, E. L.; Armstrong, N. R.; Kowalewski, T.; Pyun, J., Ferrocene Functional Polymer Brushes on Indium Tin Oxide via Surface-Initiated Atom Transfer Radical Polymerization. *Langmuir* **2010**, *26* (3), 2083-2092.
141. Gallei, M.; Schmidt, B. V. K. J.; Klein, R.; Rehahn, M., Defined Poly[styrene-block-(ferrocenylmethyl methacrylate)] Diblock Copolymers via Living Anionic Polymerization. *Macromolecular Rapid Communications* **2009**, *30* (17), 1463-1469.
142. Sheats, J. E.; Rausch, M. D., Synthesis and properties of cobalticinium salts. I. Synthesis of monosubstituted cobalticinium salts. *The Journal of Organic Chemistry* **1970**, *35* (10), 3245-3249.

143. Vanicek, S.; Kopacka, H.; Wurst, K.; Müller, T.; Schottenberger, H.; Bildstein, B., Chemoselective, Practical Synthesis of Cobaltocenium Carboxylic Acid Hexafluorophosphate. *Organometallics* **2014**, 33 (5), 1152-1156.
144. Ren, L.; Hardy, C. G.; Tang, S.; Doxie, D. B.; Hamidi, N.; Tang, C., Preparation of Side-Chain 18-e Cobaltocenium-Containing Acrylate Monomers and Polymers. *Macromolecules* **2010**, 43 (22), 9304-9310.
145. Su, X.; Tan, K. J.; Elbert, J.; Ruttiger, C.; Gallei, M.; Jamison, T. F.; Hatton, T. A., Asymmetric Faradaic systems for selective electrochemical separations. *Energy & Environmental Science* **2017**, 10 (5), 1272-1283.
146. Zhang, J.; Ren, L.; Hardy, C. G.; Tang, C., Cobaltocenium-Containing Methacrylate Homopolymers, Block Copolymers, and Heterobimetallic Polymers via RAFT Polymerization. *Macromolecules* **2012**, 45 (17), 6857-6863.
147. Fabbrizzi, L., The ferrocenium/ferrocene couple: a versatile redox switch. *ChemTexts* **2020**, 6 (4), 22.
148. Wang, Y.; Mendoza, S.; Kaifer, A. E., Electrochemical Reduction of Cobaltocenium in the Presence of β -Cyclodextrin. *Inorganic Chemistry* **1998**, 37 (2), 317-320.
149. Hultgren, V. M.; Mariotti, A. W. A.; Bond, A. M.; Wedd, A. G., Reference Potential Calibration and Voltammetry at Macrodisk Electrodes of Metallocene Derivatives in the Ionic Liquid [bmim][PF₆]. *Analytical Chemistry* **2002**, 74 (13), 3151-3156.
150. Emília, M.; Silva, N. P. R. A.; Pombeiro, A. J. L.; da Silva, J. J. R. F.; Herrmann, R.; Deus, N.; Castilho, T. J.; Silva, M. F. C. G., Redox potential and substituent effects at ferrocene derivatives. Estimates of Hammett σ_p and Taft polar σ substituent constants. *Journal of Organometallic Chemistry* **1991**, 421 (1), 75-90.
151. Shiddiky, M. J. A.; Torriero, A. A. J.; Zhao, C.; Burgar, I.; Kennedy, G.; Bond, A. M., Nonadditivity of Faradaic Currents and Modification of Capacitance Currents in the Voltammetry of Mixtures of Ferrocene and the Cobaltocenium Cation in Protic and Aprotic Ionic Liquids. *Journal of the American Chemical Society* **2009**, 131 (23), 7976-7989.
152. Lobach, A. S.; Strelets, V. V., Relationship between reduction potentials and electron affinities of fullerenes and their derivatives. *Russian Chemical Bulletin* **2001**, 50 (9), 1593-1595.
153. Artz, K.; Williams, J. C.; Allen, J. P.; Lendzian, F.; Rautter, J.; Lubitz, W., Relationship between the oxidation potential and electron spin density of the primary electron donor in reaction centers from Rhodospirillum rubrum. *Proceedings of the National Academy of Sciences* **1997**, 94 (25), 13582-13587.
154. Jirimali, H. D.; Nagarale, R. K.; Saravanakumar, D.; Shin, W., Ferrocene Tethered Polyvinyl Alcohol/Silica Film Electrode for Electrocatalytic Sulfite Sensing. *Electroanalysis* **2018**, 30 (5), 828-833.
155. Barth, A., Infrared spectroscopy of proteins. *Biochimica et Biophysica Acta (BBA) - Bioenergetics* **2007**, 1767 (9), 1073-1101.
156. Woodbridge, C. M.; Pugmire, D. L.; Johnson, R. C.; Boag, N. M.; Langell, M. A., HREELS and XPS Studies of Ferrocene on Ag(100). *The Journal of Physical Chemistry B* **2000**, 104 (14), 3085-3093.
157. Fischer, A. B.; Wrighton, M. S.; Umana, M.; Murray, R. W., An x-ray photoelectron spectroscopic study of multilayers of an electroactive ferrocene derivative attached to platinum and gold electrodes. *Journal of the American Chemical Society* **1979**, 101 (13), 3442-3446.

158. Román Santiago, A.; Yin, S.; Elbert, J.; Lee, J.; Shukla, D.; Su, X., Imparting Selective Fluorophilic Interactions in Redox Copolymers for the Electrochemically Mediated Capture of Short-Chain Perfluoroalkyl Substances. *Journal of the American Chemical Society* **2023**.
159. Clark, R. A.; Bowden, E. F., Voltammetric Peak Broadening for Cytochrome c/Alkanethiolate Monolayer Structures: Dispersion of Formal Potentials. *Langmuir* **1997**, *13* (3), 559-565.
160. Levi, M. D.; Levy, N.; Sigalov, S.; Salitra, G.; Aurbach, D.; Maier, J., Electrochemical Quartz Crystal Microbalance (EQCM) Studies of Ions and Solvents Insertion into Highly Porous Activated Carbons. *Journal of the American Chemical Society* **2010**, *132* (38), 13220-13222.
161. Tsai, W.-Y.; Taberna, P.-L.; Simon, P., Electrochemical Quartz Crystal Microbalance (EQCM) Study of Ion Dynamics in Nanoporous Carbons. *Journal of the American Chemical Society* **2014**, *136* (24), 8722-8728.
162. Sauerbrey, G., Verwendung von Schwingquarzen zur Wägung dünner Schichten und zur Mikrowägung. *Zeitschrift für Physik* **1959**, *155* (2), 206-222.
163. Auer, A.; Ding, X.; Bandarenka, A. S.; Kunze-Liebhäuser, J., The Potential of Zero Charge and the Electrochemical Interface Structure of Cu(111) in Alkaline Solutions. *The Journal of Physical Chemistry C* **2021**, *125* (9), 5020-5028.
164. Survey, U. S. G. Saline Water and Salinity. https://www.usgs.gov/special-topics/water-science-school/science/saline-water-and-salinity?qt-science_center_objects=0#qt-science_center_objects (accessed 01/31/2023).
165. Lein, N. P. H.; Fujii, S.; Tanaka, S.; Nozoe, M.; Tanaka, H., Contamination of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) in surface water of the Yodo River basin (Japan). *Desalination* **2008**, *226* (1), 338-347.
166. Zareitalabad, P.; Siemens, J.; Hamer, M.; Amelung, W., Perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) in surface waters, sediments, soils and wastewater – A review on concentrations and distribution coefficients. *Chemosphere* **2013**, *91* (6), 725-732.
167. Exner, M.; Färber, H., Perfluorinated Surfactants in Surface and Drinking Waters (9 pp). *Environmental Science and Pollution Research* **2006**, *13* (5), 299-307.
168. Bao, J.; Yu, W.-J.; Liu, Y.; Wang, X.; Jin, Y.-H.; Dong, G.-H., Perfluoroalkyl substances in groundwater and home-produced vegetables and eggs around a fluorochemical industrial park in China. *Ecotoxicology and Environmental Safety* **2019**, *171*, 199-205.
169. Xu, B.; Liu, S.; Zhou, J. L.; Zheng, C.; Weifeng, J.; Chen, B.; Zhang, T.; Qiu, W., PFAS and their substitutes in groundwater: Occurrence, transformation and remediation. *Journal of Hazardous Materials* **2021**, *412*, 125159.
170. Üner, N. B.; Baldaguez Medina, P.; Dinari, J. L.; Su, X.; Sankaran, R. M., Rate, Efficiency, and Mechanisms of Electrochemical Perfluorooctanoic Acid Degradation with Boron-Doped Diamond and Plasma Electrodes. *Langmuir* **2022**, *38* (29), 8975-8986.
171. Ehsan, M. N.; Riza, M.; Pervez, M. N.; Khyum, M. M. O.; Liang, Y.; Naddeo, V., Environmental and health impacts of PFAS: Sources, distribution and sustainable management in North Carolina (USA). *Science of The Total Environment* **2023**, *878*, 163123.
172. Veciana, M.; Bräunig, J.; Farhat, A.; Pype, M.-L.; Freguia, S.; Carvalho, G.; Keller, J.; Ledezma, P., Electrochemical oxidation processes for PFAS removal from contaminated water and wastewater: fundamentals, gaps and opportunities towards practical implementation. *Journal of Hazardous Materials* **2022**, *434*, 128886.
173. Murray, C. C.; Vatankhah, H.; McDonough, C. A.; Nickerson, A.; Hedtke, T. T.; Cath, T. Y.; Higgins, C. P.; Bellona, C. L., Removal of per- and polyfluoroalkyl substances

using super-fine powder activated carbon and ceramic membrane filtration. *Journal of Hazardous Materials* **2019**, 366, 160-168.

174. Woodard, S.; Berry, J.; Newman, B., Ion exchange resin for PFAS removal and pilot test comparison to GAC. *Remediation Journal* **2017**, 27 (3), 19-27.

175. Cotty, S. R.; Kim, N.; Su, X., Electrochemically Mediated Recovery and Purification of Gold for Sustainable Mining and Electronic Waste Recycling. *ACS Sustainable Chemistry & Engineering* **2023**, 11 (9), 3975-3986.

176. Shi, W.; Ma, J.; Gao, F.; Dai, R.; Su, X.; Wang, Z., Metal–Organic Framework with a Redox-Active Bridge Enables Electrochemically Highly Selective Removal of Arsenic from Water. *Environmental Science & Technology* **2023**, 57 (15), 6342-6352.

177. Tedesco, M.; Scalici, C.; Vaccari, D.; Cipollina, A.; Tamburini, A.; Micale, G., Performance of the first reverse electrodialysis pilot plant for power production from saline waters and concentrated brines. *Journal of Membrane Science* **2016**, 500, 33-45.

178. Tedesco, M.; Cipollina, A.; Tamburini, A.; Micale, G., Towards 1kW power production in a reverse electrodialysis pilot plant with saline waters and concentrated brines. *Journal of Membrane Science* **2017**, 522, 226-236.

179. Baldaguez Medina, P.; Ardila Contreras, V.; Hartmann, F.; Schmitt, D.; Klimek, A.; Elbert, J.; Gallei, M.; Su, X., Investigating the Electrochemically Driven Capture and Release of Long-Chain PFAS by Redox Metallopolymer Sorbents. *ACS Applied Materials & Interfaces* **2023**, 15 (18), 22112-22122.

180. Román Santiago, A.; Yin, S.; Elbert, J.; Lee, J.; Shukla, D.; Su, X., Imparting Selective Fluorophilic Interactions in Redox Copolymers for the Electrochemically Mediated Capture of Short-Chain Perfluoroalkyl Substances. *Journal of the American Chemical Society* **2023**, 145 (17), 9508-9519.

181. Liu, S.; Liu, Z.; Tan, W.; Johnson, A. C.; Sweetman, A. J.; Sun, X.; Liu, Y.; Chen, C.; Guo, H.; Liu, H.; Wan, X.; Zhang, L., Transport and transformation of perfluoroalkyl acids, isomer profiles, novel alternatives and unknown precursors from factories to dinner plates in China: New insights into crop bioaccumulation prediction and risk assessment. *Environment International* **2023**, 172, 107795.

182. Lämmer, R.; Weidemann, E.; Göckener, B.; Stahl, T.; Breuer, J.; Kowalczyk, J.; Just, H.; Boeddinghaus, R. S.; Gassmann, M.; Kling, H.-W.; Bücking, M., Evaluation of the Transformation and Leaching Behavior of Two Polyfluoroalkyl Phosphate Diesters in a Field Lysimeter Study. *Journal of Agricultural and Food Chemistry* **2022**, 70 (45), 14329-14338.

183. Sharma, S.; Shetti, N. P.; Basu, S.; Nadagouda, M. N.; Aminabhavi, T. M., Remediation of per- and polyfluoroalkyls (PFAS) via electrochemical methods. *Chemical Engineering Journal* **2022**, 430, 132895.

184. Sivagami, K.; Sharma, P.; Karim, A. V.; Mohanakrishna, G.; Karthika, S.; Divyapriya, G.; Saravanathamizhan, R.; Kumar, A. N., Electrochemical-based approaches for the treatment of forever chemicals: Removal of perfluoroalkyl and polyfluoroalkyl substances (PFAS) from wastewater. *Science of The Total Environment* **2023**, 861, 160440.

185. Asadi Zeidabadi, F.; Banayan Esfahani, E.; McBeath, S. T.; Dubrawski, K. L.; Mohseni, M., Electrochemical degradation of PFOA and its common alternatives: Assessment of key parameters, roles of active species, and transformation pathway. *Chemosphere* **2023**, 315, 137743.

186. Üner, N. B.; Baldaguez Medina, P.; Dinari, J. L.; Su, X.; Sankaran, R. M., Rate, Efficiency, and Mechanisms of Electrochemical Perfluorooctanoic Acid Degradation with Boron-Doped Diamond and Plasma Electrodes. *Langmuir* **2022**, *38* (29), 8975-8986.
187. Fernández, J. F.; Sánchez, C. R., Rate determining step in the absorption and desorption of hydrogen by magnesium. *Journal of Alloys and Compounds* **2002**, *340* (1), 189-198.
188. Zur Theorie der sogenannten Adsorption gelöster Stoffe. *Zeitschrift für Chemie und Industrie der Kolloide* **1907**, *2* (1), 15-15.
189. Ho, Y. S.; McKay, G., Pseudo-second order model for sorption processes. *Process Biochemistry* **1999**, *34* (5), 451-465.
190. Gallei, M.; Klein, R.; Rehahn, M., Silacyclobutane-Mediated Re-Activation of “Sleeping” Polyvinylferrocene Macro-Anions: A Powerful Access to Novel Metalloblock Copolymers. *Macromolecules* **2010**, *43* (4), 1844-1854.
191. Ma, L.; Huang, L.; Xu, Y.; Liu, C.; Wang, F.; Xing, H.; Ma, S., Dynamics and Model Research on the Electrosorption by Activated Carbon Fiber Electrodes. *Water* **2021**, *13* (1).
192. Zhao, X.; Jia, B.; Sun, Q.; Jiao, G.; Liu, L.; She, D., Removal of Cr(6+) ions from water by electrosorption on modified activated carbon fibre felt. *R Soc Open Sci* **2018**, *5* (9), 180472.
193. Lee, D.-H. R., Taegong; Shin, Junho; Kim, Young Ho; , Equilibrium and kinetic studies of an electro-assisted lithium recovery system using lithium manganese oxide adsorbent material. *Carbon letters* **2018**, *28*, 87-95.
194. Azizian, S., Kinetic models of sorption: a theoretical analysis. *Journal of Colloid and Interface Science* **2004**, *276* (1), 47-52.

Appendix A: Chapter 2 Supplementary Figures and Tables

A.1 Adsorption studies and solution analysis

Chemicals and preparation of PFAS solutions. All PFAS chemicals were obtained from Sigma-Aldrich and Santa Cruz Biotechnology. Individual PFASs were dissolved in deionized water to prepare 7.5 or 10 mM stock solution. All stock solutions were stored in refrigerator at 4 °C.

Electrochemical adsorption and desorption. A BASi VC-2 voltammetry electrochemical cell with a three-electrode configuration was used for all the electrochemical tests with Ag/AgCl as a reference electrode. To investigate the uptake capacity, isotherm, and kinetics of PFOA by P(TMA_x-co-TMPMA_{1-x})-CNT, 5 mL solutions containing appropriate amounts of PFOA and 20 mM NaCl was used, with Pt being used as a counter electrode. Appropriate potential onto P(TMA_x-co-TMPMA_{1-x})-CNT electrode was applied as needed for 0.5 or 1 h for electrosorption. Regeneration of P(TMA_x-co-TMPMA_{1-x})-CNT redox electrode was accomplished by reversing polarity and applying negative potentials (-0.5, -0.6, -1.0, -1.5 V) for 0.5 or 1 h in clean 20 mM NaCl solution. A cycling study was carried out using P(TMA₅₁-co-TMPMA₄₉)-CNT, by charging it +1.0 V in the presence of 0.1 mM PFOA and 20 mM NaCl for 30 min, followed by applying -1.0 V in clean 20 mM NaCl electrolyte for 1 h, which was then analysed for released PFOA.

Boron-doped diamond electrode was supplied from IKA (part number 0040004036) and used as received. In this proof-of-concept study, no further modification on BDD was carried out due to its already known activity toward PFOA degradation.⁶³ Its wider potential window compared to traditional platinum electrode is revealed in cyclic voltammetry (**Figure A.1**). The active electrochemical area of BDD electrode was 1 cm².

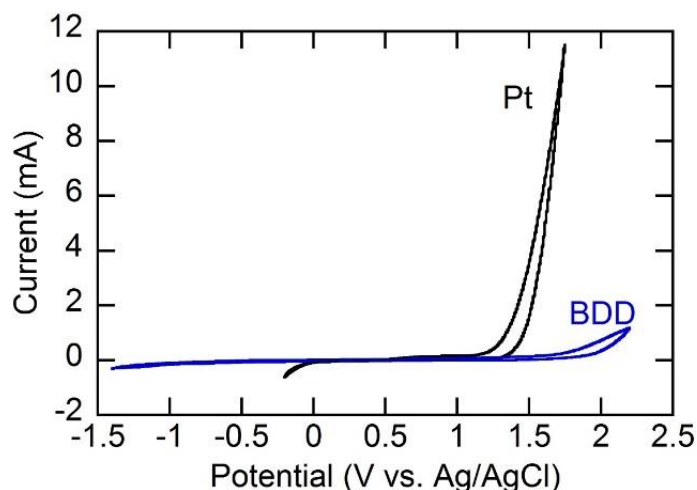


Figure A.1 Cyclic voltammetry of platinum and BDD in 0.1 M NaClO₄ (scan rate: 50 mV s⁻¹).

For a coupled P(TMA₅₁-co-TMPMA₄₉)-CNT//BDD configuration, adsorption was carried out in the presence of 0.1 mM PFOA and 20 mM NaCl for 30 min, followed by reversing polarity and applying 10 mA cm⁻² on the BDD electrode in clean 20 mM NaCl electrolyte for 5 h. All electrochemical studies were performed on a potentio/galvanostat (VSP-300 Multi Channels Potentiostat, Biologic). The PFOA uptake values are reported as the adsorption capacity normalized by the mass of the polymer.

LC-MS analysis for PFAS quantification: Concentrations of anionic PFAS compounds were measured using Waters Synapt G2Si with Waters Acquity H-class UPLC system, and the MassLynx™ 4.1 workstation was utilized for following data acquisition and processing. Waters CORTECS UPLC C18 (1.6 μm, 3.0 × 50 mm) was chosen as the chromatographic column. The temperature of the column was kept at 40 °C. Mobile phase system comprises 5 mM NH₄OAc solution (A) and acetonitrile (B), with the flow velocity of 0.5 mL min⁻¹. Injection volume of the sample was 0.1 or 1 μL for negative ionization (ESI-) mode. Gradient elution as follows: 100% A for 0–1 min, 2% A for 2–5 min, and 100% A for 6–20 min.

Fluoride analysis using ion chromatography: All the chromatographic separations were carried out on a Thermo Fisher Dionex 2100 ion chromatography system equipped with an EGC III KOH eluent generator, conductivity cell, a pump, a Chromeleon v6.8 workstation and connected to an AS-AP autosampler. A Thermo Scientific ADRS 600 4 mm suppressor was used to lower the background eluent. A Dionex IonPac AS18 (4 x 250 mm) anion exchange column with an in-line AG18 guard (4 x 50 mm) was used to separate fluoride from other species. Samples were prepped for IC by filtering through a .22 µm PTFE membrane syringe filter (Biomed Scientific) to prevent sample contaminants from eluting into the anion exchange column. A series of standard solutions were prepared from an IC multi-element standard I (certipur, USA) and diluted using deionized water produced by a Milli-Q system.

Table A.1 Fluoride calibration parameters for the analytes in standard solution. (n = 4). Eluent: 5 mM KOH; flow rate: 1.0 mL/min; Injection volume: 25 µL; detection: suppressed conductivity detector.

Analyte	Regressive equation	Coefficient of determination, R^2
F ⁻	y=2.2999x+.0316	0.9997

A.2 Performance evaluation

Adsorption isotherm. Initial PFOA concentration with 0.01, 0.05, 0.1, 0.5, 1 mM was spiked in 20 mM NaCl solution. Langmuir and Freundlich isotherm fittings were carried out using non-linear regression as shown in Eq. S1 and Eq. S2, respectively:

Langmuir: $\frac{1}{Q_e} = \frac{1}{Q_m} + \frac{1}{c_e Q_m b}$ (Eq. S1), where Q_e and Q_m (mg g⁻¹) is the amount of PFOA adsorbed at equilibrium and the maximum adsorption capacity of the adsorbent at equilibrium, respectively.

C_e (mg L⁻¹) is the equilibrium concentration of PFOA, and b (L mg⁻¹) is the equilibrium constant.

Freundlich: $Q_e = KC_e^{\frac{1}{n}}$ (Eq. S2), where Q_e is the amount of PFOA adsorbed at equilibrium. K is Freundlich constant, and n is an indicating affinity of the adsorptive energy distribution.

Table A.2 Constants of Langmuir and Freundlich isotherm for the adsorption of PFOA on P(TMA_x-co-TMPMA_{1-x})-CNT at open circuit.

Langmuir			Freundlich		
Q_m	b	R^2	K	n	R^2
839.3	0.148	0.892	213.8	4.00	0.935

Separation factor. The separation factor is defined as:

Separation factor_{PFOA⁻/Cl⁻} = $\frac{Q_{PFOA^-}/Q_{Cl^-}}{(Q_{PFOA^-})_0/(Q_{Cl^-})_0}$, where $(Q_{PFOA^-})_0$ and $(Q_{Cl^-})_0$ are the original concentration in the solution (($Q_{PFOA^-})_0$: 0.1 mM, ($Q_{Cl^-})_0$: 20 mM), and Q_{PFOA^-} and Q_{Cl^-} are isolated quantities of PFOA⁻ and Cl⁻ estimated from XPS surface analysis of fluoride and chloride (See **Table A.3**). A factor of 15 was divided to get the quantities of PFOA from fluoride.

Table A.3 XPS composition (atomic percent) of fluoride and chloride on P(TMA₅₁-co-TMPMA₄₉)-CNT electrodes after adsorption in 0.1 mM PFOA + 20 mM NaCl for 1 h at various potentials (obtained from **Figure A.9**).

Potential	Fluoride (%)	Chloride (%)
Open circuit	97.4	2.6
+1.0 V	92.0	8.0
+1.2 V	89.3	10.7
+1.4 V	88.5	14.5
+1.6 V	71.4	28.6
+1.8 V	73.1	26.9
+2.0 V	73.7	26.3

Coulombic efficiency. The Coulombic efficiency of PFOA adsorption during chronoamperometry at positive potential was estimated based on assuming one-electron process for the adsorption of anionic PFOA (which has carboxylate end):

Coulombic efficiency(%) = $\frac{n \times z \times F}{\int i \, dt} \times 100 \%$, where n is the number of moles of PFOA adsorbed; F is the Faraday constant, $z=1$ is the number of electron involved in the adsorption of one PFOA anion; i is the current passing through the circuit (see **Figure A.13**).

Defluorination performance. The defluorination performance can be evaluated using: (1) defluorination efficiency (defluorination ratio), and (2) F index.

(1) Defluorination efficiency:

$$\text{Defluorination efficiency} = \frac{C^{F^-} \text{ produced}}{C^{F^-} \text{ in PFOA, initial}}$$

(2) F index:

$$\text{F index} = \frac{C^{F^-} \text{ produced}}{C^{PFOA} \text{ degraded}}$$

Energy consumption analysis. The amount of energy consumption per a mol of produced fluoride ion during the mineralization of PFOA was estimated by dividing the amount of energy consumed by the amount of produced fluoride during the electrocatalysis on BDD anode.

$$\text{Energy consumption} \left(\frac{\text{kWh}}{\text{mol } F^-} \right) = \frac{\int (E_{WE} - E_{CE}) \times i \, dt}{n}$$

, where E_{WE} is the potential of working electrode, E_{CE} is the potential of the counter electrode, i is the current passing through the circuit (see **Figure A.13**), and n is the number of fluoride generated during each operation.

A.3 Characterization results

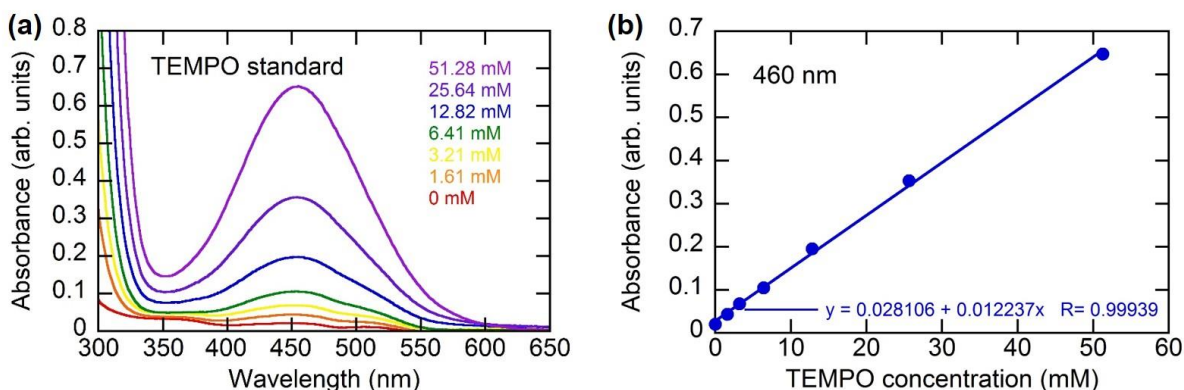


Figure A.2 (a) UV-vis absorbance of TEMPO with different concentration in chloroform, (b) Calibration curve obtained from (a) at 460 nm.

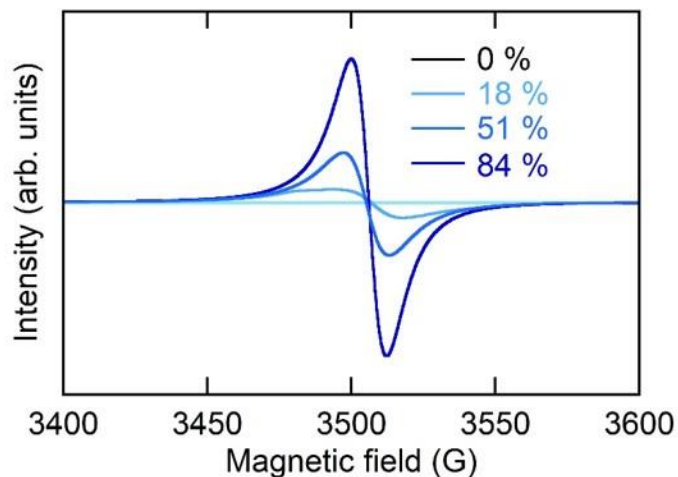


Figure A.3 EPR spectra of P(TMA_x-co-TMPMA_{1-x}) with different oxidation degrees.

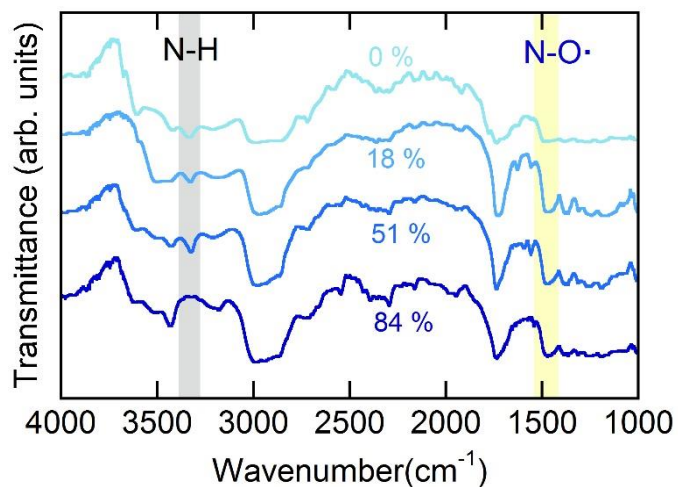


Figure A.4 Fourier-transform infrared spectroscopy spectra of P(TMA_x-co-TMPMA_{1-x}) with different oxidation degrees. The peak at 1467 cm⁻¹ is related with nitroxyl radical, while the peak at 3400-3100 cm⁻¹ is associated with amine stretch.

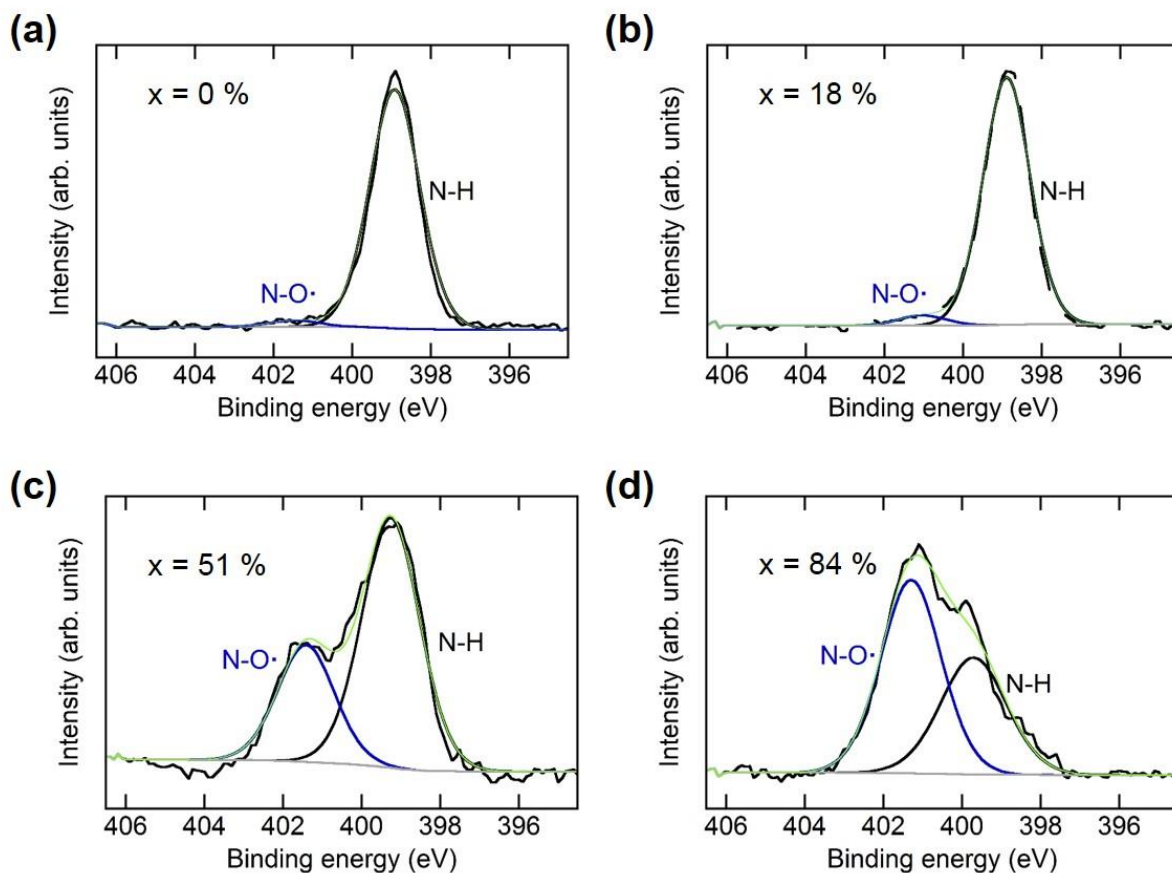


Figure A.5 High-magnification XPS N1s spectra of P(TMA_x-co-TMPMA_{1-x}) powder with different oxidation degrees: (a) PTMPMA, (b) 18%, (c) 51%, (d) 84%. The spectra indicate the presence two distinct nitrogen states of amine (black) and nitroxyl radical (blue).

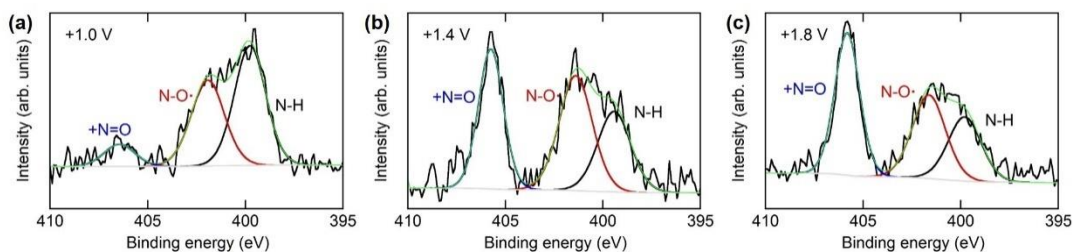


Figure A.6 High-magnification XPS N1s spectra of P(TMA₅₁-co-TMPMA₄₉)-CNT electrode after polarization at positive potentials of (a) +1.0 V, (b) +1.4 V, (c) +1.8 V vs. Ag/AgCl for 1 h. The spectra indicate the presence three distinct nitrogen states of amine (black), nitroxyl radical

Figure A.6 (cont.) (red), and oxoammonium cation (blue).

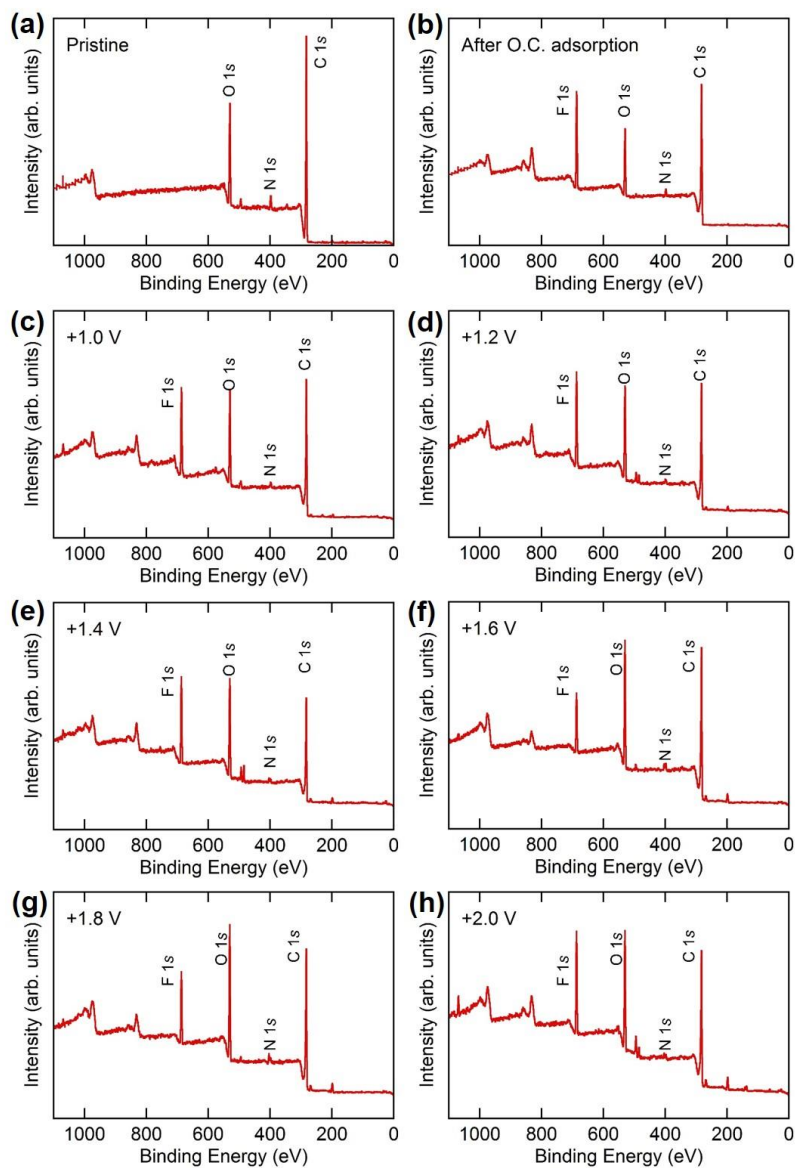


Figure A.7 XPS survey scan for (a) pristine P(TMA₅₁-co-TMPMA₄₉)-CNT electrode, and P(TMA₅₁-co-TMPMA₄₉)-CNT electrodes after adsorption in 0.1 mM PFOA + 20 mM NaCl for 1 h at (b) open circuit (c) +1.0 V, (d) +1.2 V, (e) +1.4 V, (f) +1.6 V, (g) +1.8 V, and (h) +2.0 V vs. Ag/AgCl.

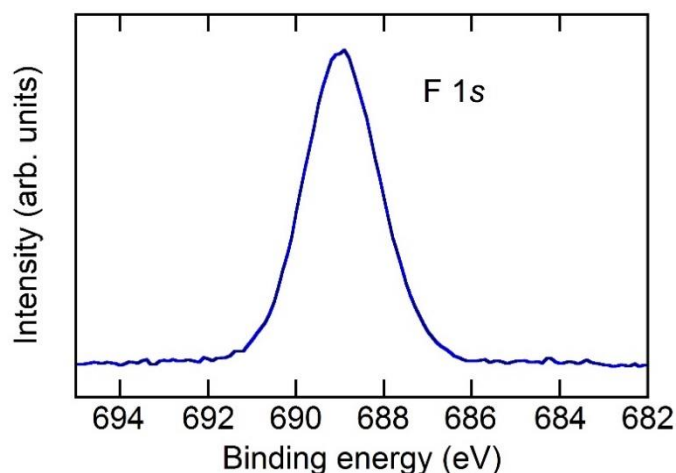


Figure A.8 High resolution XPS F1s spectrum of the surface of P(TMA₅₁-co-TMPMA₄₉)-CNT electrode after adsorption in 0.1 mM PFOA + 20 mM NaCl for 1 h at +1.0 V.

Supplementary figures for electrosorption/release and electrochemical performance

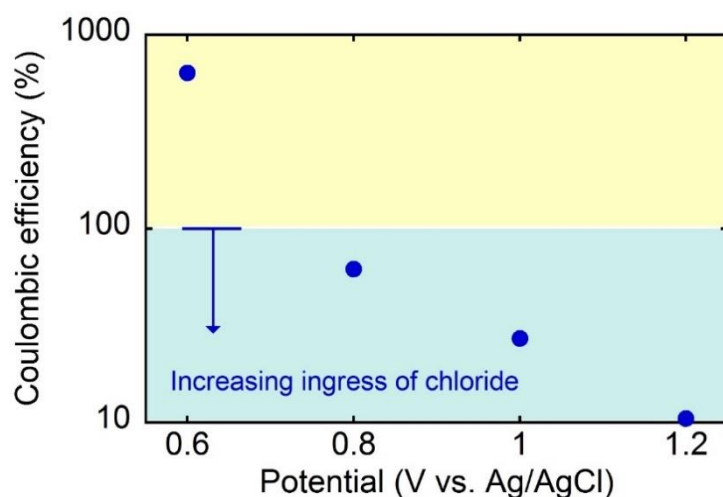


Figure A.9 Coulombic efficiency of PFOA uptake by P(TMA₅₁-co-TMPMA₄₉)-CNT electrodes after adsorption in 0.1 mM PFOA + 20 mM NaCl for 0.5 h at positive potentials. At +0.6 V vs. Ag/AgCl, the Coulombic efficiency higher than 100 % indicates PFOA binding onto the polymer electrode not only by electrostatic attraction for charge neutrality but also affinity by N-H in piperidine of TMPMA.

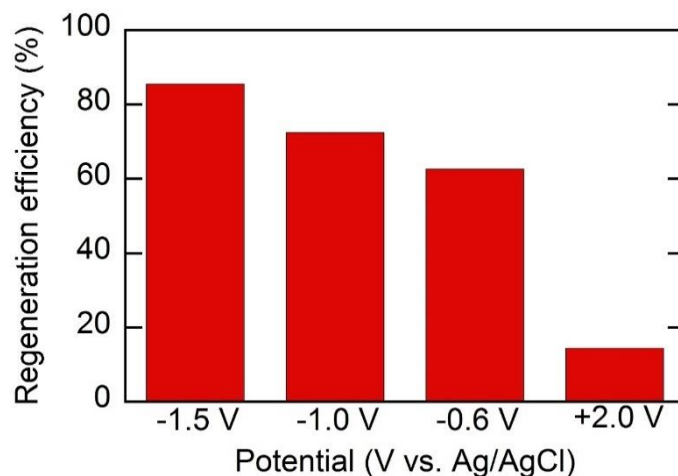


Figure A.10 Regeneration efficiency of P(TMA₅₁-co-TMPMA₄₉)-CNT electrodes. Adsorption was carried out in 0.1 mM PFOA + 20 mM NaCl at +1.0 V for 0.5 h, followed by releasing into 20 mM NaCl at various potentials (x-axis) for 1 h.

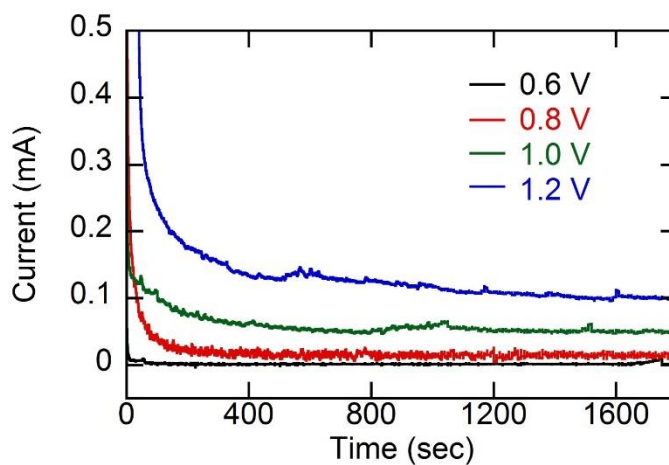


Figure A.11 Change in current during adsorption via chronoamperometry on P(TMA₅₁-co-TMPMA₄₉)-CNT electrodes. Adsorption was carried out in 0.1 mM PFOA + 20 mM NaCl for 0.5 h.

Appendix B: Chapter 3 Supplementary Figures and Tables

B.1 Methods

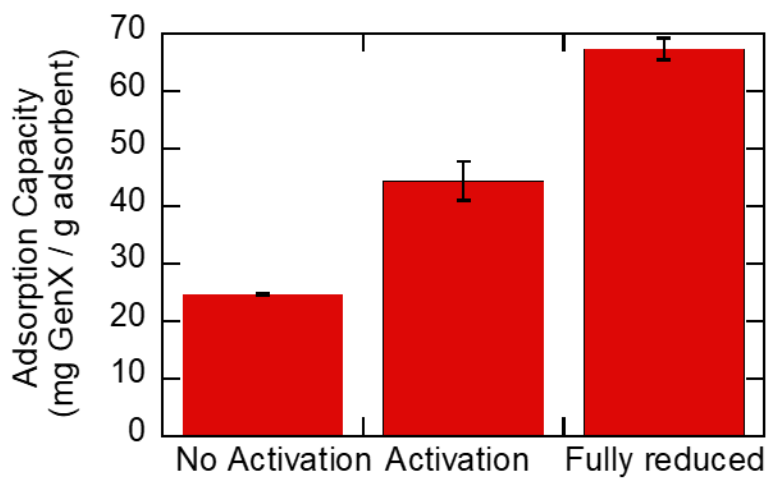


Figure B.1 Adsorption uptake of GenX with different electrode pretreatments. Experiment performed with 0.1 mM GenX and 20 mM NaCl at 0.8 V for 30 min.

B.1.1 LC/MS parameters

Table B.1 LC/MS conditions for the analysis of PFAS

LC/MS conditions	
Instrument	Waters Synapt G2Si with Waters Acquity H-class UPLC system
Column	Acquity UPLC BEH C18 1.7 μ m
Column temperature	40 °C
Mobile phase	A) H ₂ O with 5mM ammonium acetate solution B) Acetonitrile
Flow rate	0.4 mL/min
Equilibration time	2 minutes
Gradient elution profile	0–3 minutes: 30–65 % B
	3–4 minutes: 65 % B
	4–5 minutes: 65–100 % B
	5–8 minutes: 100 % B
	8.1 minutes 30% B
	10 minute 30 % B
Ionization mode	ESI negative

Injection volume for each PFAS differed depending on the compound. Longer chain PFAS, PFOA, were rapidly detected and would require a smaller injection volume and lower calibration curve concentrations. **Table B.2** indicates the summary for each LC/MS standard and injection volume.

Table B.2 LC/MS calibration curve standards concentration and injection volume.

Compound	Calibration Range (μ M)	Injection Volume (μ L)
PFOA	0-5	0.5
GenX	0-25	10
PFBS	0-25	10
PFBA	0-25	10
PFHpA	0-5	0.5

B.2 Characterization techniques

B.2.1 Scanning electron microscopy (SEM) images.

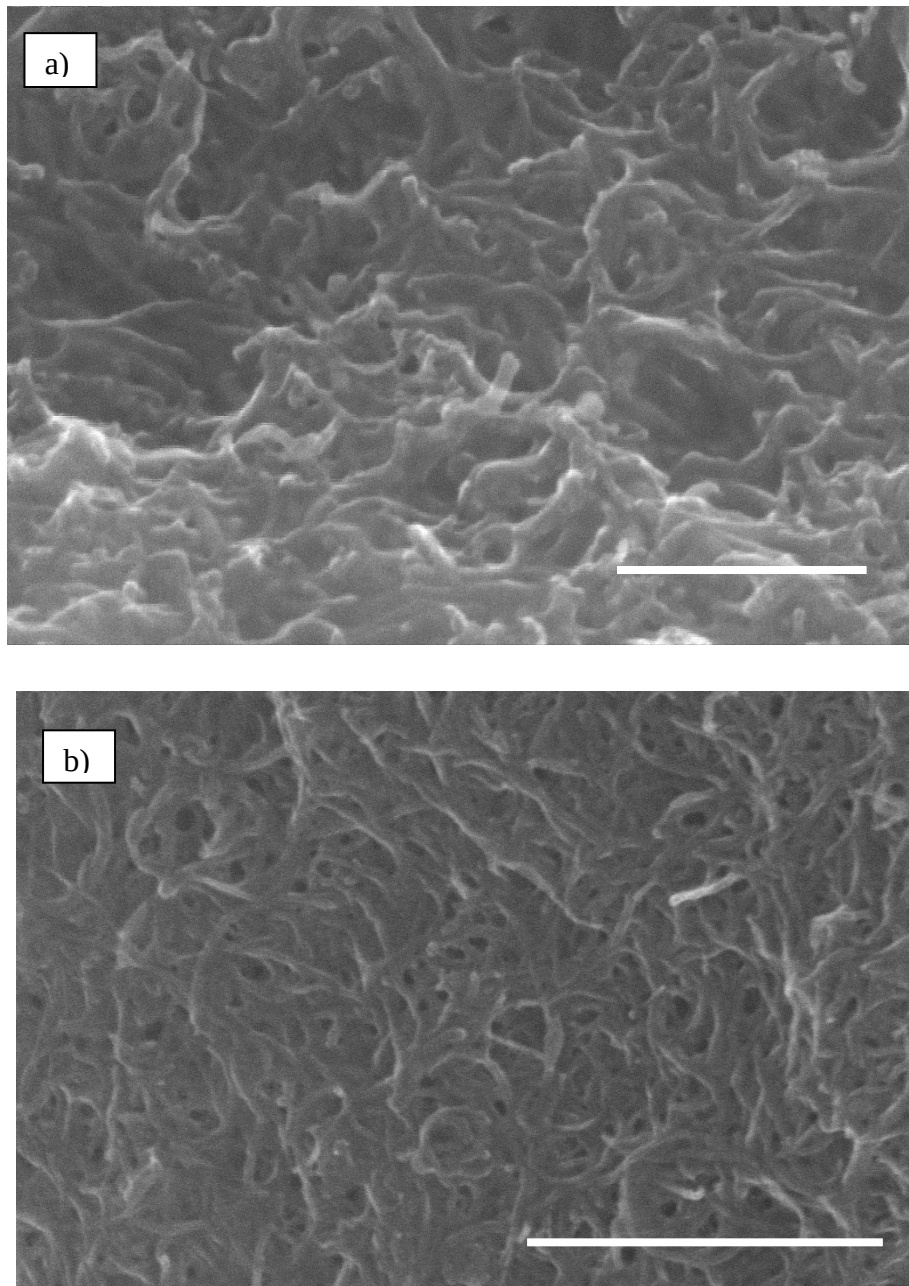


Figure B.2. (cont.)

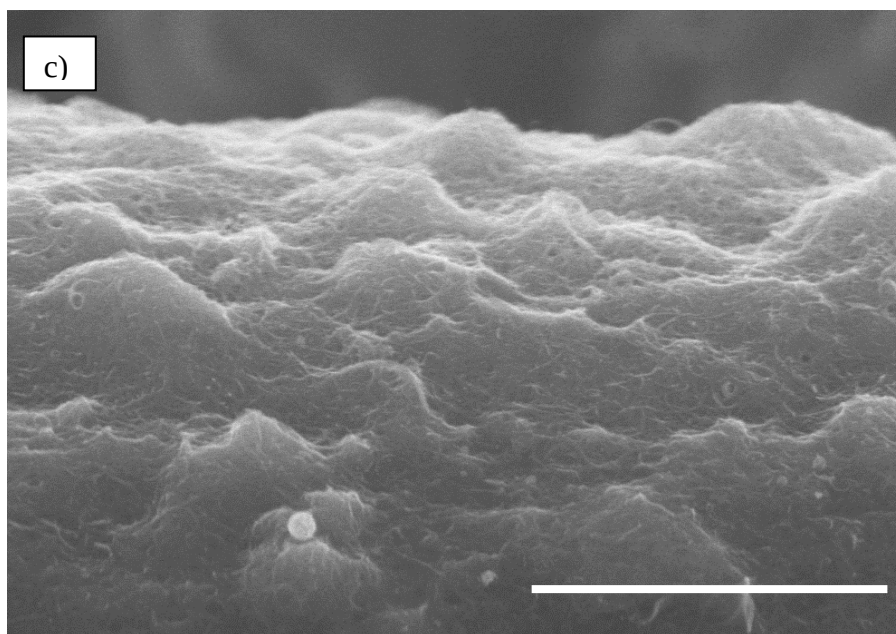


Figure B.2 (cont.) High-resolution SEM images of a PTMA-co-PTMPMA/MWCNT electrode at various magnifications. Scale bars: a) 500 nm, b) 1 μm , and c) 5 μm .

B.2.2 Electron paramagnetic resonance behavior of PTMA-co-TMPMA/MWCNT electrodes

Solid spectra for Electron paramagnetic resonance (EPR) spectroscopy were determined to prove radical behaviour of the copolymer PTMA-co-PTMPMA. The analysis was performed in a 3 mm diameter quartz EPR tube with dilution of 1 to 9 ratio of high-purity (99.999%) KNO_3 . The Bruker EMXPlus spectrometer was used with an X-band frequency of 9.8 GHz along with a Bruker ER4119HS high sensitivity resonator.

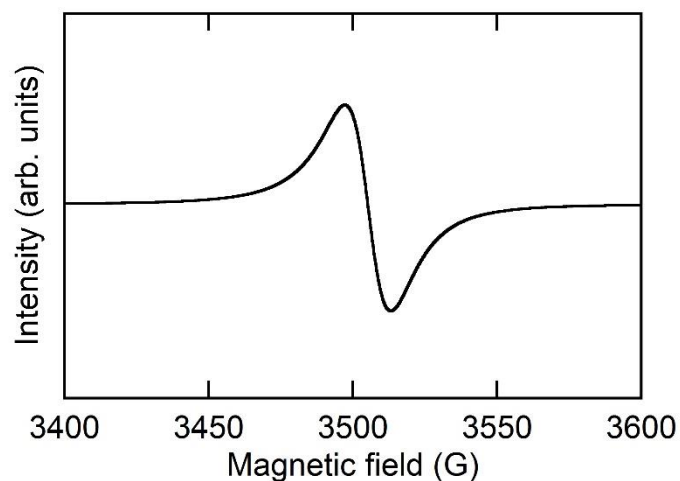


Figure B.3 Solid EPR spectra for PTMA-co-PTMPMA

B.2.3 XPS analysis

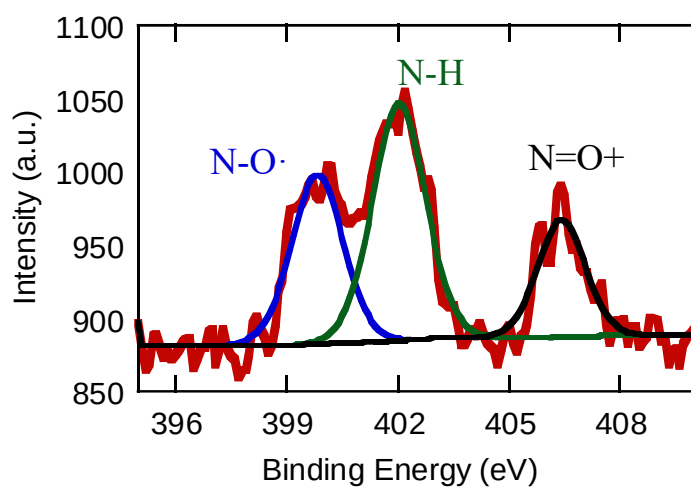


Figure B.4 High magnification XPS of N1s spectra for PTMA-co-PTMPMA electrode. Three nitrogen states can be observed.

B.2.4 Contact angle

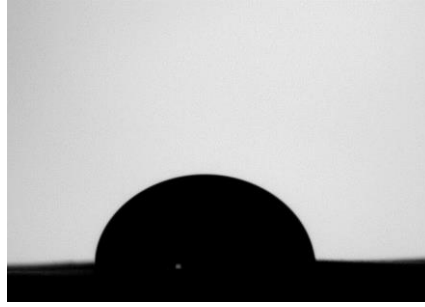


Figure B.5 Contact angle of PTMA-co-PTMPMA with 0.1 mM GenX.

B.3 Adsorption isotherms

All adsorption isotherms were performed under different equilibrium concentrations: 0.05, 0.1, 0.25, 0.5 and 0.75 mM GenX and 20 mM NaCl. Both, Langmuir and Freundlich adsorption isotherms were analyzed using their respective equations:

$$\frac{1}{Q_e} = \frac{1}{Q_m} + \frac{1}{C_e Q_m b} \quad (\text{Eq. B. 1})$$

$$Q_e = \text{GenX adsorbed at equilibrium} \left[\frac{\text{mg}}{\text{g}} \right]$$

$$Q_m = \text{maximum adsorption capacity for GenX} \left[\frac{\text{mg}}{\text{g}} \right]$$

$$C_e = \text{equilibrium concentration of GenX} \left[\frac{\text{mg}}{\text{L}} \right]$$

$$b = \text{equilibrium constant} \left[\frac{\text{L}}{\text{mg}} \right]$$

$$Q_e = K C_e^{\frac{1}{n}} \quad (\text{Eq. B. 2})$$

$$Q_e = \text{GenX adsorbed at equilibrium} \left[\frac{\text{mg}}{\text{g}} \right]$$

$$K = \text{Freundlich constant}$$

$$n = \text{Affinity of adsorptive distribution}$$

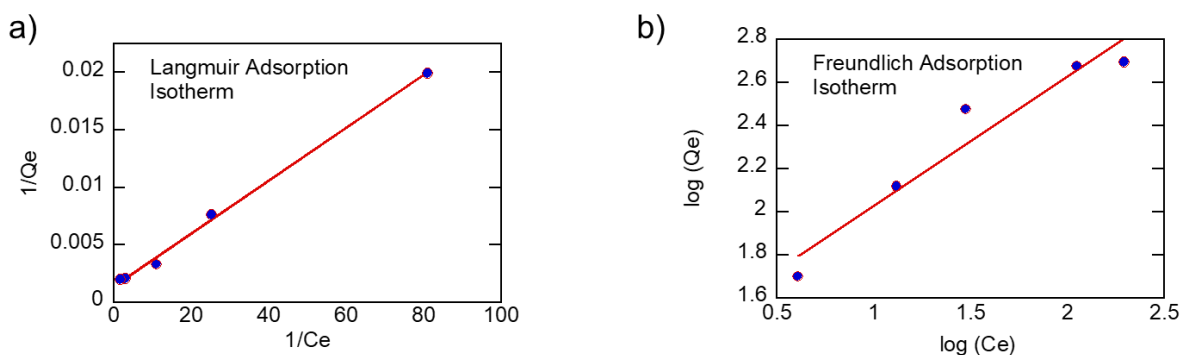


Figure B.6 Isotherm curve-fit lines for: a) Langmuir adsorption model and b) Freundlich adsorption model

Table B.3 Isotherm parameters for the removal of GenX with PTMA-co-PTMPMA. a)

Langmuir Isotherm parameters. b) Freundlich isotherm parameters

a) Langmuir isotherm parameters:

Intercept	Slope	Q_m (mg/g)	b (L/mg)	R^2
0.00141	2.29E-04	709.21986	6.14E+00	0.99737

b) Freundlich isotherm parameters:

Intercept	Slope	$1/n$	$K ((\text{mg/g})(\text{L/mg})^{1/n})$	R^2
1.43002	0.59854	0.59854	26.91659	0.93353

B.4 Kinetic study

The kinetics study was performed at open circuit and at 0.8 V vs Ag/AgCl under 2.5 mL total volume of 0.1 mM GenX and 20 mM NaCl. To obtain the rate constants of our experimental data

we used two different kinetic models for comparison. Lagergren pseudo-first-order model (**Eq. B.3**) was used as well as the pseudo-second-order model (**Eq. B.4**).^{188, 189}

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \text{ (Eq. B.3)}$$

$$q_e = \text{equilibrium uptake} \left[\frac{mg}{g} \right]$$

$$q_t = \text{uptake at a specific time} \left[\frac{mg}{g} \right]$$

$$k_1 = \text{rate constant} \left[\frac{1}{min} \right]$$

$$t = \text{time} [min]$$

$$\frac{t}{q_t} = \frac{1}{(k_2 q_e^2)} + \frac{t}{q_e} \text{ (Eq. B.4)}$$

$$k_2 = \text{rate constant} \left[\frac{g}{mg \text{ min}} \right]$$

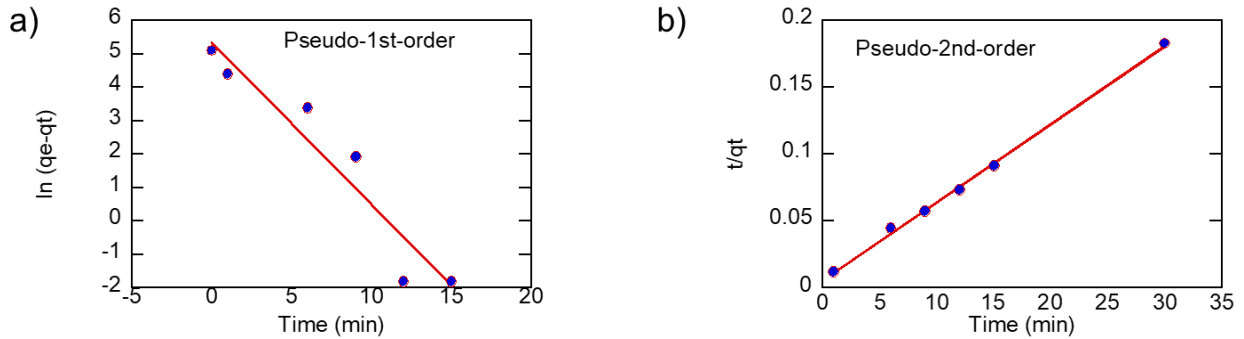


Figure B.7 Kinetics curve-fit lines for the removal of GenX using PTMA-co-PTMPMA while applying 0.8 V for 30 minutes: a) Pseudo-first-order kinetic model and b) Pseudo-second-order kinetic model.

Table B.4 Kinetic parameters for the removal of GenX using PTMA-co-PTMPMA while applying 0.8 V for 30 minutes for a) the pseudo-first-order kinetic model and b) pseudo-second-order kinetic model

a) Pseudo-first-order kinetic model

Intercept	Slope	q_e (mg/g)	k_1 (1/min)	R^2
5.35042	-0.48624	210.6968	0.01621	0.89644

b) Pseudo-second-order kinetic model

Intercept	Slope	q_e (mg/g)	k_2 (g/(mg*min))	R^2
0.00396	0.00595	168.0672	0.00894	0.99762

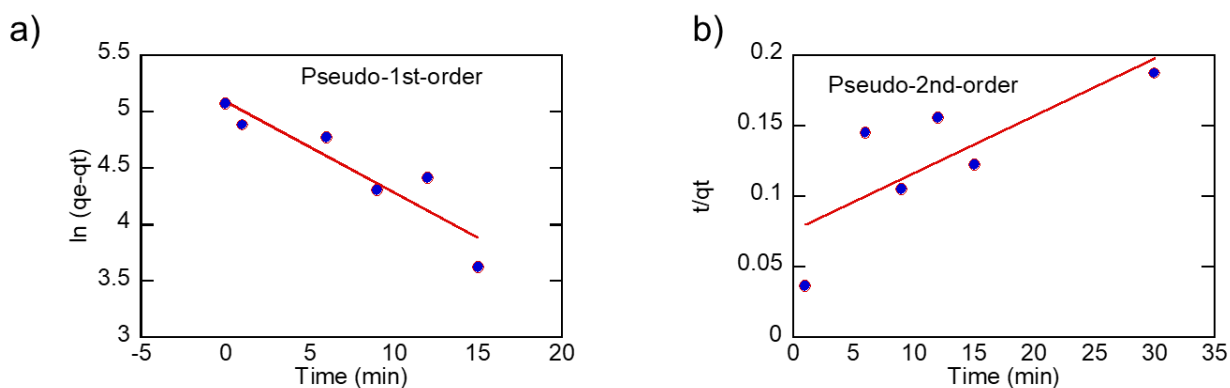


Figure B.8 Kinetics curve-fit lines for the removal of GenX using PTMA-co-PTMPMA at open circuit for 30 minutes: a) Pseudo-first-order kinetic model and b) Pseudo-second-order kinetic model

Table B.5 Kinetic parameters for the removal of GenX using PTMA-co-PTMPMA at open circuit for 30 minutes for a) the pseudo-first-order kinetic model and b) pseudo-second-order kinetic model

a) Pseudo-first-order kinetic model

Intercept	Slope (1/min)	q_e (mg/g)	k_1 (1/min)	R^2
5.09252	-0.08051	162.7996	0.00268	0.81692

b) Pseudo-second-order kinetic model

Intercept (min*g/mg)	Slope (g/mg)	q_e (mg/g)	k_2 (g/(mg*min))	R^2
0.05201	0.00534	187.2659	0.000548	0.59065

B.5 Electrochemical experiments

B.5.1 Chronopotentiometry screening

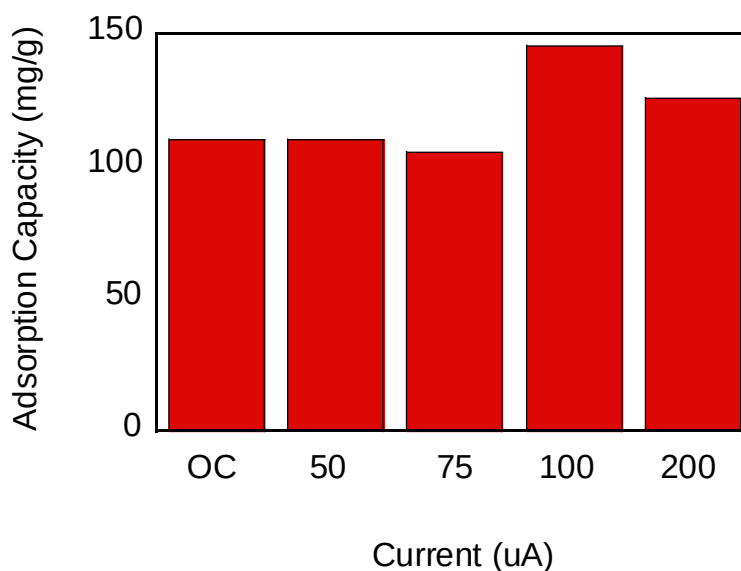


Figure B.9 Adsorption capacity of PTMA-co-PTMPMA/MWCNT electrode during chronopotentiometry with different currents in 0.1 mM GenX and 20 mM NaCl for 30 min.

S5.2 Desorption screening

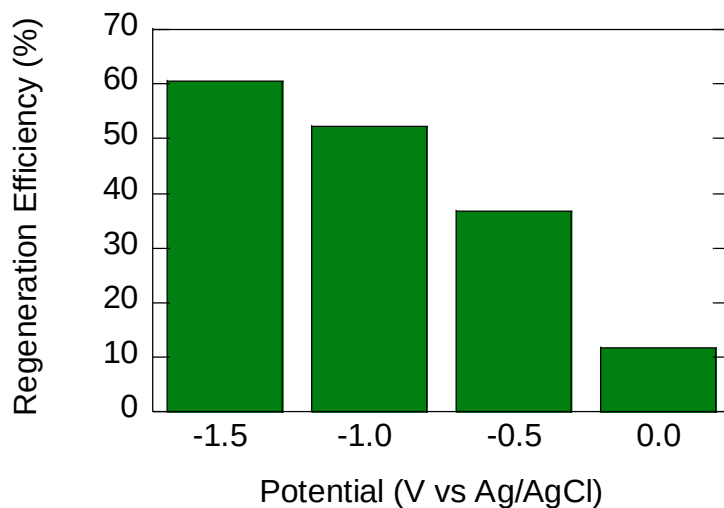


Figure B.10 Regeneration efficiency of PTMA-co-PTMPMA/MWCNT electrodes. Adsorption was carried out in 0.1 mM GenX and 20 mM NaCl at +0.8 V for 30 min. Various regenerative potentials were applied for 1 hour in 20 mM NaCl.

B.5.2 Control experiment

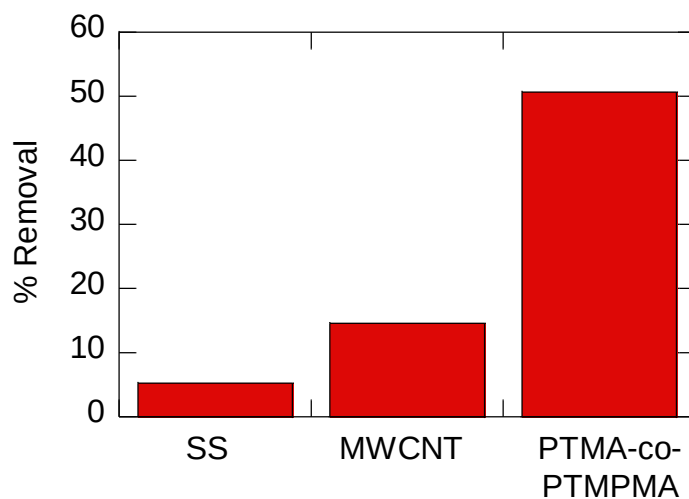


Figure B.11 Percent removal of 0.1 mM GenX + 20 mM NaCl while applying 0.8 V vs Ag/AgCl using different electrodes after 30 min of adsorption: (a) bare stainless steel mesh, (b) MWCNT, and (c) PTMA-co-PTMPMA.

B.5.3 Energy comparison for chronoamperometry screening versus chronopotentiometry screening

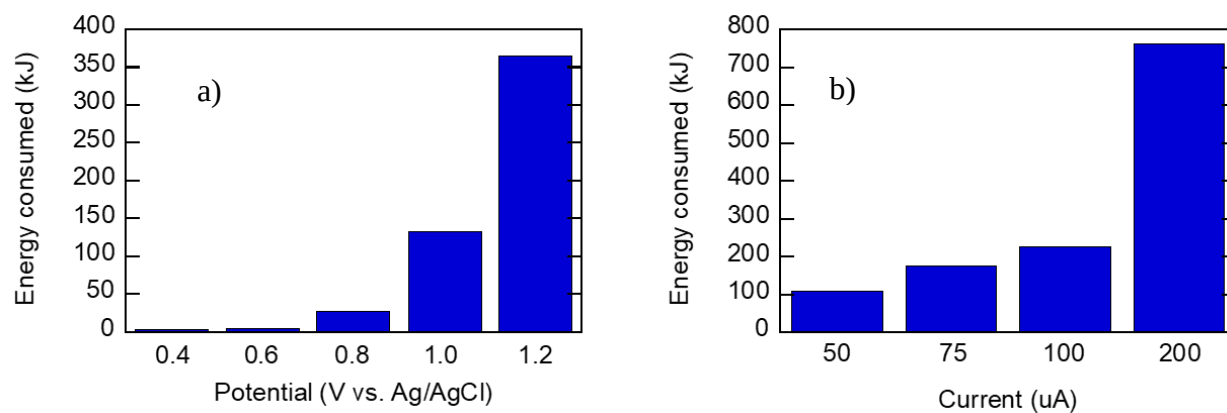


Figure B.12 Energy comparison for a) chronoamperometry and b) chronopotentiometry experiments performed for 30 min in 0.1 mM GenX and 20 mM NaCl.

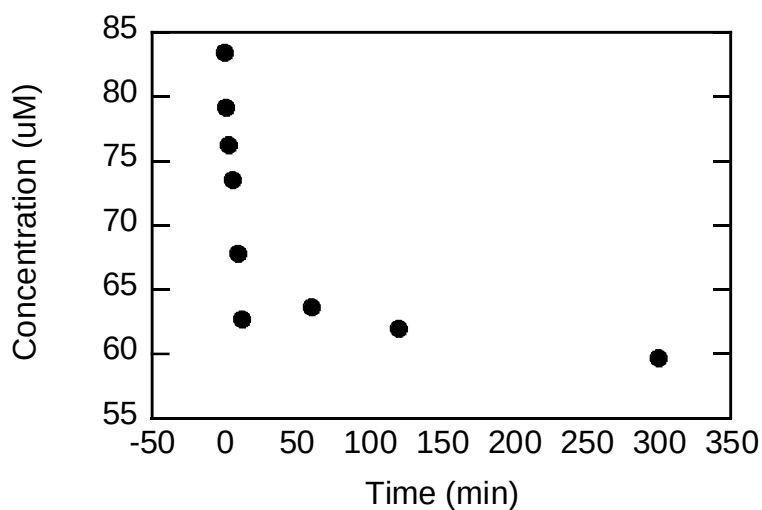


Figure B.13 Kinetics of GenX at 0.8 V in 0.1 mM GenX and 20 mM NaCl with 5 mL volume.

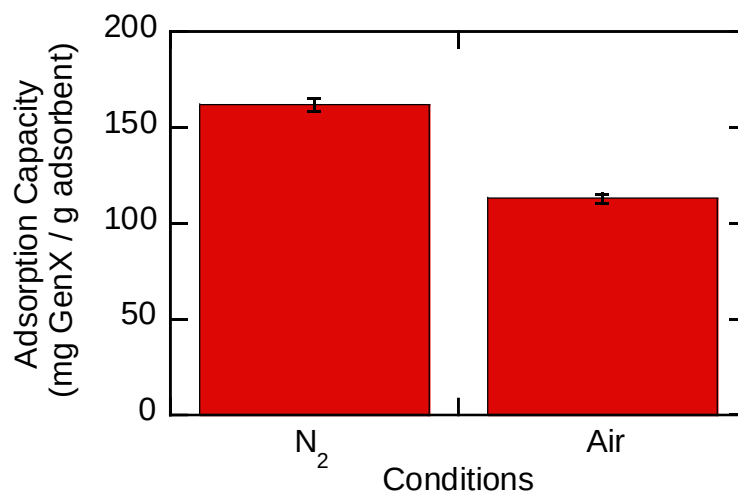


Figure B.14 Adsorption changes at +0.8 V in 1 mM GenX and 20 mM NaCl for 30 min under inert conditions with N₂ purge versus when adsorbing without N₂ purge.

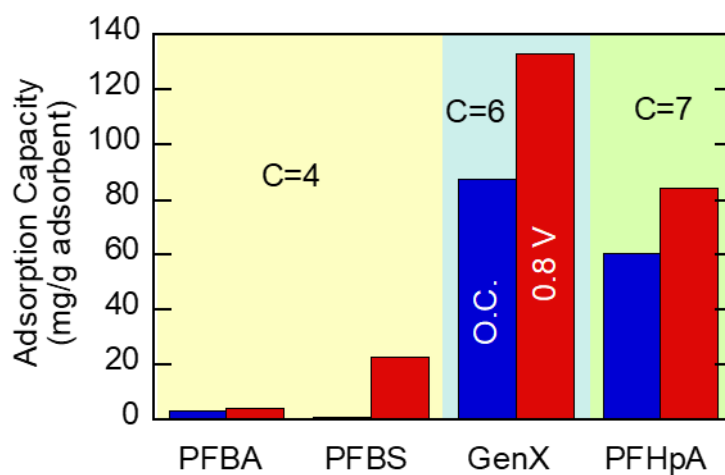


Figure B.15 Study of different short chain PFAS with PTMA-co-PTMPMA at concentrations of 0.1 mM and 20 mM NaCl.

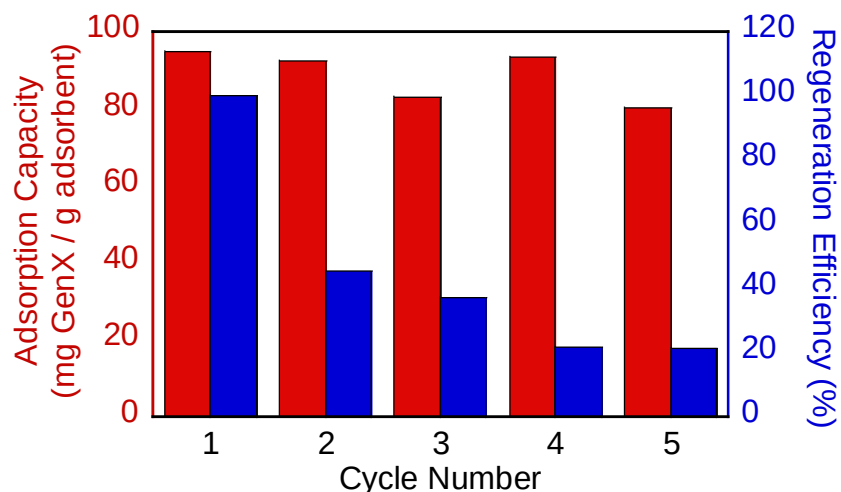


Figure B.16 Adsorption uptake for five adsorption-regeneration cycles of 0.1 mM GenX and 20 mM NaCl. Adsorption was performed for 30 minutes with 0.8 V vs Ag/AgCl and desorption was done by releasing in 20 mM NaCl and applying -1 V vs Ag/AgCl for 1 hour.

B.5.4 Electrochemical measurements

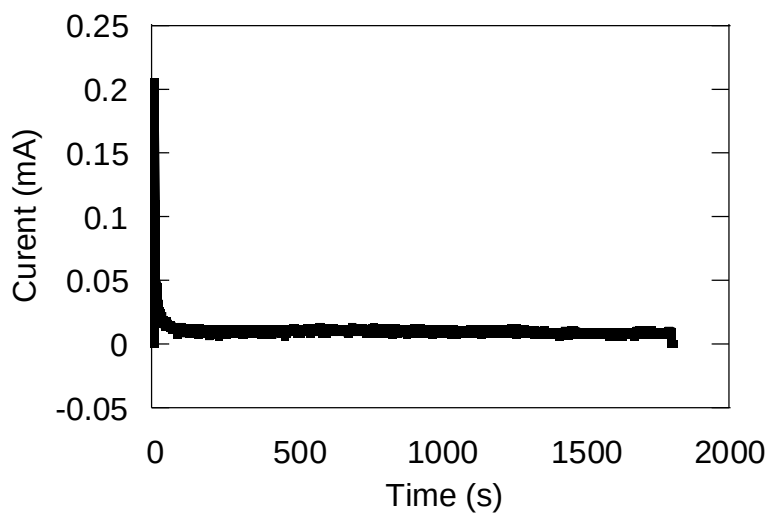


Figure B.17 Typical current behavior during adsorption via chronoamperometry with PTMA-co-TMPMA/MWCNT electrode. This adsorption experiment was under chronoamperometry at +0.8 V for 30 min in 0.1 mM GenX and 20 mM NaCl.

B.6 Other experimentations

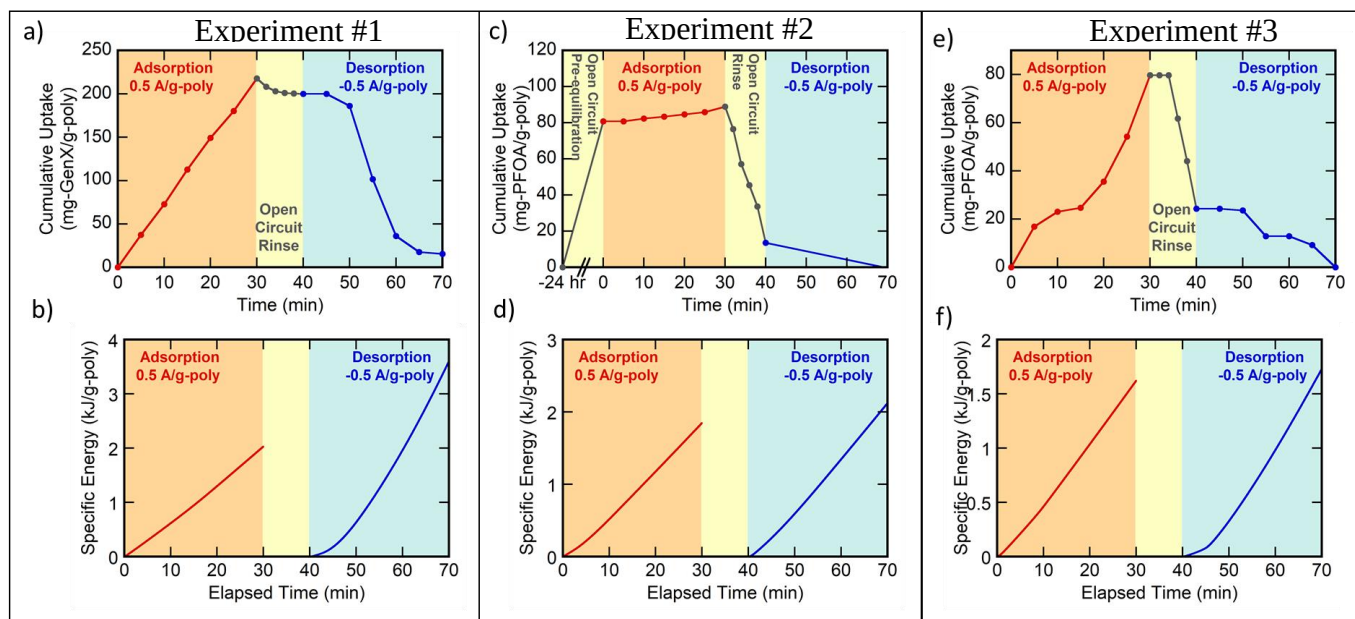


Figure B.18 (a),(c), and (e) Flow cell adsorption experiments. Uptake is determined based only on the polymer mass load. (b), (d), and (f) Flow cell energy analysis determined with the polymer mass load. (a) adsorption-release of GenX after pre-treating the PTMA-co-PTMPMA electrode and pre-equilibrating for 8 hours. The counter electrode was Ti for this experiment. (c) adsorption and release of PFOA after pre-treating the PTMA-co-PTMPMA electrode and pre-equilibrating for 8 hours. (e) adsorption and release of PFOA after only activating the PTMA-co-PTMPMA electrode. The counter electrode in this case was Pt coated/Ti plate.

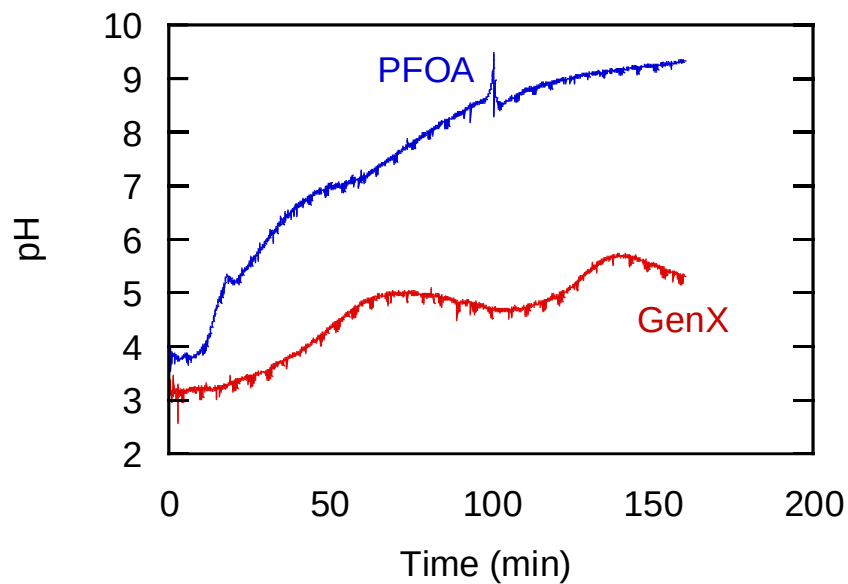


Figure B.19 pH performance with PTMA-co-TMPMA/MWCNT electrode. This adsorption experiment was under chronoamperometry at +0.8 V during 30 min in 0.1 mM GenX and 20 mM NaCl.

B.6.1 Possible fragmentation

A possible route for fragmentation occurrence was detected after six desorption cycles. Further analysis must be implemented to fully quantify LC spectra with detectable trace peaks.

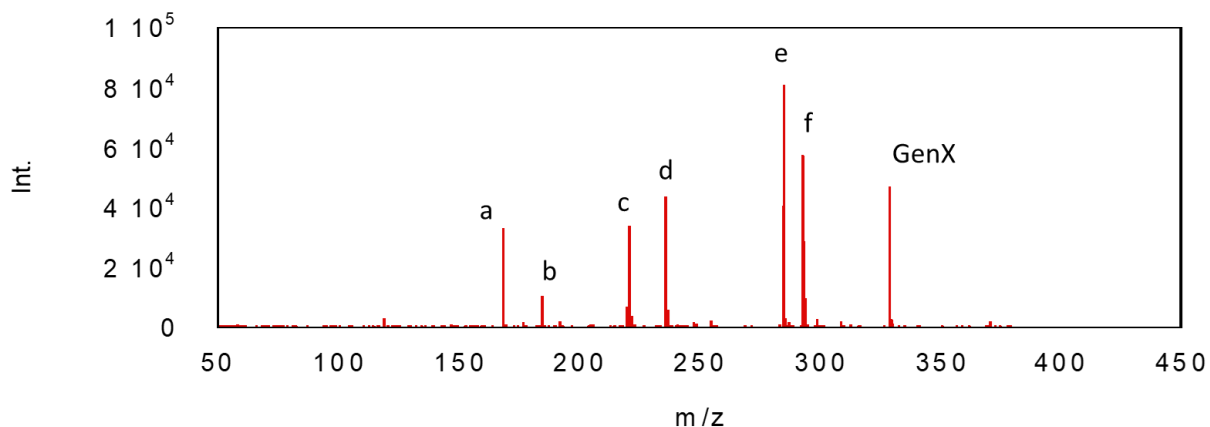


Figure B.20 Electron ionization mass spectrum for GenX desorption after 6 cycles.

Table B.6 LC/MS peak analysis of **Figure B.20**.

Peak	Molecular weight (Da)	Molecular fragment
a	168.9892	C_3F_7^-
b	184.9836	$\text{C}_3\text{HF}_7\text{O}^-$
c	221.15	$\text{C}_4\text{H}_2\text{F}_7\text{NaO}^-$
d	236.1	$\text{C}_4\text{HF}_9\text{O}^-$
e	284.9771	$\text{C}_5\text{HF}_{11}\text{O}^-$
f	293.1751	$\text{C}_5\text{F}_9\text{Na}_2\text{O}^-$

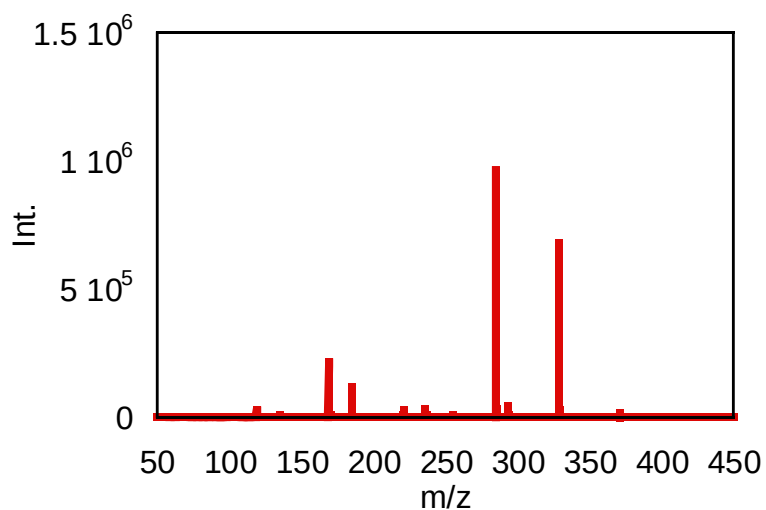


Figure B.21 Electron ionization mass spectrum for GenX stock solution of 0.1 mM GenX and 20 mM NaCl. Mass spectra was analyze on $m/z = 328.967 \pm 0.05$ Da.

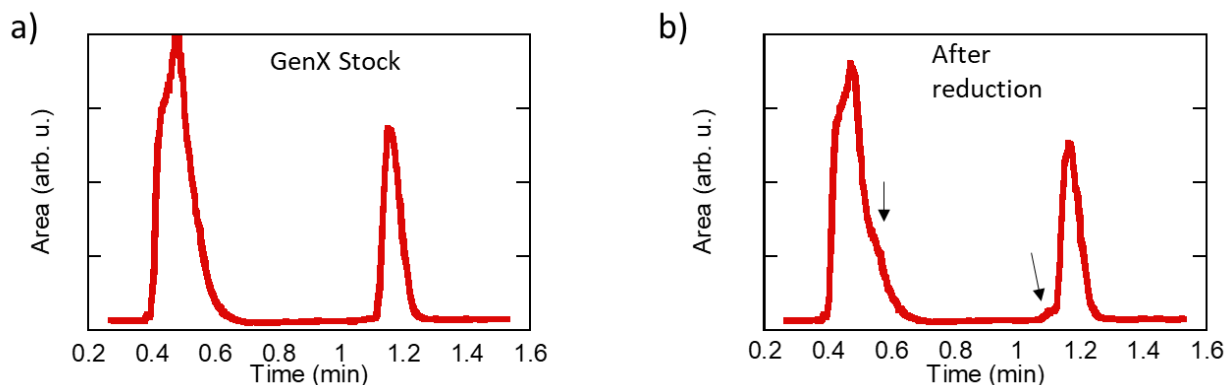


Figure B.22 (a) LC/MS Chromatogram of GenX stock (0.024 mM GenX + 20 mM NaCl) and (b) LC/MS chromatogram of a sample after being reduced for one hour on 0.024 mM GenX + 20 mM NaCl.

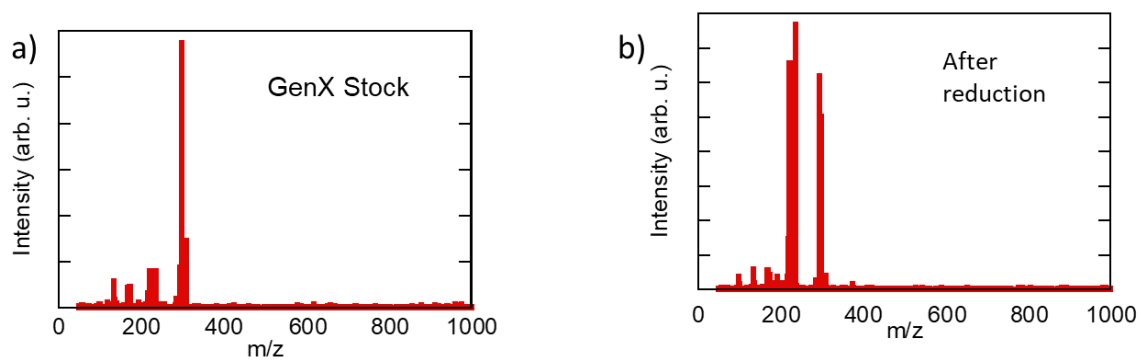


Figure B.23 (a) Electron ionization mass spectrum for 0.024 mM GenX + 20 mM NaCl stock. (b) Electron ionization mass spectrum for 0.024 mM GenX + 20 mM NaCl being reduced for 1 hour at -1 V vs Ag/AgCl with PTMA-co-PTMPMA. Both spectrums are being analyzed at 1.097 min. Notable peaks at 98.9473 and 220.8866 $\pm$ 0.0500 Da have been generated. This could correspond to $\text{C}_2\text{HFNaO}_2^-$ and $\text{C}_4\text{H}_2\text{F}_7\text{NaO}^-$, respectively.

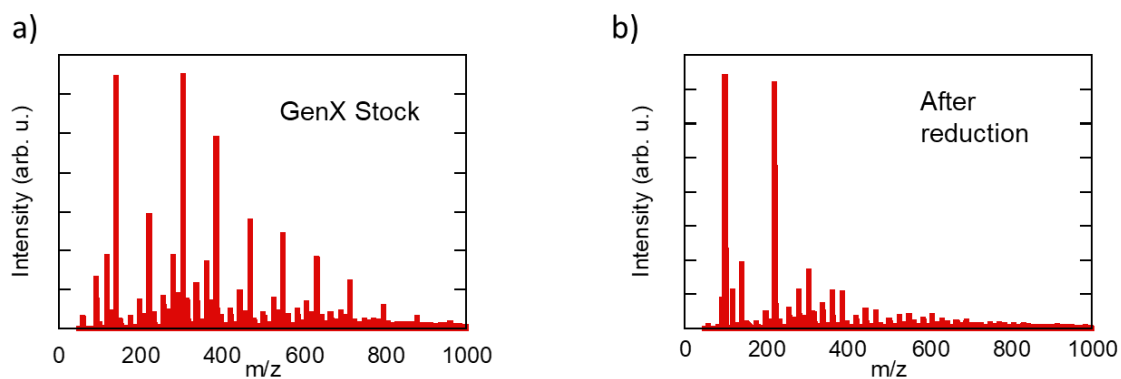


Figure B.24 (a) Electron ionization mass spectrum for 0.024 mM GenX + 20 mM NaCl stock. (b) Electron ionization mass spectrum for 0.024 mM GenX + 20 mM NaCl being reduced for 1 hour at -1 V vs Ag/AgCl with PTMA-co-PTMPMA. Both spectrums are being analyzed at 0.537 min. Notable peaks at 221.1531, 236.1041, and 293.1749 $\pm$ 0.0500 Da have been generated. This could correspond to $\text{C}_4\text{H}_2\text{F}_7\text{NaO}^-$, $\text{C}_4\text{HF}_9\text{O}^-$, and $\text{C}_5\text{F}_9\text{Na}_2\text{O}^-$, respectively.

Appendix C: Chapter 4 Supplementary Figures and Tables

C.1 Polymer characterizations

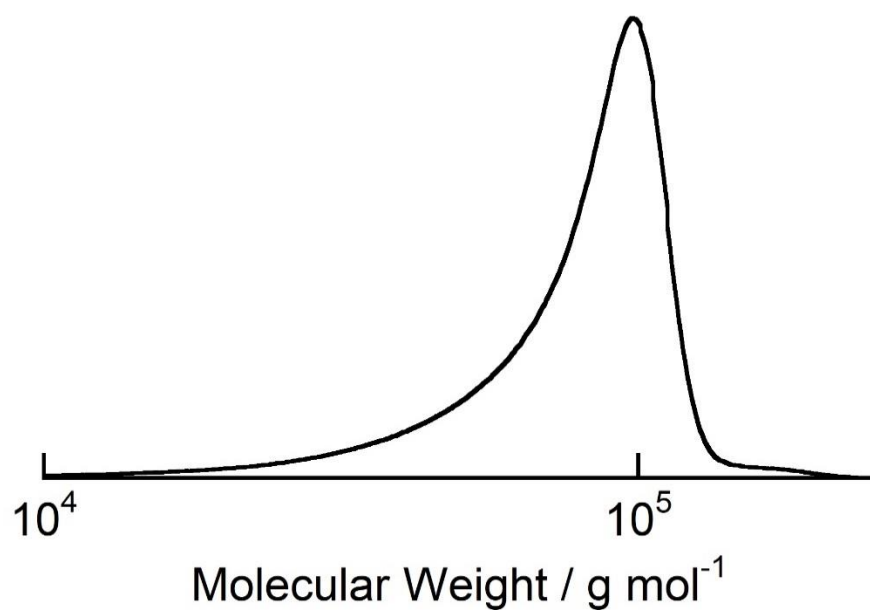


Figure C.1 Molecular weight distribution of PFMMA. Determined by GPC in THF using PS calibration.

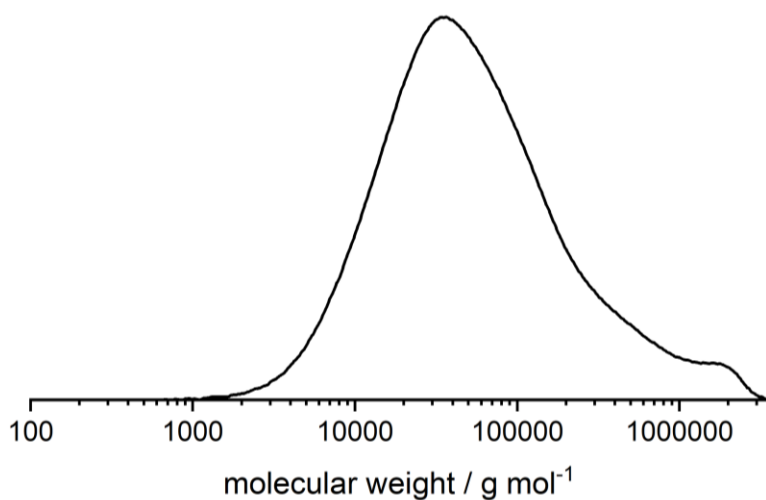


Figure C.2 Molecular weight distribution of PFPMAm. Determined by GPC in DMF/LiBr using PMMA calibration.

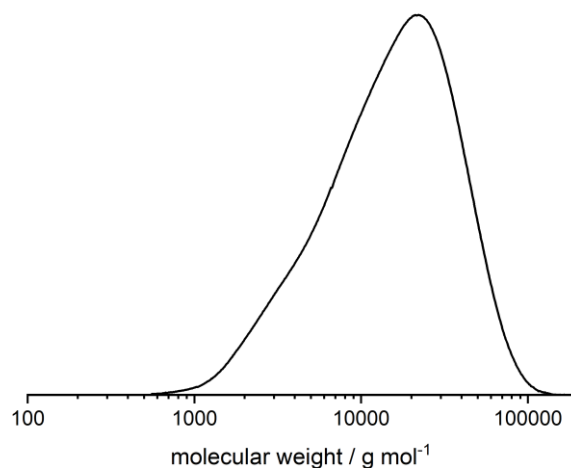


Figure C.3 Molecular weight distribution of PFcMA. Determined by GPC in THF using PS calibration.

Table C.1 ^1H NMR analysis of Fc peak intensity.

Polymer	Chemical shift δ (S, 5H)[ppm]	Chemical shift δ (2H)[ppm]
2-(methacryloyloxy)ethyl ferrocencarboxylate	4.18 ¹⁴⁰	4.40 ¹⁴⁰ , 4.81 ¹⁴⁰
Vinyl Ferrocene	4.10 ¹⁹⁰	4.20 ¹⁹⁰ , 4.36 ¹⁹⁰
Ferrocenylmethyl Methacrylate	4.10 ¹⁴¹	4.11 ¹⁴¹ , 4.22 ¹⁴¹
3-ferrocenyl propyl methacrylamide	4.09	4.05, 4.03

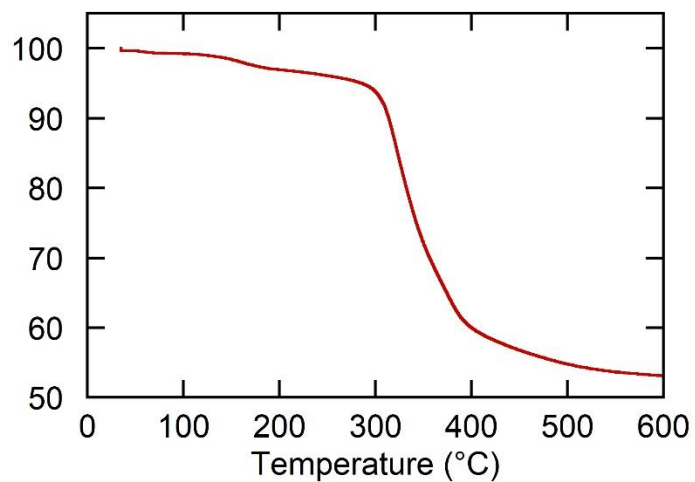


Figure C.4 TGA of MAECoPF₆.

C.2 Other characterization

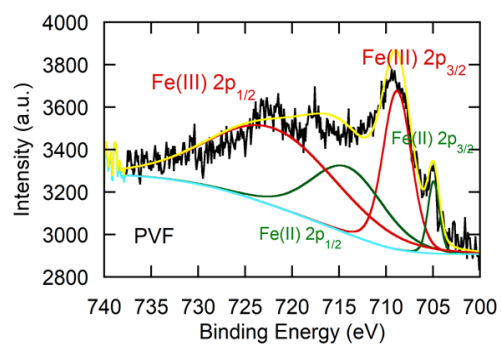


Figure C.5 XPS 2p Fe region for PVF.

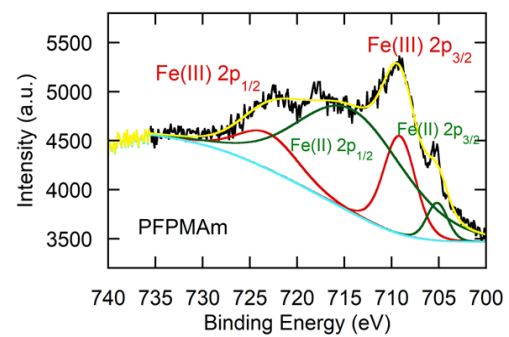


Figure C.6 XPS 2p Fe region for PFPMAm.

Table C.2 XPS separation factors per electrode after 30 minutes adsorption of 0.1 mM PFOA + 20 mM NaCl.

Polymer	F ⁻ (Atomic %)	Cl ⁻ (Atomic %)	Separation Factor
PFcMA	94.33	5.67	222
PVF	96.47	3.53	364
PFMMA	88.9	11.1	107
PFPMAm	99.0	1.0	1320
PMAECOPF₆	98.87	1.13	1167

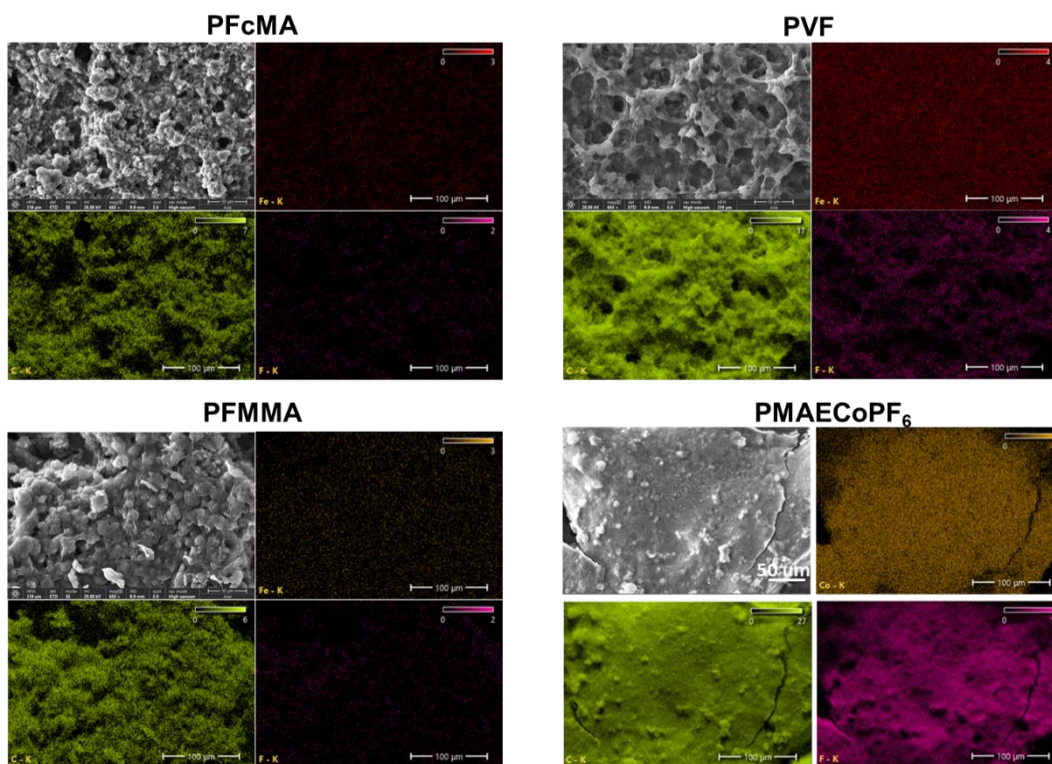


Figure C.7 SEM EDS images of PFcMA, PVF, PFMMA, and PMAECOPF₆. After electrosorption of 0.1 mM PFOA + 20 mM NaCl at the polymer's optimal potential for 30 min.

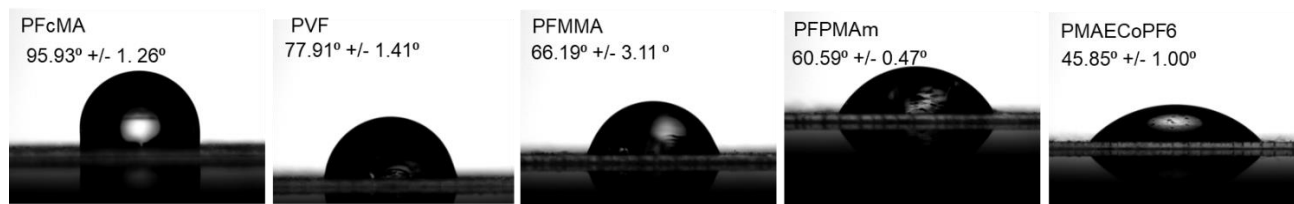


Figure C.8 Contact angle experiments on top of a glass electrode and 50 μL of the respective redox polymer. The droplet solution used was a 0.1 mM PFOA + 20 mM NaCl solution.

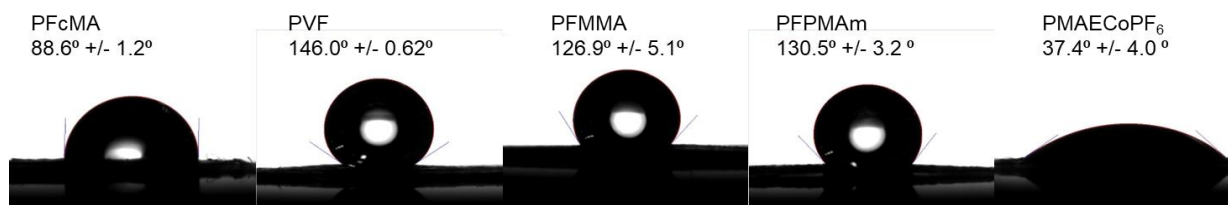


Figure C.9 A Ti mesh was covered with approximately 1 mg of the ink solution, composed of the carbon nanotubes dispersed with the polymer, of each material, concentrations of 4 mg polymer/mL. Before each contact angle analysis, the electrode surface was flattened with a clean glass substrate to prevent any uneven interference. The droplet was deionized water $>18\text{ M}\Omega$.

Table C.3 Contact angle error for results shown in **Figure 5.2d**.

Polymer	Angle Error (+/- °)
PFcMA	0.47
PVF	0.58
PFMMA	0.12
PFPMAm	0.66
PMAECOPF ₆	0.49

C.3 Electrosorption and electrodesorption screenings and other experiments

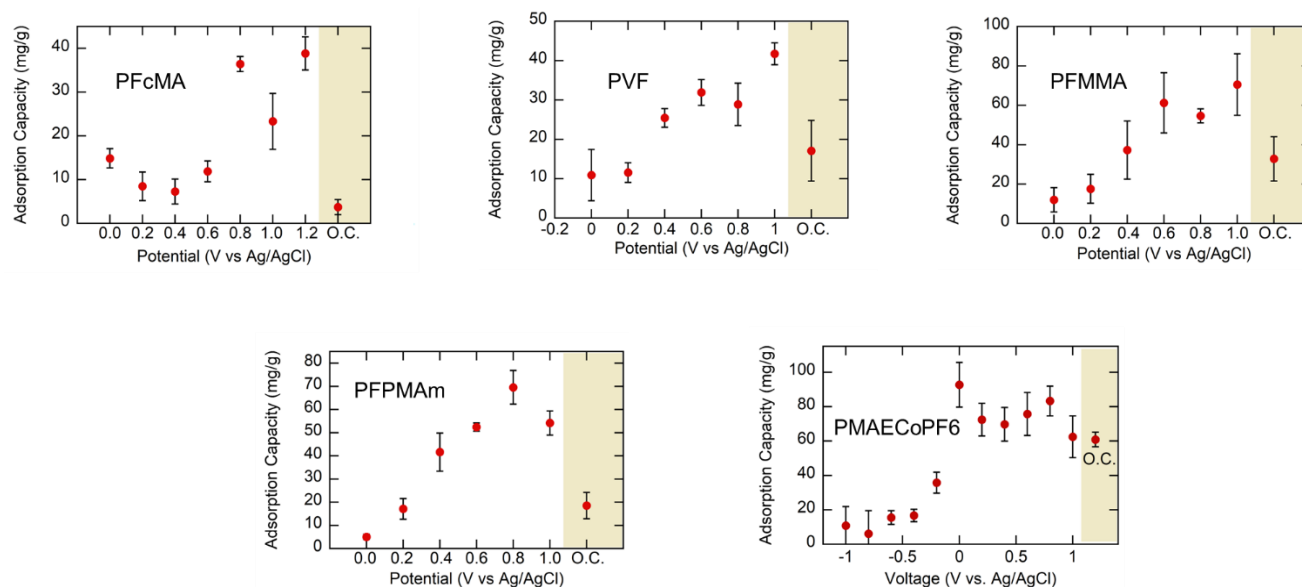


Figure C.10 Adsorption Potential screenings for all the polymers.

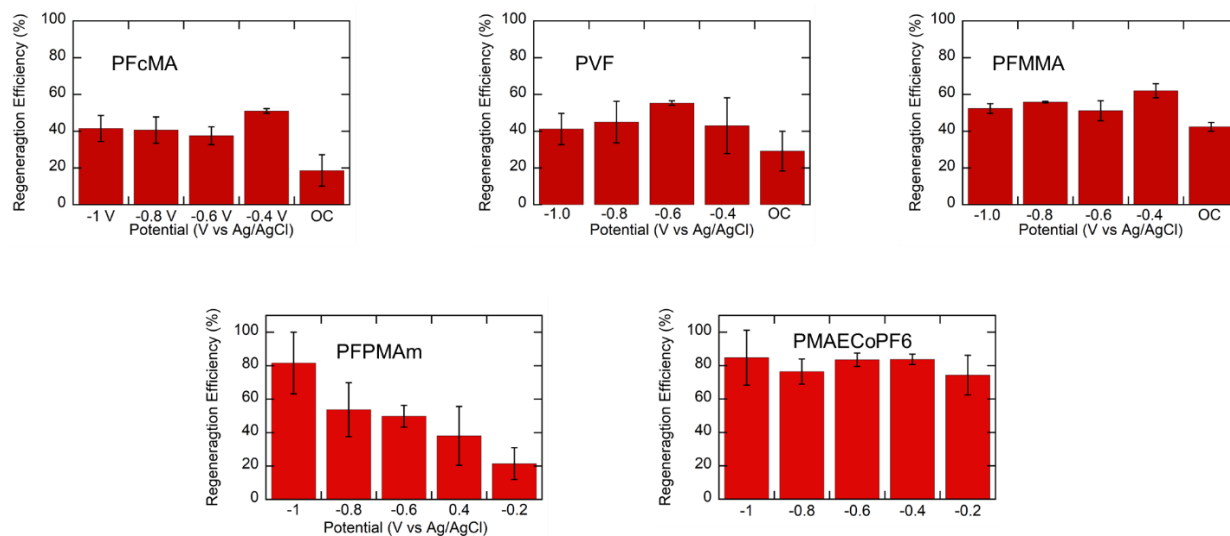


Figure C.11 Desorption screenings for all the polymers after adsorbing at 0.8 V vs Ag/AgCl for 30 minutes. These regeneration efficiencies were obtained based on the amount of PFOA capture during the adsorption process.

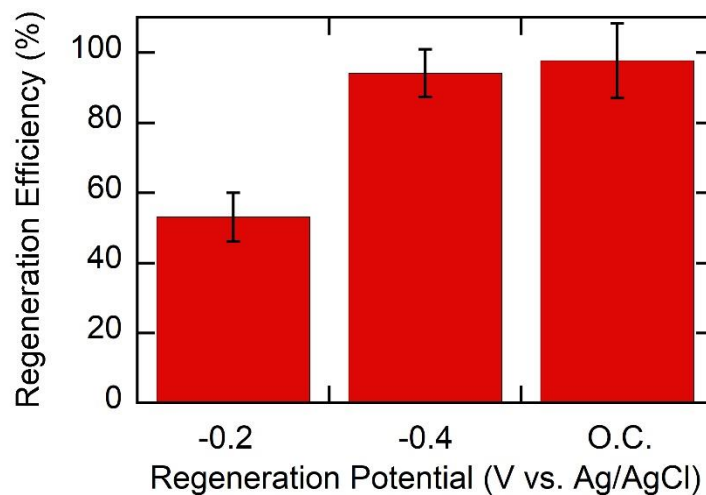


Figure C.12 Ion exchange experiment. Regeneration efficiency of PMAECoPF6 at different potentials after adsorbing 0.1 mM PFOA + 20 mM NaCl. The regeneration was performed under 1M NaCl solution.

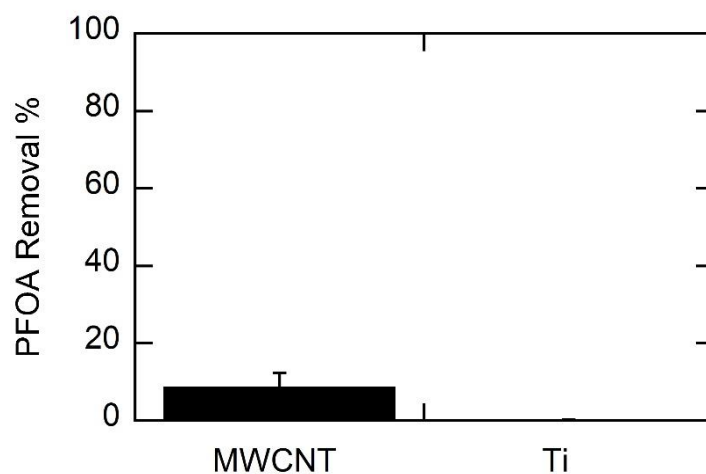


Figure C.13 Control experiments using multiwalled-carbon nanotubes (MWCNT) and a Titanium (Ti) sheet for PFOA electrosorption at 0.8 V vs Ag/AgCl in a 0.1 mM PFOA + 20 mM NaCl solution for 30 minutes.

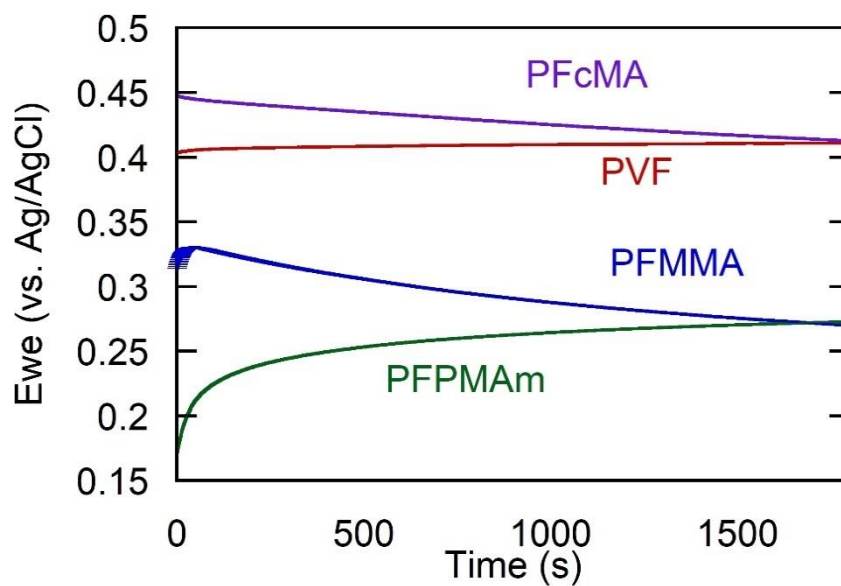


Figure C.14 Current profile of all the ferrocene containing metallopolymer at open circuit after adsorbing 0.1 mM PFOA + 20 mM NaCl for 30 minutes.

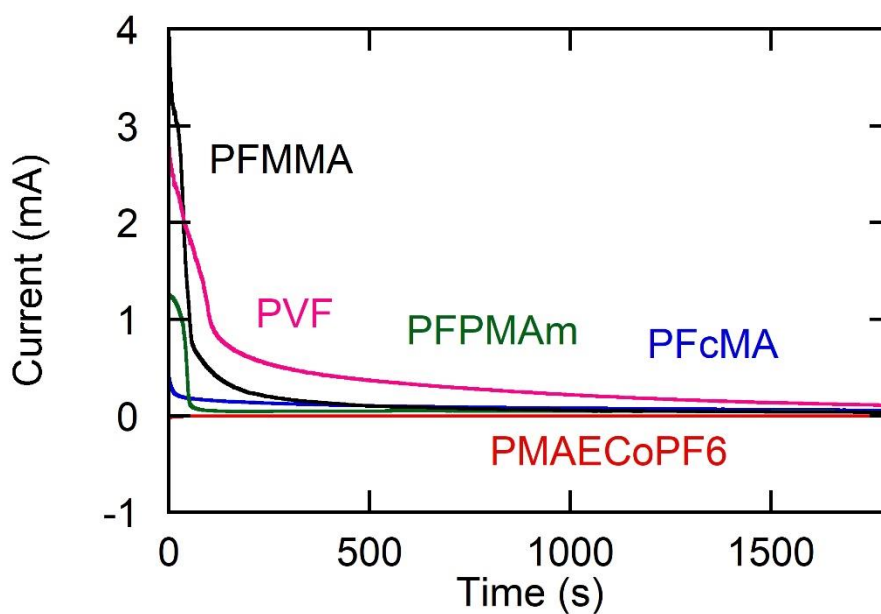


Figure C.15 Current profile of all the metallopolymer at optima potential after adsorbing 0.1 mM PFOA + 20 mM NaCl for 30 minutes.

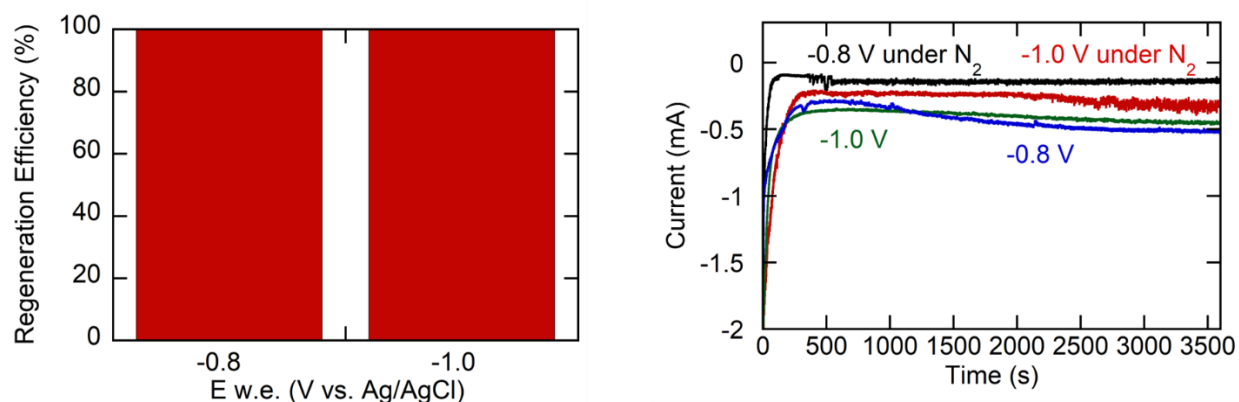


Figure C.16 PMAECoPF₆ regeneration efficiency under N₂ purge and its corresponding current profiles.

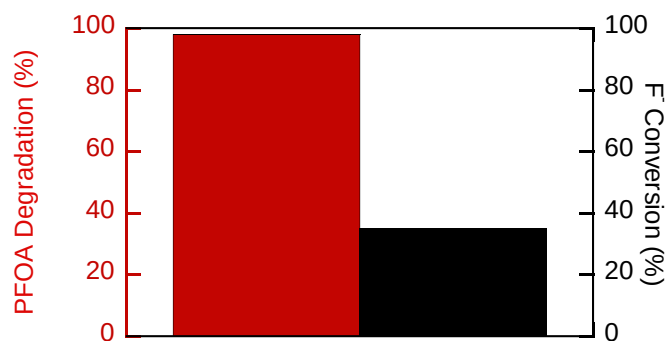


Figure C.17 PFOA degradation and conversion after 5 hours in 0.08 mM PFOA + 20 mM NaCl at 10 mA/cm² using boron doped diamonds (BDD).

C.4 Kinetic models

For our experiments we were able to compare the pseudo-first order kinetic model and the pseudo-second-order (PSO) kinetic model. Based on our fit results, **Table C.4**, we determined that the PSO model best describes our system's performance. A pseudo-second-order reaction rate are determined by the sorbate uptake and it has been studied for different electrosorption systems.^{11,}

^{46, 191-193} The equation given for this second order reaction is the following:^{189, 194}

$$q(1 + q_e k_2 t) = q_e^2 k_2 t \quad (\text{Eq. C.1})$$

Where q is the adsorption capacity (mg/g), q_e is the adsorption capacity at equilibrium (mg/g), k_2 is the pseudo-second-order reaction constant (min^{-1}), and t is time (min). Fitting of the curves for the PSO describes well the presence of a redox reaction based on the oxidative/reductive sites occupied on the metallopolymer sorbent.¹⁸⁹ Also, in this case, we can imply that the electrosorption process is the equivalent to the chemisorption reaction that describes the PSO, mainly occurring through the redox faradaic step when switching valences when oxidizing and reducing the electrodes.¹⁸⁹

Table C.4 Kinetic trends for electrosorption kinetics experiments on Fc containing metallopolymer.

Polymer	K_{obs} Pseudo-1 st -order (min^{-1})	R^2	K_2 Pseudo-2 nd -order ($[\text{mg/g}]^{-1}\text{min}^{-1}$)	R^2
PFcMA	0.0045	0.54	0.0025	0.88
PVF	0.0037	0.58	0.0046	0.97
PFPMAm	0.0035	0.52	0.00127	0.79
PFMMA	0.0056	0.96	0.0009	0.86

Table C.5 Kinetic trends for electrodesorption kinetics experiments on Fc containing metallopolymer.

Polymer	K_2 Pseudo-2 nd -order ($\%^{-1}\text{min}^{-1}$)	R^2
PFcMA	0.00123	0.9971
PVF	0.0165	0.9982
PFPMAm	0.0256	0.9939
PFMMA	0.00900	0.9952

C.5 Environmental relevant concentrations

Table C.6 Champaign-Urbana Sanitary district water specifications.

Compound	Concentration (mg/L)
Carbonaceous Biochemical Oxygen Demand (CBOD)	5.0
Total suspended solids (TSS)	7.7
Ammonia as N	12.3
Phosphorus as P	0.6

Table C.7 Ultra diluted experiment of 15 ppb using PMAECoPF₆ after 3 hours of operation at 0.0 V vs Ag/AgCl.

Compound	Initial Concentration (ppb)	Final Concentration (ppb)	PFOA Removal (%)
PFOA	15.0	6.60	56.0